APPLICATIONS OF TIME-DEPENDENT QUANTUM MECHANICS
TO RESONANTLY-ENHANCED LINEAR AND NONLINEAR OPTICAL
PROCESSES

A Dissertation in
Chemistry
by
Daniel W. Silverstein

© 2013 Daniel W. Silverstein

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2013
The dissertation of Daniel W. Silverstein was reviewed and approved* by the following:

Lasse Jensen  
Associate Professor of Chemistry  
Dissertation Advisor, Chair of Committee

Barbara J. Garrison  
Head of the Chemistry Department  
Shapiro Professor of Chemistry

John Asbury  
Associate Professor of Chemistry

Victor Nistor  
Professor of Mathematics

*Signatures are on file in the Graduate School.
Abstract

The interaction of radiation with matter allows many interesting properties of a molecule or material to be quantified. When the incident radiation is energetically tuned to be equivalent to the energy of an electronic transition, resonance enhancement occurs. This enhancement greatly increases the intensity of the detected signal and is of interest for characterizing molecules with optical processes including Raman and hyper-Raman scattering. Resonantly enhanced Raman and hyper-Raman spectra allow for coupling between electronic and vibrational motion to be quantified. This vibrational-electronic (vibronic) coupling is important for understanding electron transfer events in molecules, which is a central concept in molecular electronics and solar energy harvesting. Because Raman and hyper-Raman obey complementary selection rules, it is possible to obtain different molecular-level information from both techniques. To understand both processes, it is vital to have methods for simulating resonance Raman and resonance hyper-Raman scattering based on first principles calculations. We have examined the accuracy of density functional theory (DFT) calculations for the optical properties of metal clusters and electron transfer complexes. These studies allowed a detailed comparison of several exchange-correlation energy functionals commonly used in the literature, demonstrating that long-range corrected DFT is necessary to accurately describe optical properties in such systems. We also extended a wavepacket dynamics model for simulating linear optical properties, including one-photon absorption and resonance Raman scattering, to include nonlinear optical properties, such as two-photon absorption and resonance hyper-Raman scattering. Interpretation of the derived expressions shows that it is possible to simulate each technique using a common set of parameters. It is illustrated through applications to small molecules and the fluorescent dye rhodamine 6G that these expressions can be employed generally in cases where vibronic effects are important and when the harmonic oscillator approximation is valid. Finally, we show that our implementation of analytical excited state energy gradients in the framework of time-dependent density functional theory allows for the efficient simulation of linear optical properties for large molecules. This reduces time and number of calculations required to generate a resonance Raman spectrum, while maintaining accuracy.
# Table of Contents

List of Figures xi  
List of Tables xvi  
List of Symbols xviii  
Acknowledgments xix  

I Introductory Material 1  

Chapter 1  
Introduction 2  
Overview of Dissertation 4  

Chapter 2  
Overview of Density Functional Theory and Linear and Nonlinear Optical Properties 9  
2.1 Density Functional Theory 9  
2.2 Description of Linear and Nonlinear Optical Processes 12  
2.3 One-Photon Absorption and Resonance Raman Scattering 14  
2.4 Two-Photon Absorption 19  
2.5 Resonance Hyper-Raman Scattering 20  
2.6 Enhanced absorption of molecules near metal clusters 23  
2.6.1 Enhanced electronic excitations 23  
2.6.2 Surface-enhanced Infrared Absorption 26  
2.7 Enhanced Nonlinear Optical Properties by Metal Surfaces 29  
2.7.1 Surface-enhanced Hyper-Raman Scattering 30
II Describing electronic structure with density functional theory 36

Chapter 3
Assessment of the accuracy of long-range corrected functionals for describing the electronic and optical properties of silver clusters 37
3.1 Introduction . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 38
3.2 Theory . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 39
  3.2.1 Long-Range Corrected Functionals . . . . . . . . . . . . . . . . 39
  3.2.2 Ionization Potentials . . . . . . . . . . . . . . . . . . . . . . . . 41
3.3 Computational Details . . . . . . . . . . . . . . . . . . . . . . . . . . . 41
3.4 Results and Discussion . . . . . . . . . . . . . . . . . . . . . . . . . . . 43
  3.4.1 Ionization Potentials . . . . . . . . . . . . . . . . . . . . . . . . 43
  3.4.2 Absorbance Spectra . . . . . . . . . . . . . . . . . . . . . . . . 46
    3.4.2.1 Spectral Analysis . . . . . . . . . . . . . . . . . . . . 47
    3.4.2.2 DFT and Experimental Plasmon-like Peak Positions . 49
  3.4.3 Spectral Modeling by the Different Functionals . . . . . . . . . 50
3.5 Conclusion . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 53

Chapter 4
Understanding the Resonance Raman Scattering of Donor-Acceptor Complexes using Long-Range Corrected DFT 55
4.1 Introduction . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 56
4.2 Theory . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 57
4.3 Computational Details . . . . . . . . . . . . . . . . . . . . . . . . . . . 60
4.4 Results and Discussion . . . . . . . . . . . . . . . . . . . . . . . . . . . 62
  4.4.1 Hexamethylbenzene/TCNE . . . . . . . . . . . . . . . . . . . . . 62
  4.4.2 Carbazole/TCNE . . . . . . . . . . . . . . . . . . . . . . . . . . 67
4.5 Conclusions . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 75

III Vibronic coupling simulations of linear and nonlinear optical processes 77

Chapter 5
Vibronic Coupling Simulations for Linear and Nonlinear Optical Processes: Theory 78
5.1 Introduction . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 79
5.2 Analysis of Spectral Types . . . . . . . . . . . . . . . . . . . . . . . . 81
  5.2.1 One-Photon Absorbance . . . . . . . . . . . . . . . . . . . . . . 81
  5.2.2 Resonance Raman Scattering . . . . . . . . . . . . . . . . . . . . 84
  5.2.3 Two-Photon Absorbance . . . . . . . . . . . . . . . . . . . . . . 86
  5.2.4 Resonance Hyper-Raman Scattering . . . . . . . . . . . . . . . 89
Chapter 6
Vibronic Coupling Simulations for Linear and Nonlinear Optical Processes: Simulation Results

6.1 Introduction ............................................. 107
6.2 Computational Details .................................. 108
6.3 Results and Discussion .................................. 111
   6.3.1 Ammonia ............................................ 111
   6.3.2 Formaldehyde ....................................... 116
   6.3.3 Carbon Disulfide ................................... 119
   6.3.4 para-Nitroaniline ................................. 121
6.4 Conclusions .............................................. 128

Chapter 7
Probing One-Photon Inaccessible Electronic States with High Sensitivity: Wavelength Scanned Surface Enhanced Hyper-Raman Scattering

7.1 Experimental Section .................................... 136

Chapter 8
Probing Two-Photon Properties of Molecules: Large Non-Condon Effects Dominate the Resonance Hyper-Raman Scattering of Rhodamine 6G

Chapter 9
Surface-Enhanced Hyper-Raman Scattering Elucidates the Two-Photon Absorption Spectrum of Rhodamine 6G

9.1 Introduction .............................................. 146
   9.1.1 Nonlinear Spectroscopy of R6G ..................... 147
   9.1.2 Resonance Hyper-Raman Calculations .............. 149
9.2 Experimental Methods .................................... 151
   9.2.1 Experimental Setup ................................ 151
   9.2.2 SERS/SEHRS Sample Preparation and Use ........ 152
11.5 Conclusion and Future Work ................................. 202

VI Outlook and Future Directions ............................ 204

Chapter 12
Outlook ....................................................... 205
12.1 Dissertation Summary ..................................... 205
12.2 Future Directions for Vibronic Coupling Simulations ........ 206
  12.2.1 Analytical Transition Dipole Moment Gradients ...... 206
  12.2.2 Analytical Polarizability Gradients ..................... 207
  12.2.3 First Hyperpolarizabilities with Lifetime ............. 207
  12.2.4 Two-Photon Transition Moments ....................... 208
  12.2.5 Vibronic Approach for Simulating Chiroptical Properties ... 208
  12.2.6 Vibronic Simulations Including Duschinsky Rotations . 208
  12.2.7 Investigation of Solvation Effects on Resonance Hyper-Raman
        Scattering .................................................. 209

Appendices ......................................................... 210

Appendix A
Supplementary Information for “Assessment of the accuracy of long-
range corrected functionals for describing the electronic
and optical properties of silver clusters” ........................ 211
  A.1 Supplementary Information for Results Section ........... 211
      A.1.1 Absorbance Spectra .................................. 211

Appendix B
Supplementary Information for “Understanding the Resonance
Raman Scattering of Donor-Acceptor Complexes using
Long-Range Corrected DFT” .................................... 222
  B.1 Fitting Procedures ........................................ 222
  B.2 Hexamethylbenzene/TCNE .................................. 223
  B.3 Carbazole/TCNE ............................................ 224

Appendix C
Supplementary Information for “Vibronic Coupling Simulations for
Linear and Nonlinear Optical Processes: Simulation
Results” .................................................................. 235
  C.1 Additional Results for Ammonia ......................... 235
  C.2 Additional Results for Formaldehyde .................... 240
  C.3 Additional Results for Carbon Disulfide ................. 243
  C.4 Additional Results for p-Nitroaniline ................. 249
Appendix H
Derivation of Time-Dependent Density Functional Theory Energy Gradients

H.1 Initial Details .................................................. 313
  H.1.1 Equivalence of Notations .................................. 313
  H.1.2 Simplifying $G[\vec{X}, \vec{Y}, \omega]$ ..................... 315
  H.1.3 The Lagrangian Functional .............................. 317
H.2 Derivatives of the Lagrangian Functional (MO Coefficients) ........... 320
  H.2.1 Derivative of the Overlap Matrix (Term 3) ............... 320
  H.2.2 Derivative of the Fock Matrix (Term 2) .................. 321
  H.2.3 Derivative of the $G$ Functional (Term 1) ............... 326
    H.2.3.1 Preliminary work-up of Terms I and II ............... 327
    H.2.3.2 Derivative of the $\mathbf{A}+\mathbf{B}$ matrix (Term I) . 327
    H.2.3.3 Derivative of the $\mathbf{A}-\mathbf{B}$ matrix (Term II) ... 331
  H.2.4 Simplifying Derivatives of $G$ (Term 1) .................. 332
    H.2.4.1 Occupied-Occupied Block of $Q$ ..................... 333
    H.2.4.2 Occupied-Virtual Block of $Q$ ....................... 337
    H.2.4.3 Virtual-Occupied Block of $Q$ ....................... 339
    H.2.4.4 Virtual-Virtual Block of $Q$ ......................... 339
H.3 Final form of the Lagrangian functional derivatives ................ 340
H.4 Gradient of the excitation energy ............................. 343
  H.4.1 Reduction in dimension of $G[\vec{X}, \vec{Y}, \omega]$ .......... 350

Bibliography ....................................................... 351
# List of Figures

2.1 One-photon absorption process ........................................ 14  
2.2 Resonance Raman scattering process .................................. 16  
2.3 Two-photon absorption process ....................................... 19  
2.4 Resonance hyper-Raman scattering process ............................ 21  
2.5 Simulated absorption spectra of 20 Å silver nanoparticles with and without molecular dye coatings ........................................ 24  
2.6 Change in excitation energies of rhodamine 6G and crystal violet due to interactions with Ag$_{2057}$ ........................................ 25  
2.7 Simulated and experimental surface-enhanced infrared absorption spectra of p-nitrobenzoate ........................................ 28  
2.8 Two-photon absorption cross sections for gold particles ............ 29  
2.9 Measured and simulated surface-enhanced hyper-Raman spectra for pyridine ........................................ 32  
2.10 Simulated surface-enhanced hyper-Raman spectra for pyridine on Ag$_{20}$ ........................................ 34  
3.1 Ionization potentials calculated for silver clusters using several exchange-correlation functionals ........................................ 44  
3.2 Absorption spectra for the $D_{2d}$ isomer of Ag$_8$ .................... 46  
3.3 Absorption spectra for the $T_d$ isomer of Ag$_8$ .................... 47  
3.4 Absorption spectra for Ag$_{20}$ ........................................ 49  
3.5 Comparison of plasmon-like peak positions from theory and experiment for silver clusters ........................................ 51  
3.6 Spurious electronic states in the absorption spectra of silver clusters ........................................ 53  
4.1 Structure of the hexamethylbenzene-tetracyanoethylene complex ........................................ 62  
4.2 Simulated and experimental absorption spectra of the hexamethylbenzene-tetracyanoethylene complex ........................................ 63  
4.3 Simulated and experimental resonance Raman spectra of the hexamethylbenzene-tetracyanoethylene complex ........................................ 64  
4.4 Structure of the carbazole-tetracyanoethylene complex ........................................ 67  
4.5 Simulated and experimental absorption spectra of the carbazole-tetracyanoethylene complex ........................................ 69
4.6 Simulated and experimental resonance Raman spectra of the carbazole-tetracyanoethylene complex including the lowest two charge-transfer states .......................................................... 70
4.7 Simulated and experimental resonance Raman spectra of the carbazole-tetracyanoethylene complex including the first charge-transfer state .................................................. 71
4.8 Simulated and experimental resonance Raman spectra of the carbazole-tetracyanoethylene complex including the second charge-transfer state ............................................. 72
4.9 Plots of the interference in resonance Raman scattering between the lowest two charge-transfer states of the carbazole-tetracyanoethylene complex ......................................... 74

6.1 Simulated (LC-PBE and CCSD) and experimental one-photon absorption spectra for the $S_1$ state of NH$_3$ ................................................................. 113
6.2 Simulated (LC-PBE and CCSD) and experimental resonance Raman spectra for the $S_1$ state of NH$_3$ ................................................................. 114
6.3 Simulated (LC-PBE and CCSD) and experimental resonance hyper-Raman spectra for the $S_1$ state of NH$_3$ ................................................................. 115
6.4 Simulated two-photon absorption spectra for the $S_1$ state of CH$_2$O using LC-PBE and CCSD ................................................................. 118
6.5 Simulated resonance hyper-Raman spectra for the $S_1$ state of CH$_2$O using LC-PBE and CCSD ................................................................. 118
6.6 Simulated one-photon absorption spectra for the $S_4$ and $S_5$ states of CS$_2$ using LC-PBE and CCSD ................................................................. 120
6.7 Simulated (B3LYP and LC-PBE) and experimental one-photon absorption spectra for the $S_1$ state of para-nitroaniline ................................................................. 124
6.8 Simulated (B3LYP and LC-PBE) and experimental resonance Raman spectra for the $S_1$ state of para-nitroaniline ................................................................. 125
6.9 Simulated (B3LYP and LC-PBE) and experimental two-photon absorption spectra for the $S_1$ state of para-nitroaniline ................................................................. 127
6.10 Simulated (B3LYP and LC-PBE) resonance hyper-Raman spectra for the $S_1$ state of para-nitroaniline ................................................................. 128

7.1 Surface-enhanced hyper-Raman spectra of rhodamine 6G at $\lambda_{ex} = 1046$, 940, 840, and 751 nm ................................................................. 133
7.2 Simulated and experimental one- and two-photon absorption spectra of rhodamine 6G, and peak ratios showing the modes that track with each electronic state ................................................................. 134
7.3 Molecular orbitals and normal modes of rhodamine 6G ................................................................. 135

8.1 Comparison of experimentally measured resonance hyper-Raman and surface-enhanced hyper-Raman spectra with simulated resonance hyper-Raman spectra at $\lambda_{ex} = 825$ nm for rhodamine 6G ................................................................. 140
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.5</td>
<td>Resonance Raman spectra from analytical and numerical excitation energy gradients</td>
<td>200</td>
</tr>
<tr>
<td>11.6</td>
<td>Future molecules for study with excitation energy gradients</td>
<td>202</td>
</tr>
<tr>
<td>A.1</td>
<td>Absorption spectra for Ag$_4$</td>
<td>212</td>
</tr>
<tr>
<td>A.2</td>
<td>Absorption spectra for Ag$_5$</td>
<td>214</td>
</tr>
<tr>
<td>A.3</td>
<td>Absorption spectra for Ag$_6$</td>
<td>215</td>
</tr>
<tr>
<td>A.4</td>
<td>Absorption spectra for Ag$_7$</td>
<td>216</td>
</tr>
<tr>
<td>A.5</td>
<td>Absorption spectra for Ag$_{10}$</td>
<td>217</td>
</tr>
<tr>
<td>A.6</td>
<td>Absorption spectra for Ag$_{12}$</td>
<td>218</td>
</tr>
<tr>
<td>A.7</td>
<td>Absorption spectra for Ag$_{14}$</td>
<td>219</td>
</tr>
<tr>
<td>A.8</td>
<td>Absorption spectra for Ag$_{16}$</td>
<td>220</td>
</tr>
<tr>
<td>A.9</td>
<td>Absorption spectra for Ag$_{18}$</td>
<td>221</td>
</tr>
<tr>
<td>B.1</td>
<td>Plots of the interference using experimental data between the two lowest charge-transfer states of the carbazole-tetracyanoethylene complex at 488, 601, and 723 nm</td>
<td>233</td>
</tr>
<tr>
<td>B.2</td>
<td>Plots of the interference using B3LYP between the two lowest charge-transfer states of the carbazole-tetracyanoethylene complex at 488, 601, and 723 nm</td>
<td>233</td>
</tr>
<tr>
<td>B.3</td>
<td>Plots of the interference using LC-$\omega$PBE between the two lowest charge-transfer states of the carbazole-tetracyanoethylene complex at 488, 601, and 723 nm</td>
<td>234</td>
</tr>
<tr>
<td>C.1</td>
<td>Simulated one-photon absorption and resonance Raman spectra using B3LYP for the S$_1$ state of NH$_3$</td>
<td>237</td>
</tr>
<tr>
<td>C.2</td>
<td>Simulated resonance Raman spectra including the B term using LC-PBE and CCSD for the S$_1$ state of NH$_3$</td>
<td>238</td>
</tr>
<tr>
<td>C.3</td>
<td>Simulated two-photon absorption spectra using LC-PBE and CCSD for the S$_1$ state of NH$_3$</td>
<td>238</td>
</tr>
<tr>
<td>C.4</td>
<td>Simulated two-photon absorption and resonance hyper-Raman spectra using B3LYP for the S$_1$ state of NH$_3$</td>
<td>239</td>
</tr>
<tr>
<td>C.5</td>
<td>Simulated one-photon absorption spectra using LC-PBE and CCSD for the S$_1$ state of CH$_2$O</td>
<td>241</td>
</tr>
<tr>
<td>C.6</td>
<td>Simulated one-photon absorption spectra using B3LYP for the S$_1$ state of CH$_2$O</td>
<td>241</td>
</tr>
<tr>
<td>C.7</td>
<td>Simulated two-photon absorption and resonance hyper-Raman spectra using B3LYP for the S$_1$ state of CH$_2$O</td>
<td>242</td>
</tr>
<tr>
<td>C.8</td>
<td>Simulated one-photon absorption and resonance Raman spectra of CS$_2$ using B3LYP</td>
<td>245</td>
</tr>
<tr>
<td>C.9</td>
<td>Simulated resonance Raman spectra of CS$_2$ using LC-PBE and CCSD</td>
<td>246</td>
</tr>
<tr>
<td>C.10</td>
<td>Simulated two-photon absorption and resonance hyper-Raman spectra of CS$_2$ using CCSD</td>
<td>247</td>
</tr>
</tbody>
</table>
C.11 Simulated two-photon absorption and resonance hyper-Raman spectra of \( \text{CS}_2 \) using LC-PBE .................................................. 247
C.12 Simulated two-photon absorption and resonance hyper-Raman spectra of \( \text{CS}_2 \) using B3LYP .................................................. 248
C.13 Frontier orbitals of para-nitroaniline, calculated with LC-PBE .......... 249

D.1 Comparison of the experimental and fitted spectrum obtained for \( \lambda_{\text{ex}} = 880 \) nm. .................................................. 252
D.2 SEHRS of R6G on Ag \([\text{R6G}]=10^{-10}\) M at 880 nm. Raw data (left) and baseline corrected data (right). ............................................. 253
D.3 Comparison of the simulated nonresonant hyper-Raman spectrum of rhodamine 6G with the experimental SEHRS spectrum at 1050 nm .... 255

E.1 Relative contributions of the Franck-Condon and Herzberg-Teller terms of the \( S_1 \), \( S_2 \), and \( S_3 \) states to the total resonance hyper-Raman scattering of rhodamine 6G at 825 and 1046 nm ................................. 260
E.2 Relative contributions of the Franck-Condon and Herzberg-Teller terms of the \( S_1 \), \( S_2 \), \( S_3 \) states to the total resonance hyper-Raman scattering of rhodamine 6G at 1046, 891, 825, and 791 nm ........................................... 261

F.1 Frontier orbitals of Rubpy from B3LYP ......................................... 268
F.2 Frontier orbitals of Rubpy from LC-PBE ........................................... 269

G.1 Example ground state electronic structure for a molecule with 3 occupied and 3 virtual orbitals. Energies and indices are shown and referred to in the text. The table indicates the energy differences for all possible electronic transitions (single excitations only) ........................................... 308
List of Tables

3.1 Ionization potentials calculated for Ag$_8$ isomers using several exchange-correlation functionals .................................................. 45

4.1 Excitation energies and transition dipole moments for the lowest two charge-transfer states of the carbazole-tetracyanoethylene complex .............................. 68

5.1 Summary of prefactors to integrals for Franck-Condon and Herzberg-Teller terms ..................................................................................... 103

6.1 One- and two-photon response properties for the S$_1$ state of NH$_3$ ............................................................. 112

6.2 Two-photon response properties for the S$_1$ state of CH$_2$O ............................................................. 117

6.3 Simulated one- and two-photon response properties for the S$_4$ and S$_5$ states of CS$_2$ .................................................................................. 119

6.4 One- and two-photon response properties for para-nitroaniline ............................................................. 122

10.1 Normal mode assignments of Rubpy ................................................................................................................................. 176

11.1 Definitions of the exchange-correlation functionals ................................................................................................. 195

11.2 Comparison of displacements from analytical and numerical gradients ............................................................. 201

B.1 Simulation parameters and mode assignments using experimental data for absorbance and resonance Raman scattering of the hexamethylbenzene-tetracyanoethylene complex ................................................................. 224

B.2 Simulation parameters and mode assignments using B3LYP for absorbance and resonance Raman scattering of the hexamethylbenzene-tetracyanoethylene complex .................................................................................. 225

B.3 Simulation parameters and mode assignments using LC-ωPBE for absorbance and resonance Raman scattering of the hexamethylbenzene-tetracyanoethylene complex .................................................................................. 225

B.4 Normal modes of the free hexamethylbenzene and tetracyanoethylene molecules compared to the hexamethylbenzene-tetracyanoethylene complex .................................................................................. 226

B.5 Simulation parameters for absorbance and resonance Raman scattering of the carbazole-tetracyanoethylene complex using experimental data ................................................................. 227
B.6 Assignments of the normal modes in the carbazole-tetracyanoethylene complex based on experimental data ........................................ 228
B.7 Simulation parameters for absorbance and resonance Raman scattering of the carbazole-tetracyanoethylene complex using B3LYP .... 229
B.8 Simulation parameters for absorbance and resonance Raman scattering of the carbazole-tetracyanoethylene complex using LC-ωPBE ... 230
B.9 Assignments of the normal modes in the carbazole-tetracyanoethylene complex based on B3LYP calculations .......................... 231
B.10 Normal modes of the free carbazole and tetracyanoethylene molecules compared to the carbazole-tetracyanoethylene complex .... 232

C.1 Simulation parameters for the S$_1$ state of NH$_3$ .......................... 236
C.2 Simulation parameters for the S$_1$ state of CH$_2$O .......................... 240
C.3 Simulation parameters for the S$_4$ state of CS$_2$ .......................... 243
C.4 Simulation parameters for the S$_5$ state of CS$_2$ .......................... 244
C.5 Simulation parameters of para-nitroaniline from first principles calculations and experimental data ................................. 250

F.1 Excited state properties of Rubpy from B3LYP and LC-PBE ........ 263
F.2 Lineshape function simulation parameters for Rubpy used with B3LYP and LC-PBE ............................................................... 264
F.3 Normal mode frequencies and dimensionless displacements for the 8 most important normal modes of Rubpy ...................... 265
F.4 Normal mode frequencies and dimensionless displacements for the 9 most important normal modes of Rubpy-d24 ..................... 266
F.5 Assignments of the transitions involved in the allowed states of Rubpy from B3LYP ................................................................. 267
F.6 Assignments of the transitions involved in the allowed states of Rubpy from LC-PBE ................................................................. 267
List of Symbols

Below are a list of the most common subscripts.

\( k, l \) General Indices

\( i, j \) Occupied Molecular Orbitals

\( a, b \) Virtual/Unoccupied Molecular Orbitals or Normal Modes, Depending on Context

\( p, q, r, s \) General Molecular Orbitals

\( \mu, \nu, \kappa, \lambda \) Atomic Orbitals

\( \alpha, \beta, \gamma \) Cartesian Coordinates

Symbols will be defined as they are introduced, but the most common symbols are found below:

\( \rho \) Electron Density

\( \phi \) A Kohn-Sham Molecular Orbital

\( \chi \) An atomic orbital

\( \omega \) Incident frequency

\( \lambda \) Incident wavelength

\( \alpha_{\alpha\beta} \) Polarizability

\( \beta_{\alpha\beta\gamma} \) First Hyperpolarizability

\( Q \) Mass-Weighted Normal Coordinate

\( q \) Dimensionless Normal Coordinate

\( \Delta \) Dimensionless Displacement
Acknowledgments

I first want to thank Prof. Lasse Jensen for his all of his assistance and guidance on my Ph.D. research. I originally came to the Pennsylvania State University not knowing whether I wanted to either do experimental or theoretical work. My final decision to join the Jensen group afforded me a lot of worthwhile experience that I think will be broadly applicable in the field of quantum chemistry. Lasse immediately recognized my mathematical talent and directed much of my early work towards derivations of complicated formulas. He also facilitated me learning computer programming in a variety of languages so that I could also implement programs and work with other scientists on quantum chemistry software. These skills will be instrumental for future work on my career. I also want to thank Lasse for his support, patience, and understanding during the difficult times outside of research I experienced at the start of my fourth year.

Of course, much of this work also benefited from discussions with past and current members of the Jensen group so I want to thank them as well. I would like to thank Dr. Seth Morton for his enthusiasm towards computer programming, because I feel that he made me a better programmer by challenging me to program with a high standard. I want to thank Krista Kane for her help and being a role model early in my graduate studies. I would like to thank Justin Moore for being available to brainstorm approaches to programming in NWChem, and also with understanding the insanity that is the NWChem integral package. I also thank Dhabih Chulhai, Zhongwei Hu, and Philip Weiss for helpful comments and interesting questions during group meetings.

A large portion of this work could never have been done without collaborations with people at other research labs. I thank Prof. Jon Camden for catalyzing many projects involving his group and the Jensen group. Many of the projects presented in my dissertation would not have been possible without support from Jon’s group. From Jon’s group, I thank Chris Bennett and Nasrin Misraleh-Kohan for helping me understand how their spectroscopy experiments work and also allowing me to compare data I simulated with data they collected. From the Pacific Northwest National Laboratory, I appreciate the assistance of Dr. Niri Govind and Dr. Hubertus Van Dam with implementing features in NWChem.

I could not have done a lot of this research without the High Performance Computing group at Penn State, particularly the Research Computing and Cyberinfrastructure unit that maintains the university supercomputers. In particular, I thank Jason Holmes who
provided a lot of technical support when calculations ran incorrectly. I also want to thank the Pacific Northwest National Laboratory and TeraGrid for alloting time for us to use their supercomputers for my first two projects.

I would like to thank my parents, Kim and Bob Silverstein, for all of their support during my graduate research and encouragement throughout my education. I want to thank my brother Tim Silverstein for being a strong role model throughout my life and supporting my work in chemistry. Finally, I want to thank my wife, Carrie, for helping me get through graduate school and supporting me during the difficult months during my graduate research.
Dedication

To my family, friends, and teachers.
Part I

Introductory Material
Introduction

When electromagnetic radiation interacts with a molecule, the electronic structure and interactions with the surrounding environment of the molecule can be characterized. If the energetic location where a molecule absorbs (the excitation energy) is known, the probability of the radiation-molecular interaction can be greatly increased by selecting the energy of the radiation to match that of the molecular absorption. Matching the energy of the incident radiation to the excitation energy leads to an effect called resonance enhancement. Resonance enhancement allows techniques that yield low detectable signal, such as Raman and hyper-Raman spectroscopy, to become powerful characterization methods.\textsuperscript{1–3}

Raman scattering is an inelastic light scattering process that occurs when a molecule absorbs a photon with frequency $\omega_L$ and scatters a photon with frequency $\omega_s = \omega_L \pm \omega_v$, where $\omega_v$ is the frequency of a vibrational normal mode. This difference in the incident and scattered frequencies allows Raman scattering to characterize molecules based on their vibrational signatures.\textsuperscript{4} Under nonresonant conditions, where the incident photon energy is far from the molecule’s excitation energy, Raman scattering is known to probe the electronic ground state. When the incident photon is tuned to one of the molecule’s excitation energies, resonance Raman scattering occurs and information about the resonant electronic state is obtained.\textsuperscript{4–6}

Resonance Raman scattering (RRS) has been applied for a variety of interesting processes, such as: studying protein conformations in light-harvesting proteins for photosynthesis\textsuperscript{7} and substrate binding in heme proteins,\textsuperscript{8,9} characterizing molecular electronic devices,\textsuperscript{10,11} identifying pigments in fibers and inks for forensic applications,\textsuperscript{12,13} and detecting pigments in human skin\textsuperscript{14,15} for identification of cancerous cells.\textsuperscript{16} Although RRS is a standalone technique that can detect low concentrations of molecules with
high sensitivity, surface-enhanced spectroscopy is frequently exploited where the enhancement from RRS is combined with the enhancement from the strong electric field surrounding rough metal surfaces. Most modern experimental applications of RRS involve surface-enhanced resonance Raman scattering (SERRS), a technique that is capable of detecting single molecules. It is particularly appealing that the metal surface quenches fluorescence, which is a major interference in RRS, without significantly altering the peak ratios in the RRS spectrum.

Resonance hyper-Raman scattering (RHRS) is the analogue of RRS where the absorption of two photons initiates the process. Although it can, in principle, be used for many of the applications described for RRS, RHRS has been employed far less frequently than RRS owing to its low signal intensity and long acquisition times during experiments. These problems are resolved by using surface-enhanced resonance hyper-Raman scattering (SERHRS). A significant advantage of RHRS and SERHRS is that both are capable of probing electronic states that are forbidden in one-photon spectroscopies, resulting from the differing selection rules for two-photon processes. However use of SERHRS is not widespread, mainly resulting from two problems. First, due to the complicated nature of interactions between the metal surface and the molecule, SERRS is not well understood. The same enhancement mechanisms are expected to be important in SERRS and SERHRS because the processes differ in the number of incident photons, but can be used for the same systems. As a result, most effort is expended on understanding SERRS because it is easier to detect. The second issue is that theoretical methods for simulating RHRS are not well developed. This problem results mostly from the lack of experimental data to compare with and the difficulty in calculating the required molecular response properties from first principles calculations.

In this dissertation, theoretical studies of RRS and RHRS will be presented, enabling a detailed comparison of simulations with experimental data. We have investigated different types of exchange-correlation functionals from density functional theory (DFT) for determining the electronic and optical properties of metals and molecules. These studies demonstrate the accuracy of several different approximations in DFT. We have also extended a model commonly used to simulate absorption and RRS to include two-photon absorption and RHRS with a common set of parameters from first principles calculations. With these simulations it is possible to interpret complicated behavior involving the coupling of vibrations to electronic motion for a variety of experimentally observable methods. We then demonstrate the application of analytical excitation energy gradients using time-dependent density functional theory, which will allow efficient simulations of
absorption and Raman scattering processes for large molecules.

Overview of Dissertation

In the following, a brief outline of each chapter will be presented. Chapters 2 through 9 are adapted here from published work.

Chapter 2: Overview of Density Functional Theory and Linear and Nonlinear Optical Properties

The quantum mechanical description of electronic structure with density functional theory is presented. A detailed discussion of the molecular level properties and optical processes is given, including: one-photon absorption, resonance Raman scattering, two-photon absorption, and resonance hyper-Raman scattering. These topics, along with surface-enhanced absorption and surface-enhanced nonlinear optical properties, are presented to illustrate the scope of the thesis.

Chapter 3: Assessment of the accuracy of long-range corrected functionals for describing the electronic and optical properties of silver clusters

A study of electronic and optical properties of silver clusters demonstrates the accuracy of density functional theory calculations compared with experimental data. It is determined that ionization potentials are most correctly described by a series of exchange-correlation functionals called long-range corrected functionals. The plasmon-like features of larger silver clusters are also found to be well described by long-range corrected functionals.

Chapter 4: Understanding the Resonance Raman Scattering of Donor-Acceptor Complexes using Long-Range Corrected DFT

One-photon absorption and resonance Raman scattering are simulated to investigate the accuracy of describing photo-induced electron transfer events in the donor-acceptor complexes: hexamethylbenzene-tetracyanoethylene and carbazole-tetracyanoethylene. In comparing simulated resonance Raman spectra to experimental spectra, we find that the global hybrid functional B3LYP does not accurately describe the potential energy surface of charge transfer states, but the long-range corrected hybrid LC-ωPBE
substantially improves the potential energy surface. Interference between overlapping electronic states is also described.

Chapter 5: Vibronic Coupling Simulations for Linear and Nonlinear Optical Processes: Theory
A general framework for simulating linear and nonlinear optical properties including vibronic coupling is presented. The evaluation of integrals for vibrational overlaps, including Franck-Condon and Herzberg-Teller terms, is derived. Models for broadening effects of optical spectra are also described.

Chapter 6: Vibronic Coupling Simulations for Linear and Nonlinear Optical Processes: Simulation Results
Simulations based on the expressions in Chapter 5 are shown for ammonia, formaldehyde, carbon disulfide, and para-nitroaniline. Good agreement is observed between theoretical and experimental spectra, although some breakdowns of the harmonic oscillator model for small molecules are observed.

Chapter 7: Probing One-Photon Inaccessible Electronic States with High Sensitivity: Wavelength Scanned Surface Enhanced Hyper-Raman Scattering
A study of wavelength-scanned surface-enhanced hyper-Raman scattering is presented for the fluorescent dye, rhodamine 6G. It is found that resonance hyper-Raman simulations, including only the Franck-Condon term, are identical to resonance Raman simulations, making it impossible to assign the experimental observations with a vibronic model. Good agreement is observed between the simulated nonresonant hyper-Raman spectrum of rhodamine 6G and resonant SEHRS spectra, indicating that the nonresonant term may be significant in hyper-Raman experiments.

Chapter 8: Probing Two-Photon Properties of Molecules: Large Non-Condon Effects Dominate the Resonance Hyper-Raman Scattering of Rhodamine 6G
By implementing non-Condon terms for simulations using the vibronic theory of resonance hyper-Raman scattering, we demonstrate that rhodamine 6G experiences non-Condon effects in its surface-enhanced hyper-Raman spectrum. This new method is tested over a variety of wavelengths and
shown to reproduce the experimental spectrum. It is shown that interference of non-overlapping electronic states can be quantified using resonance hyper-Raman scattering simulations.

Chapter 9: Surface-Enhanced Hyper-Raman Scattering Elucidates the Two-Photon Absorption Spectrum of Rhodamine 6G
We describe the findings in Chapter 8 in detail by showing that non-Condon effects are important in both two-photon absorption and resonance hyper-Raman scattering of rhodamine 6G. The symmetry of rhodamine 6G is found to be an important cause of the non-Condon effects in both spectroscopies.

Chapter 10: Investigation of Linear and Nonlinear Raman Scattering for Isotopologues of Ru(bpy)$_2^{2+}$
A detailed analysis of absorption and Raman scattering of the molecule tris(2,2'-bipyridine)ruthenium(II) is presented. For the absorption spectra, the exchange-correlation functionals B3LYP and LC-PBE indicate that multiple metal to ligand charge transfer excitations are present, yielding a complicated absorption peak shape. Simulated resonance Raman and resonance hyper-Raman spectra are capable of reproducing the observed features in the experimental SERS and SEHRS spectra near the absorption maximum. Wavelength scanning over the absorption spectrum indicates complicated vibronic coupling that is not captured in the theoretical model. Reasons for the discrepancies are discussed.

Chapter 11: Efficient calculations of optical processes: analytical excited state energy gradients with time-dependent density functional theory
An implementation of analytical excited state energy gradients in the framework of time-dependent density functional theory is added to the quantum chemistry program NWChem. Although it is possible to simulate one-photon absorption and resonance Raman scattering using finite difference of the excitation energies, this is computationally inefficient. Analytical gradients are shown to be efficient for simulating one-photon absorption and resonance Raman scattering for large molecules.

Chapter 12: Outlook
Several potential future projects using the methods described in this dissertation are proposed.
In addition to these chapters, there are seven appendices.

**Appendix A:** Supplementary Information for “Assessment of the accuracy of long-range corrected functionals for describing the electronic and optical properties of silver clusters”
Supporting information for Chapter Assessment of the accuracy of long-range corrected functionals for describing the electronic and optical properties of silver clusters.

**Appendix B:** Supplementary Information for “Understanding the Resonance Raman Scattering of Donor-Acceptor Complexes using Long-Range Corrected DFT”
Supporting information for Chapter Understanding the Resonance Raman Scattering of Donor-Acceptor Complexes using Long-Range Corrected DFT.

**Appendix C:** Supplementary Information for “Vibronic Coupling Simulations for Linear and Nonlinear Optical Processes: Simulation Results”
Supporting information for Chapter Vibronic Coupling Simulations for Linear and Nonlinear Optical Processes: Simulation Results.

**Appendix D:** Supplementary Information for “Probing One-Photon Inaccessible Electronic States with High Sensitivity: Wavelength Scanned Surface Enhanced Hyper-Raman Scattering”
Supporting information for Chapter Probing One-Photon Inaccessible Electronic States with High Sensitivity: Wavelength Scanned Surface Enhanced Hyper-Raman Scattering.

**Appendix E:** Supplementary Information for “Probing Two-Photon Properties of Molecules: Large Non-Condon Effects Dominate the Resonance Hyper-Raman Scattering of Rhodamine 6G”
Supporting information for Chapter Probing Two-Photon Properties of Molecules: Large Non-Condon Effects Dominate the Resonance Hyper-Raman Scattering of Rhodamine 6G.

**Appendix F:** Supplementary Information for “Investigation of Linear and Nonlinear Raman Scattering for Isotopologues of Ru(bpy)$_3^{2+}$”
Supporting information for Chapter Investigation of Linear and Nonlinear Raman Scattering for Isotopologues of Ru(bpy)$_3^{2+}$.

Appendix G: Derivation of Linear Response Equations in Time-Dependent Density Functional Theory
Expressions for the linear response equations in time-dependent density functional theory are derived.

Appendix H: Derivation of Time-Dependent Density Functional Theory Energy Gradients
Expressions for the excited state energy gradients using time-dependent density functional theory are derived in detail. Some discussion of the implementation of the gradients is presented.
Overview of Density Functional Theory and Linear and Nonlinear Optical Properties


2.1 Density Functional Theory

The accurate determination of electronic structure for molecules requires the application of quantum chemistry.31 Because of the growing interest for investigating systems with large numbers of atoms, many methods are too computationally demanding for studying molecules with more than a few atoms. Owing to its high efficiency compared to other methods, density functional theory (DFT) has become the method of choice for describing the electronic ground state and electronic excited state properties of molecules.32–41

The general framework for DFT calculations is based on the Hohenberg-Kohn theorem.42 There are two parts to this theorem: (1) the Hamiltonian of the system and ground state wavefunction are uniquely determined by the ground state electron density; (2) the correct ground state electron density minimizes the density functional for the electronic energy. The electronic energy functional for the ground state is written in the form,

\[ E[\rho] = \int \rho(r) v(r) dr + F_{HK}[\rho] \]  

(2.1)

where \( \rho(r) \) is the electron density, \( v(r) \) is the external potential arising from nuclear charges, and \( F_{HK}[\rho] \) is a universal functional of the electron density. Unfortunately, the
density functional is not known, so practical applications of DFT require approximations to it. A widely used approach for performing DFT calculations involves the Kohn-Sham method, where the density functional is written

\[ F_{HK}[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] \]

\[ = \sum_{i=1}^{N_{elec}} \int \phi_i(r) \left( -\frac{1}{2} \nabla^2 \right) \phi_i(r) dr + \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|r_2 - r_1|} dr_1 dr_2 + E_{xc}[\rho] \]  

(Eq. 2.2)

In Eq. 2.2, \( T_s[\rho] \) is the kinetic energy of a non-interacting representation of the system, \( J[\rho] \) is the Coulomb potential energy, and \( E_{xc}[\rho] \) is the exchange-correlation (XC-) energy functional. The foundation of the Kohn-Sham method is that a reference system of non-interacting electrons is defined to possess the same electron density of the molecule. By using this approach, we can determine the ground state electron density as

\[ \rho(r) = \sum_{i} n_i |\phi_i(r)|^2 \]  

(Eq. 2.3)

where \( n_i \) are the occupation numbers of the orbitals \( \phi_i(r) \).

To determine the Kohn-Sham orbitals that yield the electron density that minimizes the ground state energy, an auxiliary functional is used

\[ \Omega[\rho] = E[\rho] - \mu \int \rho(r) dr \]  

(Eq. 2.4)

Here, \( \mu \) is a Lagrange multiplier enforcing that the total electron density equals the number of electrons in the system. Resulting from the definition of the electron density, minimization of the auxiliary functional is achieved by taking the functional derivative with respect to the electron density or equivalently, a functional derivative with respect to the Kohn-Sham orbitals. The latter derivative yields

\[ \frac{\delta \Omega[\rho]}{\delta \phi_i} = 0 = \frac{\delta E[\rho]}{\delta \phi_i} - \mu \phi_i(r) \]

\[ = -\frac{1}{2} \nabla^2 \phi_i(r) + v(r)\phi_i(r) + \left( \int \frac{\rho(r_1)}{|r_2 - r_1|} dr_1 \right) \phi_i(r) + V_{xc}[\rho] \phi_i(r) - \mu \phi_i(r) \]  

(Eq. 2.5)
Eq. 2.5 uses the functional derivative of the XC-energy functional or XC-potential, $V_{xc}[\rho]$, 

$$V_{xc}[\rho] = \frac{\delta E_{xc}[\rho]}{\delta \rho}$$  \hspace{1cm} (2.6)$$

Rearrangement of Eq. 2.5 results in

$$\left[ -\frac{1}{2} \nabla^2 + v(r) + \int \frac{\rho(r_1)}{|r_2 - r_1|} dr_1 + V_{xc}[\rho] \right] \phi_i(r) = \mu \phi_i(r)$$

$$\hbar KS[\rho(r)]\phi_i(r) = \epsilon_i \phi_i(r)$$  \hspace{1cm} (2.7)$$

The Lagrange multiplier $\mu$ is determined to be the orbital energy, $\epsilon_i$, by analogy to the Hartree-Fock equations. Determination of the Kohn-Sham orbitals and ground state density then results from solving a set of one-electron equations defined in Eq. 2.7.

The accuracy of results determined in the Kohn-Sham formulation of DFT involves the approximation made in the XC-energy functional. Numerous types of functionals exist, but in general we may write: $E_{xc} = E_x + E_c$ in many situations, where $E_x$ is the exchange energy functional and $E_c$ is the correlation energy functional. The classification of the functional depends on its variables. A simple approximation to the XC-energy functional is the local density approximation (LDA), where the exchange and correlation are dependent only on the electron density, $\rho(r)$. For molecules LDA typically underestimates molecular properties like bond lengths and atomization energies. Because the electron density of molecules is normally inhomogeneous, improvements to LDA are accomplished by including dependence on the gradient of the electron density, $\nabla \rho(r)$, in a class of functionals belonging to the generalized gradient approximation (GGA). Deficiencies from LDA in total energies, atomization energies, and bond lengths are generally improved by GGAs. More in depth investigations of the accuracy of various approximations to the XC-energy functional have been described for ground state and excited state properties, so the reader is referred to those references for more general discussion.

Studying excited state properties of molecules can be accomplished using time-dependent density functional theory (TDDFT). In the framework of response theory, TDDFT calculations determine the perturbed electron density in the presence of an external field, enabling simulations of various spectroscopies. TDDFT allows for the determination of properties including excitation energies, transition dipole moments
(or oscillator strengths), frequency-dependent polarizabilities,\textsuperscript{60,61} excited state geometries,\textsuperscript{62–64} and excited state dipole moments.\textsuperscript{64,65} A detailed derivation of the TDDFT equations is given in Appendix G.

Although traditional XC-energy functionals such as LDA or GGAs are appropriate for valence excitations, they are inadequate for describing Rydberg excitations,\textsuperscript{66} charge-transfer excitations,\textsuperscript{67–69} and polarizabilities for long conjugated chains.\textsuperscript{70} These inadequacies have been traced to the incorrect behavior of the electronic repulsion operator for large interelectronic separation. Range-separated hybrid functionals, where the electronic repulsion operator $r_{12}^{-1}$ is partitioned as a short range interaction described by DFT exchange and long range interaction described by Hartree-Fock (HF) exchange (i.e. $E_x = E_x^{SR} + E_x^{LR}$),\textsuperscript{40,71–74} are capable of correcting the shortcomings of traditional XC-energy functionals for excited state properties.\textsuperscript{37,75–77} The choice of the XC-energy functional is vital for accurately determining properties of excited electronic states, and requires knowledge of the chemical problem being investigated.

\section*{2.2 Description of Linear and Nonlinear Optical Processes}

Spectroscopy is defined as the interaction of light with matter. This interaction can be used to characterize any type of atom, molecule, or material that is present based on the frequency or wavelength of the photons used. In general, any phenomenon that changes the optical properties of a material and is caused by interaction with light is defined as an \textit{optical process}.\textsuperscript{78} Optical processes can be further categorized based on the number of incident electromagnetic fields involved. A \textit{linear optical process} is an event characterized by interactions with a single incident field. The name “linear” is derived from examining the response of the system with respect to the intensity of incident light. For a linear optical process, the plot of the system’s response versus incident light intensity is linear with a slope equal to unity. Analogously, \textit{nonlinear optical processes} involve interactions with multiple incident photons. For instance, an event involving the interaction of a system with two incident photons is “quadratic” because the plot of the response of the system versus incident light intensity is quadratic (a parabola). Although it is possible to investigate the response of the system with respect to other types (for instance, magnetic) perturbing fields,\textsuperscript{78–80} here we will focus on the perturbations resulting from an external electric field.

The response of a molecule to an electric field is generally written based on Taylor series expansion of the dipole moment (see Refs. 81, 82 and Appendix 13 of Ref. 4), as
shown below.

\[
\mu_{\alpha}(F) = \mu_{\alpha}^{0} + \alpha_{\alpha\beta}(-\omega_{s};\omega_{s}) F_{\beta} + \frac{1}{2!} \beta_{\alpha\beta\gamma}(-\omega_{s};\omega_{1},\omega_{2}) F_{\beta} F_{\gamma} + \frac{1}{3!} \gamma_{\alpha\beta\gamma\delta}(-\omega_{s};\omega_{1},\omega_{2},\omega_{3}) F_{\beta} F_{\gamma} F_{\delta} + \ldots
\]  

(2.8)

In Eq. 2.8 the dipole moment of the system (\(\mu_{\alpha}(F)\)) is determined in the presence of an electric field \(F\). For the repeated indices \(\alpha, \beta, \gamma, \ldots\), which define the Cartesian axes of the molecular reference frame, we make use of Einstein summation convention. The specific quantities in the Taylor series expansion are the permanent dipole moment \(\mu_{\alpha}^{0}\), polarizability \(\alpha_{\alpha\beta}\), first hyperpolarizability \(\beta_{\alpha\beta\gamma}\), and second hyperpolarizability \(\gamma_{\alpha\beta\gamma\delta}\).

Based on the expansion in the electric fields it is possible to associate the quantities in Eq. 2.8 various molecular optical properties. Taking derivatives of \(\mu_{\alpha}(F)\) gives

\[
\left( \frac{\partial \mu_{\alpha}(F)}{\partial F_{\beta}} \right)_{F=0} = \alpha_{\alpha\beta}(-\omega_{s};\omega_{s})
\]  

(2.9)

\[
\left( \frac{\partial^{2} \mu_{\alpha}(F)}{\partial F_{\beta} \partial F_{\gamma}} \right)_{F=0} = \frac{1}{2!} \beta_{\alpha\beta\gamma}(-\omega_{s};\omega_{1},\omega_{2})
\]  

(2.10)

\[
\left( \frac{\partial^{3} \mu_{\alpha}(F)}{\partial F_{\beta} \partial F_{\gamma} \partial F_{\delta}} \right)_{F=0} = \frac{1}{3!} \gamma_{\alpha\beta\gamma\delta}(-\omega_{s};\omega_{1},\omega_{2},\omega_{3})
\]  

(2.11)

From Eqs. 2.9, 2.10 and 2.11 it becomes clear that the polarizability, first hyperpolarizability, and second hyperpolarizability describe different processes based on the number of associated electric fields. Specifically, the polarizability of a molecule is related to one-photon absorption and Raman scattering, the first hyperpolarizability allows quantification of second-harmonic generation and hyper-Raman scattering, and the second hyperpolarizablility defines two-photon absorption and second hyper-Raman scattering.\(^{4,79,83,84}\)

Linear and nonlinear optical processes have advantages and disadvantages when compared with each other. Detection of linear optical properties benefits from their are relatively large intensity. For instance, in consistent units, the orders of magnitude of elements of \(\alpha_{\alpha\beta}\), \(\beta_{\alpha\beta\gamma}\), and \(\gamma_{\alpha\beta\gamma\delta}\) are \(10^{-40} C^{2} m^{2} J^{-1}\), \(10^{-50} C^{3} m^{3} J^{-2}\), and \(10^{-61} C^{4} m^{4} J^{-3}\), respectively.\(^{4}\) Measurement of quantities that depend on the first and second hyperpolarizabilities is therefore hindered significantly by whether a high intensity laser source can be used. Owing to the need for high intensity laser sources, nonlinear optical linear processes are less widely employed than their linear counterparts. However, non-
linear optical processes benefit from many advantages. The most significant advantages are easier discrimination against interfering signals, decreased risk of photodamage and photobleaching of the sample, and greater spatial resolution.\textsuperscript{85,86} Furthermore, because biological samples absorb and scatter light less efficiently in the region of 700-1000 nm,\textsuperscript{87,88} the higher wavelength photons used to measure nonlinear optical properties allow for deeper penetration into those samples than the with linear optical processes.\textsuperscript{89,90}

The remainder of this overview describes relevant examples of linear and nonlinear optical processes. Examples for the linear optical processes are one-photon absorption and resonance Raman scattering. The important nonlinear optical processes are two-photon absorption and resonance hyper-Raman scattering.

\section*{2.3 One-Photon Absorption and Resonance Raman Scattering}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure2.1}
\caption{Diagram of one-photon absorption (left) and an example of a one-photon absorption spectrum (right). $|0\rangle$ is the ground electronic state, $|j\rangle$ is an electronic excited state, and $\hbar \omega_L$ is the energy of the incident photon. Green dashed lines are vibrational levels of state $|j\rangle$.}
\end{figure}

One-photon absorption (OPA), or ultraviolet-visible spectroscopy as it is often called, is an integral part of many other linear optical processes such as resonance Raman scattering or fluorescence. OPA occurs when a material is irradiated with photons equal to the electronic excitation energy ($E^{j0}$), allowing absorption of the photon energy. A typical OPA spectrum and diagram of the process are shown in Figure 2.1. Due to its
long and rich history, there are too many studies involving OPA to discuss here. However, some relevant experimental and theoretical works are summarized to give perspective on the importance and limitations of this technique. It is also important to note the relationship between the OPA cross section ($\sigma_{OPA}$) and the polarizability ($\alpha$)

$$\sigma_{OPA} \propto \omega_L \langle \text{Im}[\alpha] \rangle$$  \hspace{1cm} (2.12)

In Eq. 2.12, $\omega_L$ is the incident frequency of the photon shone on the molecule and $\langle \rangle$ denotes orientational averaging.

Most of the earliest work on simulating absorption spectra focused on the bandshape. It is well known that the shape of an absorption spectrum for a small molecule in the gas phase exhibits vibrational features that are broadened when the spectrum is collected for the same molecule in a condensed phase.\textsuperscript{91,92} This difference is largely attributed to two factors: homogeneous broadening and inhomogeneous broadening. While homogeneous broadening is any mechanism that broadens the spectrum of a single molecule (for instance, the lifetime of the excited state), inhomogeneous broadening results from each molecule in an ensemble experiencing a different environment.\textsuperscript{5} Models for describing absorption spectra generally involve accounting for changes in the molecule’s geometry and how that impacts the absorption peak shape. A commonly employed method to obtain absorption peak shapes is the vibronic model, where vibrational-electronic coupling constants are determined and used to evaluate vibrational overlap integrals. Generally the overlap integrals are evaluated in the harmonic oscillator approximation because it is straightforward to integrate those functions analytically, and the normal modes are assumed to be uncoupled. This approximation is usually called the independent-mode, displaced harmonic oscillator (IMDHO) model.\textsuperscript{93} Early studies using those models examined gas phase and solution phase spectra of conjugated molecules\textsuperscript{94–99} and small molecules like CS\textsubscript{2} and SO\textsubscript{2}.\textsuperscript{92,100}

One problem with using OPA alone is that absorption spectra do not uniquely characterize molecules. For many molecules, the absorption bandshape is Gaussian-like so the only distinguishing feature may be the excitation energy. Furthermore, it is possible to have multiple excited states contributing to a single absorption peak, which has been demonstrated for several molecules and interpreted by including other spectroscopies for detailed analysis.\textsuperscript{101–108} The presence of multiple excited states is challenging to resolve using OPA alone and therefore a complementary technique, such as resonance Raman
Vibrational Raman scattering involves the inelastic scattering of light, occurring when a molecule absorbs photons from the incident radiation with frequency $\omega_L$ and scatters radiation with frequency $\omega_s = \omega_L \pm \omega_v$, where $\omega_v$ corresponds to the vibrational frequency of a molecular normal mode. This technique was first discovered in 1928 by Raman and Krishnan.\textsuperscript{109,110} For an intensity comparison, Raman scattering is usually compared with the more efficient fluorescence process. Raman scattering is a very weak process with cross sections on the order of $10^{-30}$ cm$^2$/molecule, whereas fluorescence has a cross section of $\sim10^{-16}$ cm$^2$/molecule.\textsuperscript{20} Although it was possible to detect small molecules in the gas phase without intense laser sources,\textsuperscript{111} the low signal intensity is restrictive for detecting Raman scattering of molecules in solution. When the laser wavelength is tuned to the excitation energy of the molecule, \textit{resonance} enhancement occurs and the technique is then called resonance Raman scattering (RRS). RRS is more sensitive than Raman scattering, owing to the enhancement of symmetric vibrations on the order of $10^2$ to $10^6$.\textsuperscript{112–114} Figure 2.2 diagrams the RRS process, and illustrates the relationship...
between RRS and OPA.

RRS has been used in many applications, including examinations of substrate binding to proteins,\textsuperscript{115–118} interpretation of electron transfer events,\textsuperscript{107,119–123} and studies of solvation dynamics.\textsuperscript{6,124–128} A large complement of accurate theoretical methods for simulating RRS have been developed,\textsuperscript{94,95,129–133} allowing for interpretation of the experimental spectra. Although many models for RRS exist, the general framework is based on the expressions derived by Albrecht and coworkers.\textsuperscript{134–136} Albrecht’s framework involves inspection of the expression for the polarizability of a molecule when the Born-Oppenheimer approximation is used to separate each molecular state into a product of electronic and vibrational wavefunctions

\[
\alpha_{\alpha\beta} = \sum_{J,j} \left[ \frac{\langle F_0 | \mu_{\alpha}^{0j} | J_j \rangle \langle J_j | \mu_{\beta}^{0j} | I_0 \rangle}{E_{J_j} - E_{I_0} - \omega - i\Gamma_j} + \frac{\langle F_0 | \mu_{\alpha}^{0j} | J_j \rangle \langle J_j | \mu_{\beta}^{0j} | I_0 \rangle}{E_{J_j} - E_{I_0} + \omega - i\Gamma_j} \right] \tag{2.13}
\]

In Eq. 2.13, \(|j\rangle\) is the excited electronic state, \(|0\rangle\) is the ground electronic state, \(|J\rangle\) is an intermediate vibrational level in excited state \(j\), \(|I_0\rangle\) and \(|F_0\rangle\) are the initial and final vibrational levels in the ground state, \(E_{J_j}\) is the energy of state \(|J\rangle\), \(E_{I_0}\) is the energy of state \(|I_0\rangle\), and \(\Gamma_j\) is the homogeneous broadening parameter. The quantities \(\mu_{\alpha}^{0j} = \langle 0 | \mu_{\alpha} | j \rangle\) are the transition dipole moments for the transition \(j \leftarrow 0\). The resonance condition occurs when \(E_{J_j} - E_{I_0} = \omega\), and we can safely neglect the second term in Eq. 2.13 in this circumstance. The final step in the development of the theory of RRS is to do a Taylor series expansion of the transition dipole moment with respect to the normal modes. This results in

\[
\alpha_{\alpha\beta} = \sum_{J,j} \frac{\langle F_0 | (\mu_{\alpha}^{0j})^{eq} + \sum_a \left( \frac{\partial \mu_{\alpha}^{0j}}{\partial Q_a} \right) Q_a + \cdots | J_j \rangle \langle J_j | (\mu_{\beta}^{0j})^{eq} + \sum_b \left( \frac{\partial \mu_{\beta}^{0j}}{\partial Q_b} \right) Q_b + \cdots | I_0 \rangle}{E_{J_j} - E_{I_0} - \omega - i\Gamma_j} \tag{2.14}
\]

The transition dipole moment at the equilibrium position is denoted \((\mu_{\alpha}^{0j})^{eq}\), and normal coordinates are \(Q_a\) and \(Q_b\), where \(a\) and \(b\) refer to the normal modes. Scrutiny of Eq. 2.14 shows that it can be written based on individual terms

\[
A_{\alpha\beta} = \sum_{J,j} (\mu_{\alpha}^{0j})^{eq} (\mu_{\beta}^{0j})^{eq} \frac{\langle F_0 | J_j \rangle \langle J_j | I_0 \rangle}{E_{J_j} - E_{I_0} - \omega - i\Gamma_j} \tag{2.15}
\]
\[ B_{\alpha\beta} = \sum_{J,j} (\mu_0^j)^{eq} \sum_{b} \left( \frac{\partial \mu_0^j}{\partial Q_b} \right) \frac{\langle F_0 | J_j \rangle \langle J_j | Q_b | I_0 \rangle}{E_j - E_{I_0} - \omega - i\Gamma_j} \]

\[ + \sum_{J,j} \sum_{a} \left( \frac{\partial \mu_0^j}{\partial Q_a} \right) (\mu_0^j)^{eq} \frac{\langle F_0 | Q_a | J_j \rangle \langle J_j | I_0 \rangle}{E_j - E_{I_0} - \omega - i\Gamma_j} \]  
\[ \tag{2.16} \]

\[ C_{\alpha\beta} = \sum_{J,j} \sum_{a} \left( \frac{\partial \mu_0^j}{\partial Q_a} \right) \sum_{b} \left( \frac{\partial \mu_0^j}{\partial Q_b} \right) \frac{\langle F_0 | Q_a | J_j \rangle \langle J_j | Q_b | I_0 \rangle}{E_j - E_{I_0} - \omega - i\Gamma_j} \]  
\[ \tag{2.17} \]

\[ \alpha_{\alpha\beta} = A_{\alpha\beta} + B_{\alpha\beta} + C_{\alpha\beta} + \ldots \]  
\[ \tag{2.18} \]

where \( A_{\alpha\beta} \) is the Franck-Condon term, \( B_{\alpha\beta} \) is the first Herzberg-Teller term, and \( C_{\alpha\beta} \) is the second Herzberg-Teller term. When a transition \( j \leftarrow 0 \) is strongly allowed, meaning \((\mu_0^j)^{eq}\) is large, it is expected that the A-term is the most significant. In cases involving weakly allowed states\textsuperscript{137} and nonresonant conditions,\textsuperscript{138} the B- and C-terms become important. After the polarizability is determined, a RRS spectrum can be evaluated using the squared modulus of the transition polarizability based on Eq. 2.19.

\[ I_{\text{RRS}} \propto \omega_j^4 |\alpha|^2 \]  
\[ \tag{2.19} \]

RRS is not without limitations. One of the largest interferences in RRS is fluorescence. Although it is possible in many cases to “correct” the RRS spectrum for broad background fluorescence (see, for instance, Figures 6 and 8 in Ref. 1), this can decrease the quality of the RRS spectrum. Because many of the strongest Raman scatterers are also fluorescent dyes, this introduces a complicated problem. A common method for reducing background fluorescence involves taking Raman spectra of molecules near roughened metal surfaces, in a technique called surface-enhanced Raman scattering (SERS).\textsuperscript{139–142} Surface enhancement substantially improves the sensitivity of Raman scattering and can be combined with RRS for significant enhancement of the Raman scattering signal. Further information on SERS can be found in Refs. 18,142–145.
2.4 Two-Photon Absorption

Two-photon absorption (TPA) is the simultaneous absorption of two photons that results in an electronic transition \( j \leftarrow 0 \). This process is drawn in Figure 2.3. By comparing the spectra presented in Figures 2.1 and 2.3, it is clear that OPA and TPA spectra may look very different. Furthermore, the \( 2 \leftarrow 0 \) transition is forbidden in OPA while it is clearly allowed in TPA. This demonstrates that TPA can probe different excitations than OPA. The likelihood of absorbing two photons simultaneously is related to the two-photon absorption cross section \( \sigma_{TPA} \), which is defined in Eq. 2.20.

\[
\sigma_{TPA} \propto \omega_L^2 \langle \text{Im}[\gamma] \rangle
\]  

Historically, TPA was first predicted in 1931 by Göppert-Mayer\textsuperscript{146} and demonstrated experimentally for various systems 30 years later.\textsuperscript{147-153} Interest in this technique grew with the development of two-photon excited fluorescence microscopy\textsuperscript{154} and the diverse applications of TPA and other nonlinear optical properties.\textsuperscript{155}

 Much like OPA is the initial step in many linear optical processes, TPA initiates numerous nonlinear optical properties depending on the absorption of two photons. TPA
can be used for photodynamic therapy, microfabrication, optical power limiting, and three-dimensional optical data storage. The only limitation of TPA involves the low probability of occurrence because the absorption of two photons usually relies on a transition through an intermediate virtual state. For a molecule absorbing at 350 nm (\(\sim 28000 \text{ cm}^{-1}\)), the lifetime of an intermediate virtual state is \(\sim 10^{-15}\) seconds compared to \(\sim 10^{-8}\) seconds for allowed molecular transitions, meaning that TPA must occur on a very short timescale. Resulting from the short lifetime of virtual states and the requirement that two photons be in the same area simultaneously, the cross sections observed for TPA are small values on the order of \(10^{-50}\) cm\(^4\) sec photon\(^{-1}\). Designing optimal chromophores with large TPA cross sections is therefore an important field for applications of nonlinear optical properties.

Development of theory for TPA is a less mature field than for linear optical properties. Early theoretical efforts by the groups of Peticolas and McClain were instrumental for relating the complicated quantum mechanical expressions involved in calculating two-photon transition probabilities to related quantities for one-photon processes and illustrating how the orientationally averaged TPA can be determined for an ensemble. TPA was also shown to be capable of determining symmetry of electronic states and for locating electronic states that are forbidden in OPA spectra. Calculations of TPA cross sections from first principles methods are mostly attributed to the work of Jørgensen, Ågren and coworkers. Semi-empirical methods have also been employed successfully for studying TPA cross sections. Only recently it has become possible to calculate TPA cross sections from first principles calculations where resonance exists with an intermediate one-photon state and the final two-photon accessible state. This intermediate state resonance effect has been demonstrated to increase the sensitivity of TPA by several orders of magnitude and may be a future direction where theory can assist the design of TPA chromophores.

### 2.5 Resonance Hyper-Raman Scattering

Resonance hyper-Raman scattering (RHRS) involves the inelastic scattering of light, occurring when a molecule absorbs two photons at its excitation energy from the incident radiation with frequency \(2\omega_L\) and scatters radiation with frequency \(\omega_s = 2\omega_L \pm \omega_v\), where \(\omega_v\) corresponds to the vibrational frequency of a molecular normal mode. A RHRS spectrum, in relation to the TPA spectrum, is shown in Figure 2.4 alongside a diagram of the RHRS process. The first experimental observation of nonresonant hyper-Raman scatter-
Figure 2.4. Diagram of resonance hyper-Raman scattering (left). $|0\rangle$ is the ground electronic state, $|j\rangle$ is an electronic excited state, $\hbar \omega_L$ is the energy of the incident photon, and $\hbar \omega_s$ is the energy of the scattered photon. Orange dashed lines are vibrational levels of state $|0\rangle$, and blue dashed lines indicate the position of a virtual energy level. The right image shows the relationship between incident photon energy and the two-photon absorption spectrum, and an example of a resonance hyper-Raman spectrum.

From the perspective of theory, initial work on hyper-Raman scattering involved examining the selection rules\textsuperscript{205,206} and investigation of the formulas for the frequency-dependent first hyperpolarizability under nonresonant and resonant conditions.\textsuperscript{207} The work of Ziegler and coworkers\textsuperscript{208} was instrumental in the analysis of RHRS spectra. In this model, the first hyperpolarizability is written

$$\beta_{\alpha\beta\gamma} = A_{\alpha\beta\gamma} + B_{\alpha\beta\gamma} + C_{\alpha\beta\gamma} + \ldots$$  \hspace{1cm} (2.21)
where the A-term is the Franck-Condon term, the B-term is the first Herzberg-Teller term, and the C-term is the second Herzberg-Teller term. This expression is the RHRS equivalent to Albrecht’s expressions for the vibronic theory of RRS. Using the transition first hyperpolarizability, the intensity of RHRS can be determined as

\[ I_{\text{RHRS}} \propto \omega_s^4 |\beta|^2 \]  

The vibronic approach to RHRS has been investigated largely for conjugated molecules with electron donating and accepting groups.\textsuperscript{209-213} Non-Condon effects have also been described for RHRS of zinc phthalocyanine\textsuperscript{214} and systems with intermediate, near-resonant, one-photon states.\textsuperscript{215}

Much like RRS, RHRS suffers from interferences from fluorescence. Also, it has been demonstrated by Ziegler that nonresonant hyper-Raman is approximately 5 or 6 orders of magnitude smaller than nonresonant Raman.\textsuperscript{214} Surface-enhanced hyper-Raman scattering (SEHRS), where a molecule is adsorbed to a roughened metal surface, can significantly intensify the hyper-Raman signal and simultaneously quench two-photon excited fluorescence. SEHRS is described in Section 2.7.1.
2.6 Enhanced absorption of molecules near metal clusters

The plasmon resonance of metal nanoparticles has important consequences when molecules are near the metal surface. Large electric fields in proximity of the metal nanoparticle, brought about by surface plasmon resonances, lead to dramatic enhancements in the optical response of molecules. When a molecule interacts with electromagnetic radiation, absorption of photons can occur. Relevant research in the field of enhanced absorption processes is divided into two areas characterizing electronic excitations and vibrational excitations. Modeling these processes is fundamental for investigations of other surface-enhanced spectroscopies. Therefore, developing methods that can resolve the electronic structure of molecules based on linear absorption represents an important first step to understand more complicated optical properties.

2.6.1 Enhanced electronic excitations

Enhancement of electronic excitations (or more generally, surface-enhanced absorption) involves a phenomenon where molecules near a metal nanoparticle or small metal cluster scaffolds experience a greater capacity to absorb photons. Enhanced absorption was first reported for the dyes rhodamine B and nile blue on Au and Cu films by Glass et al. Garoff et al. expanded on that work to examine the absorption of rhodamine 6G on silver-island films using both measured spectra and analysis using Mie theory. Application of the theory in that work allowed for the analysis of distribution of energy absorbed from the incident radiation between the silver film and dye molecule. Craighead and Glass applied the effective-medium theory of Garnett in a study that allowed the authors to characterize the observed splitting of the plasmon resonance of silver resulting from adsorption of dyes on the surface. This section overviews investigations that describe enhanced absorption for species both chemisorbed and physisorbed to metal surfaces.

DFT and TDDFT have been applied to study tryptophan-silver cluster systems as well as complexes of both di- and tri-peptides with silver clusters. These investigations demonstrate that the optical properties of the complex are associated with charge-transfer in both directions between the molecule and metal. This indicates that the enhanced absorption results from strong electronic interactions between both parts of the complex. Bonding between the metal cluster and biomolecules also results in complicated electronic structure, as demonstrated by the analysis presented by Compagnon et al.
Corni and Tomasi\textsuperscript{225} studied enhancements of the polarizability of merocyanine dyes physisorbed to silver and copper nanoparticles with various shapes. In this model, the molecules were represented using Hartree-Fock (HF) theory, while the metal nanoparticles were described using their dielectric functions. It was shown that the imaginary part of the molecular polarizability is enhanced in this method, resulting in an increased absorption for the molecule when it is near a metal nanoparticle. Furthermore, the authors find that the image field generated by the molecule-induced metal polarization has a much smaller effect on the molecular polarizability than the reflected field of the metal. In Figure 2.5, the absorbance cross section is plotted for 20 Å silver nanoparticles with and without dye molecules surrounding them. When the dye molecules were adsorbed to the silver nanoparticles, an increase in the absorbance of the metal nanoparticles themselves and a small red shift in the absorbance maximum were observed as well.

![Figure 2.5](image)

**Figure 2.5.** Absorbance cross section of 20 Å silver nanoparticles that are uncoated (a), coated with 20 molecules of the merocyanine dye H$_2$NCH=CHCHO (b), and coated with 20 molecules of the merocyanine dye H$_2$N(CH=CH)$_2$CHO (c). Reprinted from Ref. \textsuperscript{225}.

Morton and Jensen\textsuperscript{226} examined the linear response of rhodamine 6G (R6G) and crystal violet (CV) physisorbed to quasi-spherical gold and silver nanoparticles. Their model included a quantum mechanical description of the molecule using TDDFT and an atomistic representation of the nanoparticle based on the capacitance-polarizability interaction model.\textsuperscript{227,228} For the strongest molecular excitation of both molecules, it was demonstrated that the metal nanoparticle causes an increase in oscillator strength of 10–20%. The shift of the excitation energy with respect to the excitation energy of the free molecule as a function of distance between the molecule and nanoparticle is shown.
in Figure 2.6. Because the electric field of the metal nanoparticle decays quickly as the
distance from its surface is increased, the convergence of the molecular excitation energy
as distance from the metal surface is increased follows physical intuition. This work
also discussed how orientation of the molecule on the surface and adsorption site on the
nanoparticle affect the excitation energy and oscillator strength for different excitations.

Figure 2.6. Shift in the wavelength ($\delta \lambda = \lambda(R = x) - \lambda(R = \infty)$) in the excitation energies for
the two strongest excitations for R6G on Ag$_{2057}$ (blue dots and red squares) and CV on Au$_{2057}$
(blue diamonds and red triangles). The distance $R = 0$ defines the equilibrium position for the
two molecules with respect to the nanoparticle. Reprinted from Ref. 226.

Numerous other studies have described interactions of molecules with metal nano-
structures. Arcisauskaite et al.\textsuperscript{229} applied a quantum mechanical/molecular mechanical
method (QM/MM) to study charge transfer excitation energies for pyridine–silver com-
plexes using the CAM-B3LYP exchange-correlation functional.\textsuperscript{71} This study concluded
that the charge transfer excitation energies were more strongly perturbed by silver atoms
near the metal surface. Jørgensen et al.\textsuperscript{230} described a multiconfigurational self-consistent
reaction field (MCSCRF) method applied to the linear response of CO near a metal sur-
face represented as a perfect conductor. The authors examined the lowest four excitations
of CO, noting that the excitation energies shift and that transition dipole moments may
increase or decrease depending both on the distance between the molecule and surface
and the metal’s dielectric constant. Lopata and Neuhauser\textsuperscript{231} studied the interactions of
a polar molecule with an array of collinear spherical gold nanoparticles with a split field
finite-difference time-domain (FDTD) random phase approximation (RPA) approach.
Comparing results when the molecule is present to when it was absent indicated that the molecule scatters incident energy transferred between the nanoparticles, and also that the molecule enhances the electric field between nanoparticles. Masiello and Schatz applied a many-body Green’s function approach with TDDFT to study the adsorption of pyridine on silver nanoparticles of various shapes. This study demonstrates that varying the nanoparticle shape, local surface plasmon resonance, and molecule-metal orientation and separation shifts molecular excitation energies and changes the molecule’s polarizability. Corni and Tomasi studied the interactions between molecules and a metal surface, along with how the excitation energies change when a solvent modeled including the Polarizable Continuum Model (PCM) was used. Inclusion of representations of both the metal nanoparticle and solvent environment is an important step in comparing theoretical models to experimental results, so that enhanced spectroscopies may be understood.

Recent work by Chen et al. has indicated that a hybrid method, involving a quantum mechanical description of a molecule with real-time TDDFT and classical electrodynamics description of a metal nanoparticle, can account for enhanced absorption of molecules near a nanoparticle. Using the N3 dye, it was shown that the model accounts for the strongest enhancement of absorption as the molecule is closer to the surface. Interestingly, binding the metal nanoparticle changed the relative intensities of different molecular absorption peaks.

2.6.2 Surface-enhanced Infrared Absorption

Surface-enhanced infrared absorption (SEIRA) is a technique where molecular absorption of infrared photons is enhanced in proximity to nanostructured metal surfaces. The first SEIRA investigation was performed by Hartstein et al. for molecular monolayers coated with either Ag or Au metal films in an attenuated-total-reflection (ATR) geometry. It was demonstrated that each molecule studied (4-nitrobenzoic acid, benzoic acid, and 4-pyridinecarboxylic acid) had the same enhancement of their IR spectra on the order of $10^4$. This finding indicated that the enhancement was not from a chemical mechanism, but rather from plasmon resonances of the metal deposited on the monolayers.

A general review of SEIRA that describes many experimental studies not discussed here was presented by Osawa nearly 10 years ago. SEIRA has been investigated on nonmetallic substrates such as silver halide fibers and dielectric nanoparticles of Al$_2$O$_3$ and SiC. Xue et al. used SEIRA to characterize bonding orientations of p-nitrobenzoate to a Pt surface, and also examined the electrooxidation reaction of methanol involved in direct methanol fuel cells. Nishikawa et al. studied the effects
of low reflective substrates for characterizing organic films, finding that the best SEIRA signals were obtained for those substrates with low refractive indices. Other SEIRA studies have focused on detection of biomolecules\textsuperscript{241–243} and examining electrochemical reactions, such as the reduction of nitrite.\textsuperscript{244}

One feature that is generally observed is the asymmetric peak shape of different normal modes on the SEIRA spectrum.\textsuperscript{245–251} Krauth \textit{et al.} examined asymmetric line shapes of the modes of CO adsorbed to iron films coated on MgO(001) surfaces.\textsuperscript{245} The observed Fano-like line shape\textsuperscript{252} for the main IR absorbance line has been explained by resonance of the vibrations of CO and electronic transitions between the metal and CO molecule, by applying the electron-hole pair model of Langreth.\textsuperscript{253,254} However, it should be noted that this band asymmetry has been shown to occur for molecules such as n-heptane\textsuperscript{249} that can only physisorb to a metal surface, meaning the chemical mechanism does not necessarily cause the Fano-like line shape.

Persson and Ryberg applied the coherent potential approximation (CPA) to study the chemical enhancement mechanism of SEIRA for disordered monolayers of isotopic mixtures of CO on Cu(100) surfaces.\textsuperscript{255} In this model, vibrating molecules were allowed to interact with each other via oscillating dipole fields. Comparisons between the model and experimental data showed that good agreement exists for the surface coverage-dependent frequency shifts and integrated peak absorptance, which validated the model. Estimates of the chemical enhancement resulted from an increase in the dynamic dipole moment by a factor of 2–3, attributed to charge oscillations between the orbitals of the CO molecule and metal.

Corni and Tomasi\textsuperscript{256} have simulated SEIRA spectra using DFT for p-nitrobenzoate. IR spectra were calculated for molecular orientations perpendicular to the metal surface and tangential to it as well, and were subsequently compared to SEIRA spectra measured by Osawa and Ikeda.\textsuperscript{257} The calculated spectrum for molecules oriented perpendicular to the surface is shown in Figure 2.7. Comparison of the different orientations of the p-nitrobenzoate on the metal surface indicated that perpendicular molecules absorb more strongly than those that are tangential. The authors stress that this does not mean that all of the molecules are perpendicular to the surface, though.
Figure 2.7. Simulated (“calc.”) SEIRA spectrum for p-nitrobenzoate on a spherical 2 nm conductor and measured (“exp.”) SEIRA spectrum for p-nitrobenzoate on 4 nm thick silver-island film from Ref. 257. Calculated spectrum is for the perpendicular orientation of p-nitrobenzoate on the metal surface. Reprinted from Ref. 256.
2.7 Enhanced Nonlinear Optical Properties by Metal Surfaces

Studies of nonlinear optical properties (i.e., two-photon absorbance, two-photon absorbance followed by fluorescence, second and third harmonic generation, four-wave mixing) of molecules near metal nanoparticles and of the metal nanoparticles themselves have been examined. Experiments have been performed that characterize hyper Rayleigh scattering of spatially well-defined gold nanoparticle arrays \(^{258}\) and enhancements of the third-order nonlinear susceptibility of donor-\(\pi\)-acceptor chromophores on silver nanoparticles. \(^{259}\) Ramakrishna \textit{et al.} \(^{260}\) explored two-photon absorbance for gold clusters in the size regime between Au\(_{25}\) (1.1 nm) and Au\(_{2406}\) (4 nm). Two-photon cross section results for that study are shown in Figure 2.8. It was observed that a singularity exists for plots of the absolute two-photon cross section as the size increases, which was attributed to the transition between the discrete electronic structure behavior of clusters to the nanoparticle behavior involving surface plasmon resonance. Amendola \textit{et al.} \(^{261}\) studied the stability of nonlinear absorbance measurements of gold nanoparticles with zinc phthalocyanines present during irradiation with intense laser pulses. Zinc phthalocyanines were shown to promote self-healing of the gold nanoparticles which was indicated by the stability and reproducibility of optical limiting measurements over time. In contrast, unexposed gold nanoparticles underwent fragmentation that was confirmed with optical limiting and UV–vis measurements, which demonstrates that it is possible to maintain the signal of nonlinear processes when intense sources are used.

![Figure 2.8](image-url)

**Figure 2.8.** Measured absolute two-photon absorption cross sections (a) and two-photon absorption cross sections per gold atom in the cluster (b), in units of Goeppert-Mayer (GM). Reprinted from Ref. 260.

Other research groups have examined the nonlinear optical properties of nanoparticle
aggregates. Nonlinear susceptibilities for large fractal metal clusters were investigated by Shalaev et al.,\textsuperscript{262,263} where numerical simulations of optical response properties were performed to better understand the enhancements involved in several nonlinear processes. Zhang and Stroud\textsuperscript{264} examined nonlinear susceptibilities using an effective-medium approximation, demonstrating that a large enhancement of the nonlinear susceptibility occurs near the gold plasmon resonance for Au core particles surrounded by a dielectric medium.

Prasad and collaborators\textsuperscript{265} investigated the third-order response of para-nitroaniline (PNA) near tetrahedral Au\textsubscript{4} and Au\textsubscript{20} clusters using DFT. In this work, data was compared between the exchange-correlation functionals PBE\textsuperscript{53} and CAM-B3LYP.\textsuperscript{71} Large second hyperpolarizabilities ($\gamma_{av}$) were calculated for systems where PNA was placed near the metal clusters, and it was demonstrated that these enhancements quickly decrease as the PNA-metal cluster distance is increased. This distance dependence indicated that a charge-transfer mechanism was responsible for the increased second hyperpolarizability of the complex. It was also established that the results from CAM-B3LYP and PBE were not consistent (i.e. $\gamma_{av}$ calculated from PBE for PNA near the face of an Au\textsubscript{20} tetrahedron was $4.53 \times 10^7$ a.u., whereas CAM-B3LYP found it to be $6.33 \times 10^6$ a.u. for a PNA dimer linked through an Au\textsubscript{20} tetrahedron). This was attributed to a numerical divergence in the results from the PBE functional, possibly resulting from a resonance near the wavelength used to calculate $\gamma_{av}$ that may be corrected for using damping in the calculations.

A recent thorough examination by Day et al. of the optical properties gold clusters and gold thiolated clusters was performed using DFT and coupled cluster theory.\textsuperscript{266} When examining the two photon absorption cross sections, a strong dependence on the DFT functional chosen was observed. The authors also demonstrated that the optimized geometry, which depends on the DFT functional, can lead to large differences in the optical properties for these clusters.

### 2.7.1 Surface-enhanced Hyper-Raman Scattering

Surface-enhanced hyper Raman scattering (SEHRS) is the two-photon analogue of surface-enhanced Raman scattering (SERS) in which the scattering signal is shifted relative to the second harmonic of the incident radiation ($\omega_{s} = 2\omega_{L} - \omega_{k}$, where $\omega_{k}$ is the vibrational frequency). SEHRS has predominantly been applied to characterize electronic structure of molecules by comparing to the more established SERS process.\textsuperscript{26,28,267–274} Hulteen et al.\textsuperscript{275} demonstrated that SEHRS for trans-1,2-bis(4-pyridyl)ethylene was
more sensitive to applied potential than SERS, and that only SEHRS was able to detect changes in $\Delta G_{\text{abs}}$ and presence of coadsorbed anions that change the surface environment. Other specific applications have included detection of biological molecules\textsuperscript{276,277} and investigations of chemical reactions on metal surfaces.\textsuperscript{278,279} The effect of the substrate on SEHRS spectra\textsuperscript{280–283} has been examined as well, and spectra have been measured using continuous-wave near-infrared lasers instead of more commonly used mode-locked lasers.\textsuperscript{284} While studies involving SEHRS are numerous, there are relatively few that apply theory.

The first SEHRS study was performed by Murphy \textit{et al.}\textsuperscript{285} in which $\text{SO}_3^-$ molecules were adsorbed on Ag powder. The SEHRS spectrum at 1064 nm excitation exhibited two $a_1$ symmetry modes that coincided with those measured using SERS at 514.5 nm excitation. It was observed that the hyper-Raman signal intensity decreased with time, attributed to morphological changes induced by the laser. An estimate of the enhancement factor for SEHRS was not possible with this work, which motivated future research to incorporate electronic structure calculations and elucidate this enhancement in comparison to the better understood SERS enhancement.

Golab \textit{et al.}\textsuperscript{286} investigated the SEHRS enhancement of pyridine adsorbed to roughened Ag electrodes in a detailed experimental and theoretical study. Excitation of the pyridine molecule involved a mode-locked Nd:YAG laser, allowing for measurements of SERS and SEHRS spectra. Both the SERS and SEHRS spectra had nearly the same dominant peaks, even though the SEHRS spectrum was significantly less intense than the SERS spectrum. However, the most intense peak on the SERS and SEHRS spectra differed, and relative peak intensities were shown to vary between the two methods.

Calculations in this study were performed using the $\pi$-electron model Hamiltonian of Pariser, Parr, and Pople (PPP) to determine the transition polarizability ($\alpha_{ij}$) and first hyperpolarizability ($\beta_{ijk}$) required to simulate Raman and hyper-Raman scattering, respectively. Surface atoms were not explicitly modeled. Instead, calculations of SERS and SEHRS spectra include only the elements of $\alpha_{ij}$ and $\beta_{ijk}$ perpendicular to the “surface” (here assumed to be the $y$-direction), with pyridine oriented perpendicular to the surface with the N atom down. It was demonstrated that the calculations yielded good agreement with measured spectra for relative peak intensities. Results for the simulations of the pyridine SEHRS spectrum compared to the measured SEHRS spectrum are shown in Figure 2.9. One very interesting finding was that when pyridine is tilted $15^\circ$ relative to the surface normal, the SERS spectrum remained nearly identical to when pyridine was oriented along the surface normal, but the SEHRS spectrum changes such that several $B_2$
symmetry bands gain significant intensity. It was judged that SEHRS is more sensitive to molecular orientation on the surface than SERS as a result.

Figure 2.9. Simulated bulk hyper-Raman spectrum (a), simulated SEHRS spectrum (b), and measured SEHRS spectrum (c) of pyridine at 1064 nm. Reprinted from Ref. 286.

An additional feature of this paper was the determination of the SEHRS enhancement factor. The enhancement factor was determined as

$$\frac{I_{\text{sr}}}{I_{\text{bulk}}^{\text{HR}}} = \left( \frac{I_{\text{sr}}}{I_{\text{R}}} \right) \left( \frac{I_{\text{sr}}}{I_{\text{HR}}} \right) \left( \frac{I_{\text{bulk}}^{\text{HR}}}{I_{\text{bulk}}^{\text{R}}} \right)^{-1}$$ (2.23)

On the right side of the equation, the first term is the SERS enhancement factor taken to be $10^6$. The second term was evaluated using the measured SERS and SEHRS spectra and found to be $4.6 \times 10^{-4}$, while the final term was determined using the PPP calculations for $I_{\text{HR}}^{\text{bulk}} / I_{\text{R}}^{\text{bulk}}$ and found to be $1.05 \times 10^{-11}$. Overall, the enhancement factor
in this study is $10^{13}$ for SEHRS compared to the $10^6$ for SERS, attributed primarily to increased chemical effects for hyper-Raman scattering compared to Raman scattering.

Yang and Schatz\textsuperscript{287} further investigated the enhancement factor of SEHRS, using more rigorous Hartree-Fock (HF) and Zerner’s intermediate neglect of differential overlap (ZINDO) methods to evaluate $\alpha_{ij}$ and $\beta_{ijk}$. Like the previous study by Golab et al., the surface was not explicitly modeled in the calculations. It was demonstrated that HF calculations yield more accurate bulk hyper-Raman spectra for benzene and SEHRS spectra for pyridine than the ZINDO method. Also, the most accurate data for $\alpha_{ij}$ and $\beta_{ijk}$ was obtained using basis sets including diffuse functions. Use of Eq. 2.23 in this study with the first and second terms on the right side equivalent to what was used by Golab et al. indicated that the SEHRS enhancement factor is on the order of $10^{11}$ to $10^{12}$, meaning PPP calculations overestimated the bulk ratio of hyper-Raman and Raman scattering.

Yang and collaborators\textsuperscript{288} examined the centrosymmetric molecule trans-1,2-bis(4-pyridyl)ethylene (BPE) on Ag film over nanosphere (AgFON) electrodes. The focus of this study was validating that a three-photon process (SEHRS) was occurring instead a two-step process involving second harmonic generation followed by SERS, which may be distinguished by the different selection rules for two- and three-photon processes.\textsuperscript{205,206} HF calculations were used for simulating IR, normal Raman, hyper-Raman, SERS, and SEHRS spectra in comparison to measured spectra, where the surface again was not explicitly modeled. In general, it was found that IR, normal Raman, and SERS spectra agree well with experiment in terms of frequencies and relative peak intensities. The simulated SEHRS spectrum was in worse agreement with the measured one, resulting from larger deviations in calculated frequencies and appearance of modes in the measured spectrum that are absent in the calculated one. However, the symmetry of vibrations observed on the SEHRS spectra evidenced that the process indeed follows three-photon selection rules, ruling out two-step mechanisms.

Li et al.\textsuperscript{281} compared measured and simulated normal Raman, hyper-Raman, IR, SERS, and SEHRS spectra in a study of their Ag metal nanoparticles-on-smooth-electrode (NOSE) substrate. Density functional theory (DFT) calculations were employed to simulate spectra and investigate the molecular orientation of pyridine, pyrazine, and benzene with respect to a non-explicitly modeled surface. Generally, the simulated normal Raman, IR, and SERS spectra were in good agreement with what was measured. While the simulated SEHRS spectrum for benzene compares well with the measured spectrum, simulated SEHRS spectra for both pyridine and pyrazine are in worse agreement.
Figure 2.10. Normal hyper-Raman spectrum of pyridine (a) and SEHRS spectrum of pyridine on a tetrahedral Ag\textsubscript{20} cluster (b), using a Lorentzian with full width at half maximum of 20 cm\textsuperscript{-1} to broaden the peaks. Insets contain experimental spectra from Ref. 291 for normal hyper-Raman data and Ref. 286 for SEHRS data. Reprinted from Ref. 289.

This was rationalized by the authors by discussing surface selection rules for pyridine, and comparing two orientations of pyrazine to measured results also.

Whereas the previous investigations examined the overall SEHRS enhancement factor, Valley et al.\textsuperscript{289} focused specifically on estimating the contribution from chemical enhancement to SEHRS. Time-dependent density functional theory (TDDFT) was applied to study both substituted and unsubstituted pyridines bonded in different adsorption geometries to tetrahedral Ag\textsubscript{20} clusters. This is the first study that included a representation of the surface for simulating SEHRS spectra. It was demonstrated that chemical enhancement is important in SEHRS because there were significant differences in relative peak intensities when the simulated (and measured) normal hyper-Raman and SEHRS spectra were compared, as shown in Figure 2.10. The relative peak intensities from the TDDFT calculations correctly reproduce what is observed experimentally as well. Data for the unsubstituted pyridine adsorbed to the Ag\textsubscript{20} tetrahedra indicated that the chemical enhancements are on the order of $10^2$ to $10^4$ on average, although the maximum enhancement for an individual peak was on the order of $10^4$ to $10^5$. Combining this with the estimate for the electromagnetic SEHRS enhancement factor on silver\textsuperscript{290} of $10^7$, the total SEHRS enhancement factor is $10^9$–$10^{10}$ on average, but can be as large as $10^{11}$–$10^{12}$.

This study also applies a two-state model for SEHRS chemical enhancement using an analogous series of assumptions proposed by Morton and Jensen\textsuperscript{292} for the chemical enhancement of SERS. In this model, the SEHRS chemical enhancement factor is written
\[ \text{EF}_{\text{int}}^{\text{model}} = \frac{I_{x-\text{pyr}-\text{Ag}}}{I_{x-\text{pyr}}} = A \left( \frac{\omega_x}{\omega_e} \right)^6 \]  

(2.24)

where \( \omega_x \) is the HOMO-LUMO gap of the free molecule, \( \omega_e \) is the average gap between the Ag\(_{20}\) HOMO and molecule LUMO, and A is a constant collecting transition dipole moments, change in permanent dipole moment between the ground and excited state, and derivatives of \( \omega_x \) and \( \omega_e \) with respect to the normal modes. The correct trend in chemical enhancement for SEHRS is predicted with the model, even though it sometimes yields enhancement factors differing by a factor of approximately four from those directly calculated from TDDFT results. It is clearly demonstrated that there is a large dependence of the SEHRS chemical enhancement on \( \omega_x/\omega_e \), which facilitates comparison and understanding of the larger SEHRS chemical enhancement compared to SERS.

The Ag\(_{20}\) cluster model was also extended to include the electromagnetic enhancement mechanism in Ref. 293. Chemical enhancement effects were still accounted for by having pyridine bound to the Ag\(_{20}\) cluster in a TDDFT calculation, and the large electric fields from a nanoparticle were determined from Mie theory. With this method it was demonstrated that the overall enhancement factor is \( \sim 10^9 \), which agrees with the previous study.
Part II

Describing electronic structure with density functional theory
Chapter 3

Assessment of the accuracy of long-range corrected functionals for describing the electronic and optical properties of silver clusters


Abstract

The absorption spectra and ionization potentials of silver clusters Ag$_n$ (n=4–20) are examined in the framework of Density Functional Theory (DFT) using several different methods of representing the exchange-correlation functional. Three different types of exchange-correlation functionals are used: those including gradient corrections to the density in the generalized gradient approximation, global hybrid functionals mixing in a portion of the Hartree-Fock exchange, and long-range corrected (LC-) functionals. Comparison of ionization potentials calculated using DFT to those derived from experiments demonstrate that LC-functionals more accurately represent the electronic structure of the silver clusters studied. Absorption spectra are compared to both experimental spectra and those derived using higher level theoretical calculations showing that the LC-functionals appear to correctly describe the optical transitions in the gas phase, particularly when a small redshift in the experimental spectrum is accounted for due to matrix effects. It is also demonstrated that the LC-hybrid functionals significantly reduce the occurrence of spurious states in the optical absorbance spectrum while maintaining the intensity of plasmon-like features of the spectra for larger silver clusters.
3.1 Introduction

Small noble metal (Cu, Ag, Au) particles are of great interest to study due to their complicated physical and chemical properties.\textsuperscript{294–297} Recent advances in nanoscience have demonstrated that small Au and Ag nanoclusters (< 2 nm) can be synthesized with precise control of the number of metal atoms and ligands.\textsuperscript{298–301} Small Ag and Au clusters stabilized by encapsulating the clusters in organic dendrimers have been shown to exhibit strong fluorescence at room temperature.\textsuperscript{302,303} Furthermore, small silver clusters have been shown to produce enhanced Raman signal characteristic of the scaffold used to stabilize the clusters in solution.\textsuperscript{304,305} Also, recent theoretical work has also shown that interactions between biomolecules and small clusters can lead to enhanced absorption.\textsuperscript{221,222} Thus, these nanoclusters are of great interest due to their unique optical and electronic properties and their small size makes them particularly suitable for biological sensing.\textsuperscript{221,222,304,305}

As the size of metal particles decreases to dimensions comparable to the Fermi wavelength of the electron (\(\sim 0.5 \text{ nm for Au or Ag}\)), the electronic motion becomes confined and the electronic energy levels become discrete. This smaller size is associated with optical, electronic, and chemical properties differing from those of the larger nanoparticles.\textsuperscript{306–308} Thus, due to quantum confinement, these small metal clusters show molecular-like electronic structures and the characteristic plasmon bands are replaced with discrete electronic transitions.\textsuperscript{309–311} Experimentally, optical absorbance spectra were first obtained by photofragmentation of mass-selected Ag\(_n^+\) (\(n \leq 21\)) clusters.\textsuperscript{312} Small neutral Ag\(_n\) (\(n=2–39\)) clusters have also been characterized by embedding the clusters in rare-gas matrices.\textsuperscript{313–315} It has been observed that silver clusters have large peaks on their absorbance spectra as cluster size increases.\textsuperscript{313,315} These plasmon-like peaks are characterized by broad width and large intensity on the absorbance spectra, and thus are dominant features of the absorbance spectra. They may not be considered a true plasmon or collective oscillation of electrons due to the small sizes of the clusters examined, but the emergence of the large peak on the absorption spectrum appears to be an analogue to the plasmon excitation observed in nanoparticles.

First-principles modeling has provided accurate and efficient descriptions of the electronic structure and optical properties of nanoclusters of different sizes.\textsuperscript{60,145,294–296,316–319} Absorbance spectra have been modeled theoretically using \textit{ab initio} techniques for neutral silver clusters Ag\(_n\) (\(n=2–8\)) and cationic silver clusters Ag\(_n^+\) (\(n=2–4\)) using the framework of linear response equation-of-motion coupled cluster (EOM-CC) method.\textsuperscript{320,321} EOM-CC is a wavefunction based method shown to give appreciable
accuracy in determination of excited state energies compared with configuration interaction calculations.\cite{322} Time-dependent Density Functional Theory (TDDFT) has also been used to examine optical properties for small and medium Ag\textsubscript{n} (n=2–22) clusters with the local density approximation (LDA) and BP functional.\cite{314,323} The electronic properties of small Ag\textsubscript{n} (n=1–9) clusters have also been characterized by studying the ionization potential (IP) and electron affinity (EA) values using LDA, the Bethe-Salpeter equation for the two-particle Green’s function (GWBSE), and many-body perturbation theory (MBPT).\cite{324,325}

For studying the optical properties of large systems TDDFT quickly becomes the method of choice due to the high computational requirements of more accurate methods. Although TDDFT has been demonstrated to be very accurate, it is well known that conventional exchange-correlation (XC) functionals have certain categorical failures such as describing polarizabilities of larger extended systems\cite{70,326} and charge-transfer excitations between weakly interacting systems.\cite{68,69,327,328} Recently progress has been made with the introduction of so-called long-range corrected (LC)-functionals.\cite{71,73,75,329} These functionals are based on the separation of the Coulomb operator into long- and short-range parts and show great promise for correctly describing the excited states of large molecules. However, the performance of LC-functionals for describing the optical properties of metal clusters so far has not been evaluated.

In this work we will present a systematic study of the IP and optical spectra for small Ag\textsubscript{n} (n=4–20) clusters using different LC-functionals as well as traditional generalized gradient approximation (GGA) and global hybrid functionals. The absorbance spectra are compared with both experimental spectra for all clusters, and also with EOM-CC results for n ≤ 8. Also, IP values are determined using the different functionals and compared with experimental findings.

### 3.2 Theory

#### 3.2.1 Long-Range Corrected Functionals

For electronic separation \( r_{12} \), the long-range corrected (LC-) approach takes the inter-electronic repulsion and separates it into separate short- and long-range terms, given as

\[
\frac{1}{r_{12}} = 1 - \left[ \alpha + \beta \text{erf}(\mu r_{12}) \right] \frac{1}{r_{12}} + \frac{\alpha + \beta \text{erf}(\mu r_{12})}{r_{12}}
\]  

(3.1)
where $\mu$ is the attenuation parameter, $\alpha$ is a parameter allowing the incorporation of Hartree-Fock (HF) exchange, $\beta$ is a parameter allowing for the incorporation of density functional theory (DFT) exchange, and the requirements: $0 \leq \alpha \leq 1$, $0 \leq \beta \leq 1$, $0 \leq \alpha + \beta \leq 1$ should be satisfied. This method allows for the exchange energy, $E_x$, to be split into respective short- and long-range parts

$$E_x = E_x^{SR} + E_x^{LR} \tag{3.2}$$

and the exchange correlation energy, $E_{xc}$, to be given as

$$E_{xc} = E_x^{SR} + E_x^{LR} + E_c \tag{3.3}$$

where $E_c$ is the correlation energy. In this scheme, the short range part of the exchange is calculated using DFT

$$E_x^{SR} = -\frac{1}{2} \sum_{\sigma} \int \rho_{\sigma}^{4/3} K_{\sigma} \left[ 1 - \alpha - \frac{8}{3} a_{\sigma} \beta \left( \sqrt{\pi} \text{erf} \left( \frac{1}{2a_{\sigma}} \right) + 2a_{\sigma} (b_{\sigma} - c_{\sigma}) \right) \right] dr \tag{3.4}$$

where $a_{\sigma}$, $b_{\sigma}$, and $c_{\sigma}$ are defined as

$$a_{\sigma} = \frac{\mu K_{\sigma}^{1/2}}{6\sqrt{\pi} \rho_{\sigma}^{1/3}} \tag{3.5}$$

$$b_{\sigma} = \exp \left( -\frac{1}{4a_{\sigma}^2} \right) - 1 \tag{3.6}$$

$$c_{\sigma} = 2a_{\sigma}^2 b_{\sigma} + \frac{1}{2} \tag{3.7}$$

and $K_{\sigma}$ is defined using the standard exchange functional form

$$E_x = -\frac{1}{2} \sum_{\sigma} \int \rho_{\sigma}^{4/3} K_{\sigma} dr \tag{3.8}$$

For the long-range part of the exchange, the interaction is expressed using the HF exchange integral

$$E_x^{LR} = \alpha E_x^{HF} - \frac{\beta}{2} \sum_{\sigma} \sum_{i}^{\text{occ}} \sum_{j}^{\text{occ}} \left( \int \psi_{i\sigma}^*(r_1) \psi_{j\sigma}^*(r_1) \frac{\text{erf} \left( \frac{\mu r_{12}}{r_{12}} \right)}{r_{12}} \psi_{i\sigma}(r_2) \psi_{j\sigma}(r_2) dr_1 dr_2 \right) \tag{3.9}$$
The attenuation parameter $\mu$ can be used to determine the ratio of HF and DFT exchange. As $\mu$ approaches 0, the exchange energy is purely calculated using DFT and for $\mu$ approaching $\infty$, the exchange energy is only contributed to by HF or exact exchange.

### 3.2.2 Ionization Potentials

In this work, we will compare two different approaches to determining the IP of the silver cluster. The first approach is the $\Delta$SCF method\(^{324}\) where the ionization potential is determined by

$$IP = E_{\text{tot}}(N-1) - E_{\text{tot}}(N)$$ \hspace{1cm} (3.10)

where $E_{\text{tot}}(N-1)$ is the total energy of the cationic molecule and $E_{\text{tot}}(N)$ is the total energy of the neutral molecule. This method has been found to match the even-odd oscillations of silver clusters seen experimentally for IPs. It has been found in comparing the local density approximation (LDA) to GWBSE, a two-particle Green’s function based method, that LDA significantly overestimates IP values while GWBSE yields results comparable to experiment.\(^{324}\) Another study has shown that many-body perturbation theory using the same method underestimates IP values by approximately 1 eV for silver clusters $\text{Ag}_n$ ($n=2$–$9$).\(^{325}\)

The second approach is simply to equate the IP with the negative of the highest occupied molecular orbital (HOMO) energy. This has been demonstrated to be true for the exact functional in Kohn-Sham theory.\(^{330,331}\) However, as a result of the self-interaction error in DFT this is not always true for approximate functionals.\(^{46,332}\) An important consequence for XC functionals including the self-interaction errors is that their XC potentials decay exponentially at long range like the electron density, instead of the correct asymptotic behavior.\(^{46,71,332,333}\) The incorrect decay of the XC potential results in inaccurate eigenvalues of the outer valence electrons (see Ref. 332 and references therein). This results in IP values that differ significantly from those found experimentally.

### 3.3 Computational Details

All calculations were performed using a development version of NWChem\(^{334}\) where we recently implemented several LC-functionals.\(^{335,336}\) Initial guesses for the silver cluster geometries came from previously published work.\(^{314,318,337}\) Because each cluster has many isomers, the one used was the lowest energy structure determined in previous studies. For the $\text{Ag}_8$ cluster, two different isomers of symmetry $T_d$ and $D_{2d}$ were used.
because there is evidence that both structures have nearly identical total energies.\textsuperscript{314,320} Cluster geometries were optimized using the PBE exchange-correlation functional.\textsuperscript{53} These structures were subsequently used for all calculations of absorbance spectra and ionization potentials. Silver clusters were represented using a LANL2DZ relativistic effective core potential (RECP) and corresponding basis set.\textsuperscript{338}

Several different exchange-correlation (XC) functionals were used in this study. Two of the GGA type functionals used were the PBE and BP functionals. The PBE functional involves exchange and correlation functionals derived by Perdew, Burke, and Ernzerhof to improve on the local-spin density (LSD) description of atoms and molecules.\textsuperscript{53} The BP functional includes an exchange functional of Becke\textsuperscript{49} and the correlation functional of Perdew.\textsuperscript{50} Two global hybrid functionals including a combination of HF exchange and gradient-corrected exchange and correlation were also used. The first is the B3LYP functional first proposed by Becke.\textsuperscript{338} The B3LYP functional uses 3 empirical parameters to combine the exact exchange, gradient corrected exchange, and LSD exchange with a correlation term based on the LSD approximation. The other is the global hybrid form of the PBE functional, known as PBE0.\textsuperscript{340,341} Unlike the B3LYP functional PBE0 uses no empirical parameters; instead, it uses perturbation theory to define the ratio of 25\% HF exchange and 75\% exchange from the PBE functional. Finally, a series of LC-functionals were used, including: CAM-B3LYP,\textsuperscript{71} BNL,\textsuperscript{73} LC-PBE,\textsuperscript{342} and LC-PBE0.\textsuperscript{342} The µ parameter varies depending on the LC-functional used. For the CAM-B3LYP functional, the suggested values\textsuperscript{71} of µ = 0.33, α = 0.19, β = 0.46 were used for all calculations performed in this work. A value of µ = 0.30 was used for the functionals LC-PBE (α = 0.0, β = 1.0), LC-PBE0 (α = 0.25, β = 0.75), and BNL (α = 0.0, β = 1.0).

Optical properties including excitation energies and oscillator strengths were calculated using the TDDFT linear response method\textsuperscript{343,344} in NWChem. Calculations were performed on clusters Ag\textsubscript{4} to Ag\textsubscript{8} for the smaller clusters. For the larger silver clusters, Ag\textsubscript{10} to Ag\textsubscript{20}, calculations were limited to the closed-shell clusters (even numbered clusters). This was justified by the previous work on the larger silver clusters showing similar absorbance spectra for open- and closed-shell silver clusters.\textsuperscript{314} All absorbance spectra presented in this work using DFT calculations use a Gaussian lineshape with a full-width at half maximum (FWHM) of 0.2 eV. The lineshape and FWHM were found to fit the experimental absorbance spectra optimally compared to other lineshapes, which is confirmed by the findings of Fedrigo \textit{et al.}\textsuperscript{315}
3.4 Results and Discussion

3.4.1 Ionization Potentials

The ionization potentials of the optimized structures for Ag$_4$ to Ag$_{20}$ are compared in Figure 3.1 for the different XC functionals. Experimental results are from an electron impact ionization study in liquid Ar, with an error bar of 0.1 eV for the cluster sizes investigated.$^{345}$

a. $\Delta$SCF Method. For all of the functionals, the ionization potentials determined by the $\Delta$SCF method are in good agreement with the findings from experiment. The even-odd oscillations observed in previous experimental$^{345}$ and theoretical$^{324,325}$ works are reproduced in Figure 3.1. This is particularly true for the clusters Ag$_n$, $n = 4−12$. For these clusters, $\Delta$SCF yields deviations of less than 0.4 eV for BP and PBE. There is slightly worse agreement for the LC-functionals, but in general the LC-PBE functional has comparable accuracy to the GGAs.

For the smaller clusters there are some noticeable deviations from experiment for B3LYP, BNL, and LC-PBE0. Interestingly, these functionals yield IP values that are too large for the Ag$_4$ and Ag$_5$ clusters. This results from the cationic clusters having total energies that indicate the clusters are not stable. Examining the data from the DFT calculations, it is unclear why these particular clusters result in large IP values. It is apparent, however, that the LC-PBE and CAM-B3LYP functionals do not have these problems, indicating that they may more accurately represent the total electronic structure of the silver clusters.

At larger cluster size, Ag$_n$, $n = 13−20$, the agreement with experiment is not as good for any of the XC functionals. In general the deviation from experimental results for these clusters is at least 0.4 eV. For the largest cluster studied, Ag$_{20}$, each functional gives a result differing from experiment by at least 0.9 eV. The increased deviation from experimental IPs may result from having more possible structures for larger clusters containing more atoms. It is possible that the IP measured experimentally for the larger silver clusters result from a mixture of several different clusters containing the same number of atoms. As a results, the experimental IP may reflect an averaged value from all cluster geometries that were present. This could also explain why the even-odd oscillations are not as pronounced for the experimental results as the cluster size increases. There is also the possibility that there are lower energy structures for the larger silver clusters. Using structures that do not correspond to the most energetically stable geometry for a larger cluster results in smaller IP values, and therefore the agreement
between theory and experiment deteriorates as cluster size increases.

b. Negative of the HOMO energy eigenvalue. The results (see Figure 3.1) indicate that the different functionals yield very different results for ionization potentials derived from the HOMO energy. For the GGAs BP and PBE, it is apparent that the negative of the HOMO energy significantly deviates from the experimental IP results. These functionals always yield IP values that are too small by approximately 2 eV for every silver cluster. The global hybrid functionals B3LYP and PBE0 fail to significantly improve the results from the GGAs for the IP values. In general the global hybrid functionals increase the IP by at least 0.2 eV, but this never results in IP values comparable to what is found experimentally.

For the LC-functionals, there is an improvement in the IP determined for all of the silver clusters. CAM-B3LYP produces only a small improvement with IP values differing from experiment by 1 – 2 eV. A possible reason for this is that CAM-B3LYP differs from the other LC-functionals used in that it uses a mixture of 35% DFT exchange and 65% exchange.

Figure 3.1. IP data collected using the different functional methods. On the plots, the squares (blue line) are experimental results (Ref. 345), the triangles (grey line) are from the ΔSCF method, and diamonds (purple line) are from the negative of the HOMO energy eigenvalue.
Table 3.1. IP for the two different isomers of the Ag₈ cluster using the negative of the HOMO energy eigenvalue.

<table>
<thead>
<tr>
<th>Functional</th>
<th>D₂d IP (eV)</th>
<th>T₄d IP (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP</td>
<td>4.90</td>
<td>5.16</td>
</tr>
<tr>
<td>PBE</td>
<td>4.75</td>
<td>5.00</td>
</tr>
<tr>
<td>B3LYP</td>
<td>5.12</td>
<td>5.39</td>
</tr>
<tr>
<td>PBE0</td>
<td>5.10</td>
<td>5.37</td>
</tr>
<tr>
<td>CAM-B3LYP</td>
<td>5.89</td>
<td>6.22</td>
</tr>
<tr>
<td>LC-PBE</td>
<td>6.67</td>
<td>7.05</td>
</tr>
<tr>
<td>LC-PBE0</td>
<td>6.54</td>
<td>6.92</td>
</tr>
<tr>
<td>BNL</td>
<td>6.58</td>
<td>6.95</td>
</tr>
<tr>
<td>Experiment³⁴⁵</td>
<td>7.10</td>
<td>7.10</td>
</tr>
</tbody>
</table>

HF exchange at long range, whereas the others use 100% HF exchange at long range. LC-PBE0 improves the result significantly with errors for the small cluster sizes between 0.2 and 0.6 eV. For BNL and LC-PBE, there is a substantial improvement of the results, especially for the silver clusters between Ag₄ and Ag₁₂. These two functionals yield very good agreement with experiment, with errors of 0.1 to 0.3 eV in that size regime. These results, particularly for the LC-PBE and BNL functionals, indicate that there is a significant improvement of how the electronic structure of molecules are treated with the long-range corrected DFT framework.

Like what was observed for the ∆SCF method, the deviation from experimental results increases as cluster size increases. With CAM-B3LYP as an exception, the LC-functionals see a slight improvement of the IP values between Ag₁₃ and Ag₂₀ when the negative of the HOMO energy is used to find the IP instead of the ∆SCF method. This improvement is on the order of 0.2 to 0.3 eV. Again, this deviation from experimental values for the larger clusters likely results from multiple isomers contributing to the IP determined experimentally, and also that there is uncertainty in whether lower energy structures exist for the larger clusters.

c. Comparison of two isomers of the Ag₈ cluster. It is generally accepted that the T₄d Ag₈ cluster is more stable than the D₂d isomer by approximately 0.1 eV.³¹⁴,³²⁰ The IP values calculated for the two isomers are summarized in Table 3.1. For all of the functionals used, it is clear that the T₄d structure is more stable by at least 0.2 eV, as indicated by its larger IP. GGAs and global hybrid functionals significantly underestimate the IP values, with deviations ranging between 1.7 and 2.1 eV for the T₄d structure and 2.0 to 2.35 eV for the D₂d structure. LC-functionals improved this result substantially, with
Figure 3.2. Absorbance spectra for the $D_{2d}$ isomer of the Ag$_8$ cluster using the different functionals. Spectra are plotted with labels of the XC functional or method used to obtain them. Plots of the experimental (Ref. 320) and EOM-CCSD (in oscillator strength, $f_e$, from Ref. 314) results were generated using digitizing software on the original spectra.

deviations of 0.05 to 0.9 eV for the $T_d$ structure and 0.4 to 1.2 eV for the $D_{2d}$ structure. The results indicate that LC-PBE and BNL reproduced the experimental result the best with deviations of 0.05 eV and 0.15 eV, respectively, for the $T_d$ structure. From Table 3.1 it seems likely that the $T_d$ cluster is the correct minimum energy structure, although the small separation in energy between both isomers may prevent their isolation.

3.4.2 Absorbance Spectra

Optical absorption spectra calculated for the Ag$_8$ and Ag$_{20}$ silver clusters are presented in Figures 3.2 – 3.4, where each figure contains the spectra for one of the silver clusters calculated with each XC functional. For the data using the other silver clusters (Ag$_n$, $n = 4–7, 10–18$), refer to Appendix A. Results in this section are compared to both experimental$^{314,315}$ and computational results when possible.$^{320,321}$ The experimental work measured the absorbance spectra of isolated silver clusters in rare gas matrices for silver clusters Ag$_2$ to Ag$_{21}$. Calculations of optical properties by Bončič-Koutecky et al. were performed in an EOM-CC with single and double excitations (EOM-CCSD) framework for clusters between Ag$_2$ and Ag$_8$. 
3.4.2.1 Spectral Analysis

**a. Ag<sub>8</sub>.** Absorbance spectra for the \( D_{2d} \) and \( T_d \) isomers of the eight atom cluster are shown in Figures 3.2 and 3.3, respectively. Due to the similarity in energy for both clusters,\(^{314,320} \) there is likely a mixture of both clusters yielding the complicated experimental absorbance spectrum. The experimental results show several peaks at 3.15, 3.57, 3.82, 3.90, and 4.50 eV. For the \( D_{2d} \) isomer, EOM-CCSD yields intense peaks at 3.78, 4.08, 4.09, and 4.21 eV. The \( T_d \) cluster with the same method has excitations at 3.27, 4.16, 5.68, 5.99, and 6.06 eV.

The absorbance spectrum for the \( D_{2d} \) isomer using both GGAs has transitions located at 3.50 and 3.85 eV. Compared to the experimental results and EOM-CCSD, the spectrum is redshifted slightly but the overall features of the spectrum are reproduced well with these XC functionals. The absorbance spectrum of the \( T_d \) isomer has three main transitions at 3.00, 3.90, and 4.50 eV for both GGAs. These again compare very well to the experimental results, with the peak at 3.00 eV slightly redshifted from its position on the experimental spectrum.

For the global hybrid functionals, the spectrum of the \( D_{2d} \) isomer has major transitions at 3.75 and 4.05 eV. These compare very well with EOM-CCSD results. It is apparent
that the spectra are blueshifted compared with the experimental findings, however, by about 0.2 eV. The absorbance spectrum of the $T_d$ isomer has two significant transitions at 3.15 and 4.05 eV for the global hybrid functionals. These agree well with the EOM-CCSD and have a small blueshift compared to experimental results.

Examining the results for the LC-functionals, a general trend observed for the $D_{2d}$ isomer is that the transitions are blueshifted compared to the experimental spectrum to be between 3.5 and 4.5 eV. This makes the spectra for these XC functionals much more similar to the results obtained using the EOM-CCSD method, especially for the LC-PBE functional where the two major transitions are observed at 3.76 and 4.05 eV. Overall, the same trend is observed for the $T_d$ isomer, with a noticeable blueshift of the large peak. Again, it seems that the LC-PBE functional best reproduces the results of EOM-CCSD, with transitions at 3.32 and 4.11 eV.

b. Ag$_{20}$. The results shown for the smaller silver clusters (see Appendix A) demonstrate that the XC functionals that are similar in type give similar results. That is to say, the GGAs BP and PBE give very similar absorbance spectra. This is also true for the the global hybrid functionals and LC-functionals as well. Resulting from this observation it was determined that one XC functional of each type needed to be used to compare data for the larger silver clusters. Based on the excellent agreement with experiment on calculating the ionization potentials and agreement with both EOM-CCSD and experiment for absorbance spectra, LC-PBE was selected to be one of the functionals used for the larger silver clusters. Since PBE and PBE0 are based on the same XC functional as LC-PBE, they were also chosen in order to compare a GGA, global hybrid, and LC-functional.

For the Ag$_{20}$ cluster, absorbance spectra are plotted in Figure 3.4. For this cluster the spectrum is essentially one large peak with a small shoulder. Experimental results place the large peak at 3.70 eV with a small shoulder at 3.97 eV. PBE, PBE0, and LC-PBE place the large peak at 3.51, 3.78 and 3.97 eV, respectively. PBE0 also has an additional large transition at 3.97 eV, while LC-PBE has a large transition at 4.04 eV. The PBE functional causes a redshift of the main transition, while both LC-PBE and PBE0 blueshift the position by 0.08 and 0.27 eV, respectively. From the spectra of the functionals including HF exchange, it seems both have the additional feature that could result in the small shoulder on the experimental spectrum, but it is not far enough from the peak maximum for the shoulder to appear.

The intensity of the peaks is also significantly different for each functional. LC-PBE gives an absorption coefficient of approximately 760 L mol$^{-1}$ cm$^{-1}$, whereas PBE0 and PBE yield absorption coefficients of 410 and 595 L mol$^{-1}$ cm$^{-1}$, respectively. The LC-
Figure 3.4. Absorbance spectra for the Ag_{20} cluster using the different functionals. Spectra are plotted for the C\textsubscript{s} isomer with labels of the XC functional or method used to obtain them. The plot of the experimental spectrum (Refs. 314 and 315) was generated using digitizing software.

PBE functional correctly places most of the intensity of the transition near the absorption maximum. PBE and PBE0 spread the oscillator strength out among more transitions, causing an overall decrease in the intensity of the peak and model the spectrum for the Ag_{20} cluster less accurately as a result.

3.4.2.2 Comparison of DFT and Experimental Plasmon-like Peak Positions

The absorbance spectra for the silver clusters Ag\textsubscript{n}, n = 4 – 20, show similar characteristics to one another in two different size regimes. For the smaller clusters, this range of cluster sizes goes from n = 4 to n = 6, and the spectra are characterized by several comparable intense absorption lines. The remaining silver clusters, n = 7 – 20, are likewise grouped together with similar features on the absorption spectra. For the larger clusters, the spectrum becomes primarily dominated by one peak, located between 3.40 and 4.00 eV. This is similar to the observed plasmon resonance for silver nanoparticles, which is known to be positioned at 3.78 eV.\textsuperscript{315}

Figure 3.5 presents a plot comparing the experimental location\textsuperscript{314,315} of the large plasmon-like peak, \(\omega_p^{\text{expt}}\), compared to the location of the same peak from TDDFT, \(\omega_p^{\text{theory}}\), on the absorbance spectrum from the PBE, PBE0, and LC-PBE functionals. For the Ag\textsubscript{8} cluster, the \(T_d\) isomer was selected because its spectrum is dominated by a single
peak which is more comparable to other larger clusters. For the experimental data, it has been observed by comparing experimental results for larger silver clusters with Mie theory that embedding nanoparticles and large silver clusters in an Ar medium results in a redshift of the large peak by 0.24 eV. This shift was incorporated into Figure 3.5 to compare with experimental data because the TDDFT calculations were done in vacuum.

It is clear from Figure 3.5 that the functionals PBE, PBE0, and LC-PBE differ in how accurately they model the position of the plasmon-like peak. After incorporating the matrix effects described above, it is determined that the peak position obtained from the LC-PBE functional most accurately compares to the experimental results. On average the LC-PBE functional yields a peak position that is 0.06 eV closer to the experimental value than the PBE0 functional. Both functionals result in a slight redshift of the spectrum when the matrix effects are included. The PBE functional tends to underestimate the position of the peak and has the largest average deviation from experimental values of 0.38 eV. These results indicate that the LC-PBE functional most accurately captures the optical characteristics of each cluster.

For each functional there is a large deviation on the data from the Ag\textsubscript{10} cluster. Data for this cluster is represented with unfilled shapes on Figure 3.5 for clarity. Comparing the absorption spectra for the Ag\textsubscript{10} cluster (see Appendix A) from each functional with the experimental results, it is apparent that the large plasmon-like peak present from theory is absent on the experimental absorption spectrum. As a result, the data for this cluster is in large error compared with experiment. This illustrates that the experimentally measured spectrum most likely is not for the Ag\textsubscript{10} cluster studied in this work. Instead, Harb \textit{et al.} argue that the Ag\textsubscript{10} spectrum that was measured comes from Ag\textsubscript{9}, because it is possible that the Ag\textsubscript{10} cluster fragments to form Ag\textsubscript{9}. This explanation is consistent with the finding that the Ag\textsubscript{10} spectrum in their work has many similar features with the spectrum for Ag\textsubscript{9}, and is likely the reason for the large discrepancy in Figure 3.5.

3.4.3 Spectral Modeling by the Different Functionals

Figure 3.6 presents two separate plots comparing absorption spectra for the PBE, PBE0, and LC-PBE functionals for the silver clusters Ag\textsubscript{4} to Ag\textsubscript{20}. For each of the functionals, the $T_d$ isomer of the Ag\textsubscript{8} cluster was used in making the figures. Due to the large number of states required to model the absorption spectra for the Ag\textsubscript{18} and Ag\textsubscript{20} cluster using the PBE functional at high energy, those spectra were not plotted above the 4.20 eV threshold and results are not included on the figures. However, the trend on both figures is still apparent without results for those clusters.
Figure 3.5. Plot the location of the plasmon-like peak from theory, $\omega_p^{\text{theory}}$, compared with that of experiment (Ref. 315), $\omega_p^{\text{expt}}$, for silver clusters $\text{Ag}_7$ to $\text{Ag}_{20}$. The triangles result from the PBE functional, diamonds result from the PBE0 functional, and squares result from the LC-PBE functional. Unfilled shapes correspond to the results for the $\text{Ag}_{10}$ cluster.

The plot in Figure 3.6(a) shows how the number of states changes with cluster size below a threshold of 4.20 eV. Up to $\text{Ag}_8$, both PBE0 and LC-PBE have nearly identical behavior in having low numbers of states, with LC-PBE having slightly lower numbers of states. After $\text{Ag}_8$, it becomes more clear that LC-PBE calculates fewer states than PBE0 below the threshold by approximately 10 states for each cluster. PBE generally calculates too many states below the threshold, climbing from 20 states at $\text{Ag}_8$ to 141 states at $\text{Ag}_{16}$. This result shows that the PBE functional calculates significantly more states than the PBE0 and LC-PBE functionals, indicating that PBE includes a large number of spurious states in this energy range of the absorbance spectrum. Comparing the LC-PBE and PBE0 functionals indicates that not all of the spurious states are removed by the PBE0 functional, which supports the finding that LC-PBE generally does the best job modeling the absorbance spectra compared to experiment and higher level theoretical calculations.

Figure 3.6(b) is a plot of the sum of oscillator strength below a threshold of 4.20 eV from the HOMO versus cluster size. This figure also demonstrates that both PBE0 and LC-PBE have similar behavior for the silver clusters. For almost every cluster PBE0 has a slightly larger sum of oscillator strengths compared to the LC-PBE functional, but the
difference does not appear to be significant. For the two noticeable deviations from that
trend at Ag$_{10}$ and Ag$_{18}$, the threshold is slightly too low to capture some of the near
degenerate excitations and results in a decreased sum of oscillator strength for the PBE0
functional. The data show that PBE underestimates the amount of oscillator strength
for clusters larger than Ag$_8$ by as much as 1.00 in this region of the absorption spectrum.

Comparing the results of the two figures, it is clear that the spectrum of PBE has
a significant contribution from spurious states. For example, the spectrum for the Ag$_{16}$
cluster has over 140 states below 4.20 eV, whereas LC-PBE has only 47 states below
the same threshold. For those 140 states, the sum of oscillator strength using the PBE
functional is 4.85 compared while that same sum is 5.84 for the 47 states that the LC-
PBE functional finds below 4.20 eV on the same cluster. Both effects may be explained
resulting from the inclusion of HF exchange in the XC functional as outlined below.

A twofold effect is observed on the spectrum by comparing the different descriptions
of the XC functional. First, as indicated in Figure 3.6(a), the sum of states below
4.20 eV demonstrates that the spurious states are removed as HF exchange is added.
Second, the sum of oscillator strength below 4.20 eV increases as the HF exchange is
added. This may be caused by the included spurious charge-transfer states in the PBE
absorbance spectrum. These spurious states generally have low oscillator strength, but
they are numerous in the PBE absorbance spectrum. They are not required to be dark
states, though, because spurious states have been shown to borrow oscillator strength
from bright states and become comparable in intensity to those bright states in other
systems.$^{328}$ This complicates the analysis of which states are spurious, and in the silver
clusters studied in this work it is difficult to pick out the spurious states due to the high
density of electronic states for each system. However, there is not an exact threshold of
where the spurious states may be located with respect to the bright state they borrow
intensity from. As a result, the energy cutoff used may not include all of the spurious
states required to obtain the correct sum of oscillator strength for the PBE functional.

It should be stressed that this finding implies that the PBE functional calculates a
significant number of transitions that most likely should not be present in the absorbance
spectrum for silver clusters. A likely cause for these spurious transitions are low-lying
intramolecular charge transfer states that are incorrectly described if the potential does
not have the correct asymptotic behavior.$^{71,76}$ The elimination of the low-lying charge-
transfer states using LC-functionals has been discussed for systems like π-stacked adenine
dimers,$^{342}$ indicating that correct asymptotic behavior of the potential is necessary for
correctly describing optical properties of other systems also. These spurious states are
Figure 3.6. Plots of the number of states below 4.2 eV (a) and the sum of oscillator strength below a threshold energy of 4.2 eV (b). The triangles (blue line) result from the PBE functional, diamonds (grey line) result from the PBE0 functional, and squares (purple line) result from the LC-PBE functional.

removed by adding in HF exchange giving a more physically correct description of the systems investigated in this work as well.

3.5 Conclusion

The findings in this paper show the first investigation of the electronic structure and optical properties of silver clusters with the LC-DFT scheme. Experimental work was the basis for examining how LC-functionals model the frontier orbital energies of silver clusters by comparing experimental and theoretical IP values. Results were compared to several experimental studies along with a data from the EOM-CCSD method for examining the absorbance spectra of small silver clusters. Also, the functionals PBE, PBE0, and LC-PBE were compared based on how they model optical properties by investigating the number of states and sum of oscillator strength below a threshold energy above the HOMO.

Examining the IP values, a clear trend is observed by comparing values calculated from the $\Delta$SCF method and negative of the HOMO energy. Using the $\Delta$SCF method, the IP values from theory best compare to experiment when the BP, PBE, and LC-PBE functionals are used for the smaller silver clusters $\text{Ag}_4$ to $\text{Ag}_{12}$. The negative of the HOMO energy clearly distinguishes the LC-functionals from the GGAs and global hybrids, however. Both LC-PBE and BNL yield IPs nearly identical to experiment using
this method, while the GGAs tend to give IPs that are too small by approximately 2 eV for every cluster examined. It was demonstrated by comparing the negative of the HOMO energy for the different XC functionals that the LC-functionals correctly model the electronic structure of the silver clusters, while the GGAs and global hybrid functionals do not account for the same accuracy. This results from a correct description of the XC potential at long range for the LC-functionals that is absent for the GGAs and global hybrid functionals.

Absorbance spectra calculated from TDDFT methods show two separate trends. Generally, the GGAs BP and PBE yield comparable spectral structure to experimental data but result in a redshift of peak positions when looking at the experimental and EOM-CCSD data. The global hybrid functionals tend to slightly blueshift the spectrum from the experimental positions and redshift it from the EOM-CCSD results. LC-functionals also cause a blueshift compared to experiment. A slight redshift was observed for these functionals compared to EOM-CCSD, but the spectra obtained from the LC-functionals are most comparable to those obtained with the EOM-CCSD method. These results demonstrate that the high accuracy of determining excitation energies with coupled cluster calculations can be obtained using the lower cost LC-TDDFT method.

Further examination of the absorbance spectra including Ar matrix effects show that the LC-PBE functional significantly improves the agreement with experiment for the position of the plasmon-like peak compared with PBE and PBE0 for silver clusters between Ag\textsubscript{7} and Ag\textsubscript{20}. Also, analyzing the number of states and sum of oscillator strength below a given energy threshold demonstrated that the HF exchange used in the PBE0 and LC-PBE functionals removes spurious states that are present in calculations for the same molecule with the PBE functional. From the data it was clear that LC-PBE removed more spurious states, and it was shown that removing these states does not decrease the intensity of the peaks on the spectrum. Removal of these states is important because the data indicate that they should not be present on the absorbance spectrum.
Chapter 4

Understanding the Resonance Raman Scattering of Donor-Acceptor Complexes using Long-Range Corrected DFT


Abstract

The optical properties involving charge transfer states of the donor–acceptor electron transfer complexes carbazole/tetracyanoethylene (carbazole/TCNE) and hexamethylbenzene/tetracyanoethylene (HMB/TCNE) were investigated by utilizing the time-dependent theory of Heller to simulate absorbance and resonance Raman spectra. Excited state properties were obtained using time-dependent density functional theory (TDDFT) using the global hybrid B3LYP and the long-range corrected LC-ωPBE functionals and compared with experimental results. It is shown that while reasonable simulations of the absorbance spectra can be made using B3LYP, the resonance Raman spectra for both complexes are poorly described. The LC-ωPBE functional gives a more accurate representation of the excited state potential energy surfaces in the Franck-Condon region for charge transfer states, as indicated by the good agreement with the experimental resonance Raman spectrum. For the carbazole/TCNE complex, which includes contributions from two overlapping excited states on its absorbance spectrum, interference effects are discussed and it is found that detuning from resonance with an excited state results in interference along with other factors. Total vibrational reorganization energy for both complexes is discussed, and it is found that both B3LYP and LC-ωPBE yield reasonable estimates of this quantity compared with experiment.
4.1 Introduction

Electron transfer reactions are fundamental processes involved in chemistry and biology. Some important applications of these processes include studies of photocatalysis, charge transfer (CT) in polymers, and numerous other biological and chemical processes. Resulting from those applications, investigations involving the rate of electron transfer and optimization of that process are a major research focus.

For molecules that undergo a change in oxidation state due to electron transfer, the molecular geometry changes as well. The rate of electron transfer between molecules strongly depends on molecular geometries of the donor and acceptor molecules before and after the electron transfer event. A more quantitative analysis of structural changes due to electron transfer requires knowledge of which normal modes are Franck-Condon active, because it is these modes that are strongly influenced by electron transfer. Using resonance Raman spectroscopy allows the CT state being investigated to be characterized and information about the rate of electron transfer to be quantified.

Several methods for modeling resonance Raman scattering have been developed. In the vibronic theory of Albrecht et al., the Born-Oppenheimer (BO) approximation is used to separate each vibronic state into a product of the electronic and vibrational wave functions. Then, the transition dipole moment is expanded as a Taylor series in the nuclear coordinates. This allows the Raman transition polarizability to be represented as a sum of terms, where the first is the A term (Franck-Condon) and the second is the B term (Herzberg-Teller). Another formulation is the time dependent formalism developed by Heller et al. This method uses wave packet dynamics to describe the time dependent overlap of the final state and initial vibrational wave function that propagates along the excited state potential energy surface. Unlike the vibronic theory, the time dependent method avoids the computationally demanding summation over intermediate vibrational states. Both methods can be used with harmonic approximations of the ground and excited state potential energy surfaces that are displaced along the normal coordinate, in the independent mode displaced harmonic oscillator (IMDHO) method. Excited state displacements calculated using the IMDHO method are proportional to the excited state gradient at the ground state equilibrium geometry, which can be used to model resonance Raman spectra and also be applied to studying electron transfer rates using Marcus theory.

Density functional theory (DFT) has been applied in several cases for studying vibronic structure of molecules in resonance Raman scattering. Traditional DFT exchange-correlation (XC) functionals have been shown to largely underestimate the CT
excitations of weakly interacting systems, but this effect has been demonstrated to be partially corrected using the long-range corrected (LC) DFT. Although many studies have shown the usefulness of LC-DFT for correctly describing CT excitation energies, there has not been a study of resonance Raman scattering of CT excited states using the LC-functionals. This will provide an additional validation of the LC-functionals since it is crucial to accurately describe the curvature of the excited state surface for correctly modeling resonance Raman scattering.

Here we will present a detailed study of the resonance Raman scattering of two donor-acceptor complexes using LC-DFT combined with Heller’s time-dependent theory of Raman scattering. Time-dependent density functional theory (TDDFT) is used to evaluate excited state displacements within the IMDHO method for the hexamethylbenzene/tetracyanoethylene (HMB/TCNE) and carbazole/tetracyanoethylene (carbazole/TCNE) complexes. The absorption and resonance Raman scattering spectra are then simulated using the time-dependent theory. Complexes similar to those studied in this work have been investigated using the LC-functional BNL (Baer-Neuhauser-Livshits) to investigate how the attenuation parameter in that functional can be tuned to give improved descriptions of excitation energies for CT states in comparison to experiment. For both of these systems their resonance Raman scattering have been measured experimentally, thus enabling a comprehensive comparison between theory and experiment. The low energy portion of the optical absorbance spectra for these complexes include excitations where an electron is transferred from the donor (carbazole or HMB) to the acceptor (TCNE) molecule. The complex HMB/TCNE has a single CT state on its absorbance spectrum, while carbazole/TCNE has two energetically close CT states that overlap in one band on the absorbance spectrum. For the carbazole/TCNE complex, contributions from two CT states result in interference effects, which have been observed in previous studies that focused on experimentally derived fits to resonance Raman spectra. Total vibrational reorganization energies are also compared between the XC functionals and experiment for both complexes.

4.2 Theory

Expressions for the absorbance cross section ($\sigma_a$) and Raman polarizability ($\alpha_n^{\rho\lambda}$) can be obtained by applying both the Franck-Condon (FC) and Born-Oppenheimer (BO) approximations. In the time dependent formalism, expressions for $\sigma_a$ and $\alpha_n^{\rho\lambda}$ can be rewritten as respective full- and half-Fourier transforms, resulting in
\[
\sigma_a = \frac{4\pi}{3hc} E_L \sum_n (\mu^{0n}_n)^2 \times \text{Re} \int_0^\infty \langle i | i_n(t) \rangle e^{i(E_L + \nu_{i0})t - \Gamma_n t - (1/2)\Theta^2 t^2} dt \tag{4.1}
\]

and

\[
\alpha^p_{\rho\lambda} = \sum_n \mu^{0n}_\rho \mu^{n0}_\lambda \times i \int_0^\infty \langle f | i_n(t) \rangle e^{i(E_L + \nu_{i0})t - \Gamma_n t - (1/2)\Theta^2 t^2} dt \tag{4.2}
\]

For both expressions, \(E_L\) defines the energy of the incident radiation, \(n\) defines the electronic state (where 0 is the electronic ground state), \(\mu^{0n}\) defines the electronic transition dipole moment for an excitation between electronic states 0 and \(n\), \(\nu_{i0}\) is the energy of vibrational state \(|i\rangle\), and \(|i_n(t)\rangle = e^{-i\tilde{H} t/\hbar}|i\rangle\) is the wavepacket corresponding to the time-dependent nuclear wavefunction of electronic state \(n\). The homogeneous broadening for this system is treated phenomenologically with the addition of \(\Gamma_n\), which allows for each excited state to have a different lifetime. It is often difficult to fit absorbance spectra with only the homogeneous broadening parameter \(\Gamma_n\) because the Lorentzian line shape resulting from \(\exp(-\Gamma t)\) decays too slowly, which is found to worsen the fit on the red edge of the absorption spectrum.\(^{359}\) This can be compensated by including an inhomogeneous broadening parameter, \(\Theta\), where both Eqs. 4.1 and 4.2 represent convolutions of Gaussian and Lorentzian line shapes (Voigt line shape). In particular for the Raman polarizability\(^{129,130}\) given in Eq. 4.2, the final vibrational state \(|f\rangle\) is involved in the dynamics, and the subscripts \(\rho\) and \(\lambda\) refer to \(x, y,\) and \(z\) directions of the transition dipole moment vectors and polarizability tensor elements.

In order to calculate the overlaps between different vibrational states, the IMDHO model\(^{93,132,359}\) was used. This method relies on assumptions that the ground and excited state potential energy surfaces are harmonic and have the same normal mode composition and frequencies. The excited-state displacement relative to the ground-state equilibrium position of the potential is given by the shift \(\Delta_p^n\) in dimensionless normal coordinates. Use of the IMDHO method allows for the overlap integrals to be written

\[
\langle i | i_n(t) \rangle = e^{-\sum_j s^p_j (1 - e^{-i\omega_j t}) - i(\nu_{i0} - E_{0n})t} \tag{4.3}
\]

for determining the absorption cross section and

\[
\langle f | i_n(t) \rangle = \prod_p \left\{ \frac{(-1)^{m_p}(\Delta_p^n)^{m_p}}{(2m_p m_p^{1/2})^{1/2}} (1 - e^{-i\omega_p t})^{m_p} \right\} e^{-\sum_j s^p_j (1 - e^{-i\omega_j t}) - i(\nu_{i0} - E_{0n})t} \tag{4.4}
\]
for the Raman polarizability. For these expressions, \( s^n_p = (\Delta^n_p)^2 / 2 \) are the Huang-Rhys factors and \( m_p \) is the excitation number for the kth normal mode of vibrational state \( | f \rangle \).

After determining the Raman polarizabilities, the differential Raman scattering cross section can be calculated to compare with experimental measurements.\(^4\)\(^7\)\(^9\)\(^3\)\(^6\)\(^4\) For measurements of scattered radiation 90\(^\circ\) from the direction of propagation of the incident radiation, the differential Raman scattering cross section is given by

\[
\frac{d\sigma}{d\Omega} = \frac{2}{\varepsilon_0^2 (\nu_{in} - \nu_{p0})^4} \left( \frac{45a_p^2 + 7\gamma_p^2}{45} \right) \frac{1}{1 - \exp\left[ -\frac{h\nu_{p0}}{k_B T} \right]} \tag{4.5}
\]

where \( \nu_{in} \) is the energy of the incident radiation and \( T \) is the temperature (assumed to be 300 K in the present work). The tensor invariants \( a_k \) and \( \gamma_k \) are the isotropic and anisotropic polarizability averages, given by

\[
a_p = \frac{1}{3} \left\{ (\alpha_{xx})_p + (\alpha_{yy})_p + (\alpha_{zz})_p \right\} \tag{4.6}
\]

and

\[
\gamma_p^2 = \frac{1}{2} \left\{ \left[ (\alpha_{xx})_p - (\alpha_{yy})_p \right]^2 + \left[ (\alpha_{yy})_p - (\alpha_{zz})_p \right]^2 + \left[ (\alpha_{zz})_p - (\alpha_{xx})_p \right]^2 \\
+ 6 \left[ (\alpha_{xy})_p + (\alpha_{yz})_p + (\alpha_{zx})_p \right]^2 \right\} \tag{4.7}
\]

In order to perform the integrals for obtaining the absorbance cross section and Raman polarizability, the dimensionless excited state displacements \( (\Delta^n_p) \) must be calculated. When the potential energy surface is assumed to be harmonic,\(^9\)\(^3\) \( \Delta^n_p \) relates to the partial derivative of the excited state electronic energy with respect to a ground state normal mode at the ground state equilibrium position,

\[
\left( \frac{\partial E^n}{\partial q_p} \right)_{q_p=0} = -\nu_{p0} \Delta^n_p \tag{4.8}
\]

The excited state electronic energy gradients in Eq. 4.8 are calculated using a three-point central differences formula around the ground state equilibrium geometry. For convenience, the derivatives are initially determined in mass-weighted normal coordinates, \( Q_p \), not the dimensionless normal coordinates \( q_p \). However, it is easy to convert between
the two using the relationship

\[ \frac{\partial E^n}{\partial q_p} = \left( \frac{dQ_p}{dq_p} \right) \frac{\partial E^n}{\partial Q_p} = \sqrt{\frac{\hbar}{2\pi c\nu_0}} \frac{\partial E^n}{\partial Q_p} \] (4.9)

Excited state electronic energy gradients in terms of mass-weighted normal coordinates were evaluated using formulas similar to those presented by Reiher et al. for numerical derivatives of the polarizability tensor elements, replacing the polarizability with electronic energy at positions displaced along each normal mode.

Electron transfer rates for harmonic potential energy surfaces can be quantified if the energy penalty for transferring an electron, i.e. the energy difference between the charge-separated state at the equilibrium geometry of the neutral system and equilibrium geometry of the charge-separated state, is known. This energy penalty is called the reorganization energy, \( \lambda_{\text{tot}} \). Generally, \( \lambda_{\text{tot}} \) is partitioned into two components, the solvent reorganization energy (\( \lambda_s \)) and vibrational reorganization energy (\( \lambda_v \)), as

\[ \lambda_{\text{tot}} = \lambda_s + \lambda_v \] (4.10)

The solvent reorganization energy is the energy cost resulting from solvent molecules reorienting themselves after the electron transfer takes place, in order to optimize the solvent-complex interactions. Vibrational reorganization energy results from changes in the molecular geometry due to electron transfer. For a harmonic free energy surface, the total vibrational reorganization energy can be written as a sum of single-mode contributions

\[ \lambda_v = \frac{1}{2} \sum_p (\Delta_p^n)^2 \nu_p \eta_0 = \sum_p \lambda_{v,p} \] (4.11)

Analysis of the single-mode contributions to the vibrational reorganization energy compared with what is found experimentally yields complementary information to examining the features of resonance Raman spectra.

### 4.3 Computational Details

In the long-range corrected (LC-) approach, the interelectronic repulsion is partitioned into separate short- and long-range terms, which is given for electronic separation \( r_{12} \) as

\[ \frac{1}{r_{12}} = \frac{1 - \text{erf}(\omega r_{12})}{r_{12}} + \frac{\text{erf}(\omega r_{12})}{r_{12}} \] (4.12)
where $\omega$ is the attenuation parameter, the first term on the right side of Eq. 4.12 is for the short-range part of the exchange, and the second term of the right side of that equation is used for the long-range part of the exchange. Recently, we implemented several LC-functionals into NWChem\textsuperscript{334} based on the general approach produced by Hirao and co-workers\textsuperscript{75} for constructing the short-range GGA XC functional.\textsuperscript{335,336} An alternative procedure based on a model for the PBE exchange hole has been presented by Scuseria and co-workers.\textsuperscript{74,367} LC-functionals based on this procedure, LC-$\omega$PBE and LC-$\omega$PBEh, have been shown to lead to a good description of both ground state and excited state properties.\textsuperscript{40} Here we have implemented these functionals into NWChem.\textsuperscript{334}

The ground state equilibrium geometry and normal modes for the HMB/TCNE and carbazole/TCNE complexes were determined using the B3LYP functional\textsuperscript{339} and 6-31G* basis set. Normal mode frequencies were scaled by 0.98 from the B3LYP values to obtain better agreement with experimental frequencies. Optical properties including excited state energies used for determining the dimensionless displacements were calculated using the TDDFT linear response method\textsuperscript{343,344} in NWChem. The dimensionless displacements were calculated based on the B3LYP structure and normal modes using either B3LYP or LC-$\omega$PBE for calculating the excitation energies. For the LC-$\omega$PBE functional, $\omega$ was chosen to be $0.30a_0^{-1}$. This value is based on previous applications where it was shown that this value leads to the best performance for excited state properties such as excitation energies.\textsuperscript{40,368} Excitation energies using the LC-$\omega$PBEh functional yielded very similar results to the LC-$\omega$PBE functional and are thus not reported.

Simulation parameters for the absorbance spectrum were determined by shifting the peak position and changing the peak width to match the experimental absorbance spectrum using a mixture of homogeneous and inhomogeneous broadening. Peak height was normalized to match the experimental absorbance spectrum by applying a scale factor to the DFT results. Repositioned excitation energies, and homogeneous and inhomogeneous broadening parameters for each functional were then used to simulate the resonance Raman spectra. The scale factors used to normalize the absorbance maxima were not applied to the resonance Raman spectra. Additional details of the fitting procedure are described in Appendix B.
4.4 Results and Discussion

4.4.1 Hexamethylbenzene/TCNE

The structure for the HMB/TCNE complex is shown in Fig. 4.1. In this system, the electron donor molecule is HMB and the electron acceptor is TCNE. Experimentally, the absorbance maximum is found to be located at 532 nm (2.33 eV) with a transition dipole moment estimated at 1.644 a.u. The LC-ωPBE functional places the excitation at 499 nm (2.48 eV) with a transition dipole moment of 1.218 a.u., while B3LYP finds the excitation to be at 668 nm (1.86 eV) with a transition dipole moment of 1.597 a.u. LC-ωPBE locates the excited state closer to where it is found experimentally than B3LYP. Discrepancies between the experimental and the theoretical excitation energies may be attributed to solvent effects that are not included in the TDDFT calculations and basis set dependence of the excitation energies.

Simulated absorbance spectra for the HMB/TCNE complex obtained using B3LYP and LC-ωPBE are shown in Fig. 4.2. Also, shown in Fig. 4.2 is the simulated absorbance spectrum using data fitted to the experimental spectrum taken from Ref. 107. For this complex, one symmetric peak is observed with an absorbance maximum positioned at 532 nm that corresponds to an intermolecular charge-transfer state between the HMB donor and TCNE acceptor. Calculations using LC-ωPBE find that the first excitation is the HOMO-1 to LUMO transition, which is a dark state, while the second excitation is the HOMO to LUMO transition that is a bright state. In this case, both the HOMO
Figure 4.2. Absorbance spectra for HMB/TCNE with fits (blue line) compared to the experimental absorbance spectrum (black line, Ref. 107). The fit to experimental data (labeled “Exp. Fit”) used $\Gamma = 300 \text{ cm}^{-1}$, $\Theta = 1000 \text{ cm}^{-1}$, scale factor = 0.725. Using the B3LYP functional: $\Gamma = 300 \text{ cm}^{-1}$, $\Theta = 1800 \text{ cm}^{-1}$, scale factor = 0.761. For LC-\(\omega\)PBE: $\Gamma = 300 \text{ cm}^{-1}$, $\Theta = 1400 \text{ cm}^{-1}$, scale factor = 1.29.

and HOMO-1 come from HMB and the LUMO is from TCNE. B3LYP yields similar character for the frontier molecular orbitals, however, it reorders the energy and intensity of the two excitations.

Examination of Fig. 4.2 shows that each method gives a reasonably accurate model of the experimental data. It is coincidental that each method uses the same homogeneous broadening parameter $\Gamma$, but the inhomogeneous broadening is dominant due to its much larger magnitude. The variation in the $\Delta_n^k$ values is reflected in part by the inhomogeneous broadening parameter $\Theta$ which varies from 1000 cm\(^{-1}\) for the experimental fitted data to 1800 cm\(^{-1}\) for the B3LYP functional. Also, it is apparent that each description differs because each fit is scaled by a different factor. While the $\Delta_n^k$ values from B3LYP and experiment cause the absorbance cross section to be overestimated by about 25%, using $\Delta_n^k$ values from LC-\(\omega\)PBE results in the underestimation of the absorbance cross section.
Figure 4.3. Resonance Raman spectra at 530 nm for HMB/TCNE using the optimum modeling parameters for the absorbance spectra plotted in 4.2. Data for the spectrum labeled “Exp.” are from Ref. 107. Spectra are broadened with a Lorentzian function with 10 cm\(^{-1}\) width.

by about the same factor. The scale factor that is applied to the experimental fit, in this case, is likely due to the different model for the inhomogeneous broadening used in this work compared to the original work of Myers et al.\(^{107}\)

Resonance Raman spectra simulated at 530 nm with the optimum modeling parameters for the absorbance spectra are presented in Fig. 4.3 using B3LYP and LC-\(\omega\)PBE. For comparison we also plot the simulated Resonance Raman spectrum using the data obtained by fitting to the experimental spectrum, which we will refer to as the experimental spectrum since it is essentially identical to what was found by Myers et al.\(^{107}\) A qualitative comparison of the B3LYP spectrum with the experimental resonance Raman spectrum indicates that B3LYP significantly underestimates the relative peak intensities of the high energy normal modes. Comparing the data from the LC-\(\omega\)PBE functional with the experimental resonance Raman spectrum shows that LC-\(\omega\)PBE yields much better agreement with experiment. For both experiment and LC-\(\omega\)PBE, the most intense
peak results from the C=C stretch at 1570 cm$^{-1}$ on the TCNE structure, whereas for B3LYP it involves the intermolecular donor-acceptor (D-A) stretching motion at 165 cm$^{-1}$ (see Supporting Information for complete normal mode assignments).

There are some noticeable differences between the spectrum from LC-$\omega$PBE and the experimental spectrum. The region around 1000 cm$^{-1}$ has only one important mode (due primarily to a C-CH$_3$ stretch and CH$_3$ deformation on HMB) in the experimental spectrum, but LC-$\omega$PBE indicates there are two modes with similar mode structure and intensity at 956.85 cm$^{-1}$ and 1056.58 cm$^{-1}$. Also, LC-$\omega$PBE overestimates the intensities of several modes between 1460 cm$^{-1}$ and 1500 cm$^{-1}$ relative to the large peak at 1531.11 cm$^{-1}$. It is also found that the lower frequency region (below 250 cm$^{-1}$) has some additional features, but these low-frequency modes are not very accurately described in the harmonic approximation. Inclusion of anharmonic effects in the model would be a method to test if anharmonicity is important, but this is not feasible for large molecular systems like the HMB/TCNE complex. There may also be an improvement in the description of these modes if solvent effects are included in the TDDFT calculations, which have been shown to be important for describing intramolecular CT states of rhodamine 6G.$^{362}$ It may also be important to include dispersion corrections to the XC functional in complexes such as HMB/TCNE, like those used in the DFT-D method.$^{369,370}$

Quantitative inspection of the peak intensities of the different resonance Raman spectra show that the agreement between theory and experiment is not perfect, but it is interesting that changing between the two XC functionals yields such a dramatic change in relative peak intensities. The resonance Raman spectrum simulated with LC-$\omega$PBE yields differential Raman scattering cross sections that differ by a range of factors between 4 and 10 when compared with those derived experimentally. A similar comparison between the spectrum from B3LYP and that from experiment shows that, resulting from the poor description of the high energy normal modes, the differential Raman scattering cross sections vary by a range of a factor of 2 to a large factor of approximately 50 for some of the higher energy normal modes. Based on the good agreement between spectra plotted with LC-$\omega$PBE and experiment, it appears that the long-range corrections to the XC potential are necessary for describing the electronic structure in systems where CT states are important.

Further evidence of the necessity of long-range corrections to the XC potential for the HMB/TCNE system are shown on the low energy side of the resonance Raman spectra. For the normal mode at 165 cm$^{-1}$, it is found that the motion of the system involves vibrations where the HMB and TCNE molecule change relative distance from
one another. In situations where molecules involved in a CT excitation change distance from one another, it has been shown that the excitation energy and potential energy surface are dependent on the distance $R$ between the donor and acceptor molecule. As the intermolecular distance is changed for a CT state, it is expected that the interactions between the cationic donor molecule (HMB) and anionic acceptor molecule (TCNE) behave as $1/R$, so the potential energy surface should have that behavior. Resonance Raman spectra, and especially the excited state gradients used for determining $\Delta^n_k$ values, are a useful probe of how well the excited state potential energy surface is described by the XC functional.

For B3LYP, although the magnitude of the $\Delta^n_k$ for the intermolecular D-A stretch is comparable to that determined experimentally (2.80 from B3LYP compared with -3.80 from experiment), this is likely a result of fortuitous error cancellation because the rest of the $\Delta^n_k$ values are poorly described using this functional. The experimental result for the sign of $\Delta^n_k$ for this mode was rationalized based on the fitting procedure by including the nuclear coordinate dependence on the transition dipole moment (Herzberg-Teller terms). Note that for a single contributing excited state, the sign of $\Delta^n_k$ is irrelevant as long as Duschinsky rotations are not accounted for, and also that experimentally measured resonance Raman spectra can only yield the absolute value of $\Delta^n_k$. The potential energy surface described by B3LYP displays a shape that is incorrect, likely attributed to the incorrect exponential decay of XC potential. LC-\(\omega\)PBE has a slightly worse agreement for this mode with experiment ($\Delta^n_k$ is 2.12 for LC-\(\omega\)PBE compared with -3.80 from experiment), but the rest of the spectrum is described much more similarly to the experimental results. This finding reflects the importance of asymptotic decay of the XC potential in this system.

It is also interesting to compare the methods based on the vibrational reorganization energy. The total reorganization energies for experiment, B3LYP, and LC-\(\omega\)PBE are 3517 cm\(^{-1}\), 2140 cm\(^{-1}\), and 2738 cm\(^{-1}\), respectively. Comparing these values indicates both DFT methods underestimate the reorganization energies, by approximately 1400 cm\(^{-1}\) for B3LYP and 800 cm\(^{-1}\) for LC-\(\omega\)PBE. This partially reflects that both B3LYP and LC-\(\omega\)PBE underestimate the value of $\Delta^n_k$ for almost every mode when compared with the fit determined experimentally. Another cause for the difference between the $\Delta^n_k$ values is that those calculated from TDDFT are for the HMB/TCNE complex in vacuum, but those determined experimentally include the effects of solvent. Inclusion of solvent effects can have a dramatic effect on the resonance Raman spectrum for molecules involving CT states, as was shown in a previous study of rhodamine 6G.
4.4.2 Carbazole/TCNE

The optimized structure for the carbazole/TCNE complex is shown in Fig. 4.4. Results for the calculation of vertical excitations and transition dipole moments using TDDFT with both XC functionals are compared with experimental findings in Table 4.1. For the experimental estimates for the locations of the two excitations, electronic structure calculations involving the Pariser-Parr-Pople (PPP)\textsuperscript{373} and semiempirical AM1 methods\textsuperscript{123} were used to determine that the HOMO and HOMO-1 of carbazole are energetically similar. These analyses were performed for the carbazole donor in vacuum, and therefore do not include interactions with the TCNE acceptor molecule. The calculations presented in this work include the entire complex as shown in Fig. 4.4, and when TDDFT was applied using the LC-\(\omega\)PBE functional to the carbazole/TCNE complex, it was determined that two CT states exist in energetically close proximity for this complex. When the calculation is performed using B3LYP the excitation energies are severely underestimated for both CT states, which has been observed previously in the literature and can be traced to self-interaction errors resulting from missing HF exchange.\textsuperscript{371} These states will be referred to as the CT1 and CT2 states in the discussion that follows. Having two states in the absorbance band confirms what was proposed in Refs. 123 and 373.

Inspection of the transition dipole moments in Table 4.1 indicates that each method gives a different description of both excited states. This is reflected in the very different simulation of the absorbance spectrum (see Fig. 4.5) for each method. For B3LYP, the CT2 state is more intense than the CT1 state, and as a result the CT2 state must be positioned near the absorbance maximum to obtain a good description. The LC-\(\omega\)PBE functional finds that the two states have similar intensity and are positioned nearly equidistant from the absorbance maximum. Experimentally, the transition dipole
Table 4.1. TDDFT results for the vertical excitation energies and magnitudes of the transition dipole moments compared with the experimental estimates of these values.107

<table>
<thead>
<tr>
<th>Method</th>
<th>CT1</th>
<th>CT2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ (nm)</td>
<td>Energy (eV)</td>
</tr>
<tr>
<td>B3LYP</td>
<td>1138</td>
<td>1.09</td>
</tr>
<tr>
<td>LC-ωPBE</td>
<td>549</td>
<td>2.26</td>
</tr>
<tr>
<td>Exp.123</td>
<td>626</td>
<td>1.98</td>
</tr>
</tbody>
</table>

moments were determined as fitting parameters that gave the best agreement with the resonance Raman spectra.123 In this case, it is found that the CT1 state is more intense and is positioned closer to the absorbance maximum than the CT2 state resulting from the transition dipole moments.

In Fig. 4.5, plots of the fits using the experimental, B3LYP, and LC-ωPBE Δν values (see Tables B.7 and B.8 in Appendix B) are shown. For this system, the CT1 state involves the HOMO to LUMO excitation regardless of which functional is used. The CT2 state is a transition between the HOMO-1 and LUMO for both functionals. Both functionals yield similar character for the orbitals involved in both CT states, where the HOMO and HOMO-1 are localized on the carbazole molecule and the LUMO is contributed to by the TCNE molecule. The simulated absorbance spectrum is especially good for the LC-ωPBE functional. However, both XC functionals yield a poorer fit than experimentally determined parameters for the red-edge of the absorbance maximum.

Simulated resonance Raman spectra at the absorbance maximum (601 nm) are shown in Fig. 4.6. At that wavelength both CT states have some contribution to the total resonance Raman spectrum. A simple qualitative examination of the spectra indicates again that B3LYP overestimates the contribution of the intermolecular D-A stretch at 159.78 cm⁻¹. Even if that mode were ignored, the mode at 1537.44 cm⁻¹ would not stand out on the resonance Raman spectrum even though that mode (predominantly the C=C stretch of the TCNE molecule) is the dominant feature observed experimentally. Clearly, the potential energy surfaces of the CT1 and CT2 states are poorly described by B3LYP as indicated by the resonance Raman spectrum.

LC-ωPBE yields a spectrum where the correct mode is the dominant feature of the spectrum, but also has some noticeable differences. The fact that the relative intensities of the modes at 1537.44 cm⁻¹, 1602.16 cm⁻¹ (carbazole C-H and N-H in-plane bending
Figure 4.5. Absorbance spectra for Carbazole/TCNE with fits compared to the experimental absorbance spectrum (black line, Ref. 123). In the figures, the total fit is the blue line, the fit for the CT1 state (at lower energy) is the red line, and the fit for the CT2 state (at higher energy) is the green line. For (a) we used $\Gamma_{CT1} = 300 \text{ cm}^{-1}$, $\Gamma_{CT2} = 200 \text{ cm}^{-1}$, $\Theta = 1200 \text{ cm}^{-1}$, scale factor = 0.732. Using the B3LYP functional in panel (b): $\Gamma_{CT1} = 250 \text{ cm}^{-1}$, $\Gamma_{CT2} = 300 \text{ cm}^{-1}$, $\Theta = 2200 \text{ cm}^{-1}$, scale factor = 0.893. For LC-\(\omega\)PBE in panel (c): $\Gamma_{CT1} = 300 \text{ cm}^{-1}$, $\Gamma_{CT2} = 250 \text{ cm}^{-1}$, $\Theta = 1600 \text{ cm}^{-1}$, scale factor = 2.01.

The energetic placement of the excited states to obtain good fits, and also in particular the transition dipole moments for the two states. Because the experimental fit determines that CT2 has a significantly smaller transition dipole moment, this state will not be observed having as strong of an effect on the resonance Raman spectrum. LC-\(\omega\)PBE finds that the transition dipole moments for both states have similar magnitude, causing a noticeable contribution from both states to the resonance Raman spectrum.

To determine the effects of the different excited states, resonance Raman spectra for
Figure 4.6. Resonance Raman spectra at 601 nm for carbazole/TCNE using the optimum modeling parameters for the absorbance spectra plotted in 4.5. Data for the spectrum labeled “Exp.” are from Ref. 123. Spectra are broadened with a Lorentzian function with 10 cm$^{-1}$ width.

The individual CT1 (Fig. 4.7) and CT2 (Fig. 4.8) states were simulated by only including one excited state. Comparing the results for the CT1 state alone, it is clear that LC-ωPBE gives a very similar resonance Raman spectrum compared with the experimental result. It is also distinct that the description from B3LYP is poor, likely resulting from the same incorrect behavior of the XC potential for B3LYP described above for the HMB/TCNE complex. Only a few modes around 750 cm$^{-1}$ and 1250 cm$^{-1}$ involving carbazole ring deformations and in-plane bending of C-H and N-H bonds have intensities that are overestimated by the LC-ωPBE functional.

A comparison between the resonance Raman spectra for the individual CT1 and CT2 states from the LC-ωPBE functional and experimental data gives an indication of how well each excited state is described using the LC-DFT method. The CT1 state simulated by LC-ωPBE compares well with what is found from experiment, indicating that this state is described correctly by the LC-ωPBE functional. When the CT2 state
Figure 4.7. Individual resonance Raman spectra for the CT1 state at 601 nm for the car-
bazole/TCNE complex using the optimum modeling parameters for the absorbance spectra
plotted in 4.5. Data for the spectrum labeled “Exp.” are from Ref. 123. Spectra are broadened
with a Lorentzian function with 10 cm$^{-1}$ width.

is simulated, there is a clear difference between what is observed experimentally and
using the LC-ωPBE functional, however, due to the appearance of two modes with high
intensity near 425 cm$^{-1}$ (carbazole out of plane ring deformation) and also several high
intensity modes between 1000 and 1500 cm$^{-1}$ for the LC-ωPBE model. This disagreement
stands out, but based on the agreement of LC-ωPBE with experiment for the CT1 state,
it does not seem like the description of the CT2 state potential energy surface by the
LC-ωPBE is necessarily incorrect.

Use of the experimental fit proposed in Ref. 123 would mean that observing both CT
states separately is very difficult because both overlap on the blue edge of the absorbance
maximum. Although interference effects$^{123}$ are observed between the two CT states, this
does not seem to be the reason why the $\Delta n_k$ values for the CT1 state and CT2 state are
so similar experimentally. Because of the large amount of overlap, the positioning of the
two states, and the large transition dipole moment of the CT1 state compared to the CT2 state from experiment, the CT1 state is observed to dominate the contributions to the total resonance Raman spectrum (Fig. 4.6). As a result, any wavelength used to measure a resonance Raman spectrum for the carbazole/TCNE complex would have intensities largely derived from the CT1 state. Likely, the CT2 state was only partially observed due to changes in relative peak intensities on the total resonance Raman spectrum, but its contribution was so weak that it could not be fully resolved.

Because the CT1 and CT2 states overlap to some degree in the absorbance spectrum there is a possibility that interference effects may occur in the resonance Raman spectrum. Interference can be constructive and result in an increased total differential cross section compared to the individual contributions of either CT states, or destructive which causes a reduction in peak intensities for specific modes on the total resonance Raman spectrum.
These effects are described in detail in Ref. 123 for parallel transition dipole moments and more generally in Ref. 106 for numerous situations involving different modeling parameters. Three important cases that may cause destructive interference are: having $\Delta_n^k$ values with opposite signs, the angle between the transition dipole moments of different states, and detuning from resonance.

The contribution from $\Delta_n^k$ values with opposite signs is important because for two contributing excited states the differential Raman scattering cross section is proportional to the sum of the polarizability of each state squared. This causes terms in the differential Raman scattering cross section that are products of the polarizability of each state that both depend on the $\Delta_n^k$ values as multiplicative factors. The angle between the transition dipole moments for the two states can result in components of the transition dipole moments that are opposite in sign. For the experimental spectrum, it was assumed that the transition dipoles are parallel\textsuperscript{123} but LC-$\omega$PBE finds that there is a 125.5° angle between them. This means that only the first effect is present in the total resonance Raman spectrum for the experimental data, but both are present for the LC-$\omega$PBE functional. The third effect was elaborated on in Ref. 106 and is caused by detuning from resonance with the excited states resulting in resonance deenhancement. This third effect can be observed when changing the excitation wavelength along the absorbance peak, and is clearly viewed for the experimental data where the sign of the Fourier integrals can change and result in different signs for the real and imaginary components of the polarizability. This effect is most clear when the sum-over states expression for the Raman polarizability is examined, where having an excitation wavelength greater than the vertical excitation energy creates a negative sign in the energy denominator.

The interference effects, $I$, in terms of the resonance Raman cross sections for this system can be quantified as

$$I = \left( \frac{d\sigma}{d\Omega} \right)_{\text{total}} - \left( \frac{d\sigma}{d\Omega} \right)_{\text{CT1}} - \left( \frac{d\sigma}{d\Omega} \right)_{\text{CT2}}$$  \hspace{1cm} (4.13)

where the terms on the right hand side are, respectively, the total differential Raman cross section, the differential Raman cross section for the CT1 state alone, and the differential Raman cross section for the CT2 state alone. This allows plots of interference to be made over the spectral range of the resonance Raman spectrum, like what is shown in Fig. 4.9. For each plot, data is normalized to the mode with maximum constructive interference and thus any negative peak represents destructive interference.

An obvious difference is apparent by investigating the interference patterns presented
Figure 4.9. Plots of the interference between the CT1 and CT2 states at 601 nm using Eq. 4.13. Plots are normalized to the peak with maximum constructive interference. Data for the spectrum labeled “Exp.” are from Ref. 123.

in Fig. 4.9. First, the figure derived from experimental data has constructive interference present for modes involving $\Delta n$ values that are opposite in sign for the CT1 and CT2 states. This disagrees with the analysis presented in Ref. 123, where having $\Delta n$ values with opposite signs for the CT1 and CT2 states was thought to be the only factor causing destructive interference. Because the transition dipole moments are parallel (directed along the positive z-axis), their components have the same sign and cannot result in destructive interference effects. This means that the third effect resulting from the sign of the integral must lead to the seemingly opposite picture for the constructive and destructive interference observed for the experimental data. A test calculation (data not shown) where the experimental absorbance maxima for CT1 and CT2 were shifted to the locations determined for the best fit of the LC-ωPBE functional caused the interference pattern to change from what is shown in Fig. 4.9 to a pattern similar to that found for
LC-ωPBE, indicating that this detuning effect is important for determining interference. Also, it can be shown that the interference pattern changes when data is compared at different excitation wavelengths for the experimental data (see Figure B.1 in Appendix B).

For both the B3LYP and LC-ωPBE functionals, all three interference effects are present, resulting in a different description of the interference pattern. Although the magnitude of constructive interference for the B3LYP functional, particularly on the low frequency side of the spectrum, does not agree with the description by LC-ωPBE, examination of the interference plots show that many of the same modes have constructive interference. This is surprising based on the poor description of the potential energy surfaces by B3LYP, but more importantly it demonstrates that all three effects discussed above are important for describing interference. It turns out that out of eight modes found experimentally to have destructive interference, six of these modes at 617.00, 1127.24, 1362.96, 1463.04, 1477.85, and 1626.19 cm⁻¹ were found to show destructive interference using the LC-ωPBE functional.

One final detail is the vibrational reorganization energy for the carbazole/TCNE system. Experiment finds comparable values for the CT1 and CT2 states of 1988 cm⁻¹ and 1950 cm⁻¹, respectively. The respective values are 2441 cm⁻¹ and 1456 cm⁻¹ for B3LYP and 1375 cm⁻¹ and 2606 cm⁻¹ for LC-ωPBE. Due to the different descriptions of the two CT states using B3LYP and LC-ωPBE as compared with experiment it is difficult to directly compare the individual reorganization energies. However, the sum of the reorganization energies for the two CT states are similar in all three cases.

4.5 Conclusions

This work presents the first application of the LC-DFT method to resonance Raman scattering of donor-acceptor complexes. The popular global hybrid functional B3LYP and LC-functional LC-ωPBE were compared against experimental data for the carbazole/TCNE and hexamethylbenzene/TCNE donor-acceptor complexes with important CT states in their optical absorbance spectra. Using simulations of the absorbance and resonance Raman spectra involving the time-dependent formalism of Heller et al. it was found that even though B3LYP could simulate absorbance spectra reasonably, it yielded poor descriptions of the excited state potential energy surfaces in the FC region as indicated by resonance Raman spectra. The LC-ωPBE functional simulates the absorbance spectra well and significantly improves the description of the potential energy surfaces.
in the FC region, as shown by its better agreement with the experimental resonance Raman spectrum for both complexes. For the carbazole/TCNE complex in particular the overlapping CT1 and CT2 states cause interference effects that change relative peak intensities on the resonance Raman spectrum. These effects can be traced to three factors: the sign of $\Delta n_k$ for each state, the angle between the transition dipole moments, and detuning from resonance with each state. In the analysis we showed that all three factors need to be accounted for. Finally, the total vibrational reorganization energy from both B3LYP and LC-ωPBE was compared to what was calculated experimentally using Marcus theory of electron transfer. Both functionals yield reasonable predictions of the total vibrational reorganization energy, but LC-ωPBE distributes single-mode contributions similarly to what was found experimentally based on the resonance Raman spectra. In order to improve agreement with the experimental data, it might be necessary to include solvent effects in these systems so that the $\Delta n_k$ values compare more closely with experiment for the CT states investigated in this work.
Part III

Vibronic coupling simulations of linear and nonlinear optical processes
Vibronic Coupling Simulations for Linear and Nonlinear Optical Processes: Theory


Abstract

A comprehensive vibronic coupling model based on the time-dependent wavepacket approach is derived to simulate linear optical processes, such as one-photon absorbance and resonance Raman scattering, and nonlinear optical processes, such as two-photon absorbance and resonance hyper-Raman scattering. This approach is particularly well suited for combination with first-principles calculations. Expressions for the Franck-Condon terms, and non-Condon effects via the Herzberg-Teller coupling approach in the independent-mode displaced harmonic oscillator model are presented. The significance of each contribution to the different spectral types is discussed briefly.
5.1 Introduction

Simulations of linear and nonlinear optical properties provide detailed molecular level understanding of experimental spectra. In many cases it is important to include vibronic coupling effects to obtain good agreement with experimental results. For this reason there is a significant interest in developing efficient approaches that includes these effects in the simulations of linear and nonlinear optical properties. Several approaches to understanding linear absorbance and emission bandshapes have been presented.\textsuperscript{91,100,123,125,126,132,374–381} While most of these studies invoke the Born-Oppenheimer approximation, significant process has also been made to include nonadiabatic effects.\textsuperscript{382–387} However, due to the large computational demands of accounting for coupling between different electronic states when nonadiabatic effects are important, only the most important vibrational degrees of freedom were included in the quantum representation of the system while the remaining normal modes were represented as a harmonic bath. In contrast to the large number of studies described above involving linear optical processes such as one-photon absorption (OPA), resonance Raman scattering (RRS), and fluorescence, significantly fewer studies have been devoted to vibronic structure in nonlinear optical processes such as two-photon absorbance (TPA) and resonance hyper-Raman scattering (RHRS).

Macak et al.\textsuperscript{388} examined vibronic profiles of molecules containing donating and accepting groups using a combined model incorporating Franck-Condon (FC) and Herzberg-Teller (HT) terms (or non-Condon). Lin et al.\textsuperscript{389} extended that model to examine FC and HT contributions in both OPA and TPA for 4-dimethylamino-4'-methyl-trans-stilbene. Vibronic structure has also been incorporated into TPA spectra in a small collection of other studies, showing improvement in the agreement between the models and experimental data.\textsuperscript{29,185,390–393} Other TPA studies have examined absorbance of various chromophores including donor-acceptor chromophores and thiolated gold clusters, using simpler Lorentzian or Gaussian bandshapes and delta functions to simulate spectra.\textsuperscript{181,182,266,394–399}

Nonresonant hyper-Raman scattering and also RHRS, owing in part to their inherent weakness,\textsuperscript{1,24} have been examined in even less detail. Significant contributions from Ziegler and coworkers\textsuperscript{24,196–198,400} lead to a comprehensive understanding of RHRS in terms of vibronic theory that was applied to small molecules in the gas phase.\textsuperscript{208} In that model, the transition hyperpolarizability is written as a sum of terms: $\beta_{ijk} = A + B + C + \ldots$, where $A$ refers to the FC term, $B$ is the first HT term, $C$ is the second HT term, and so forth. This decomposition parallels the analysis of the transition polarizability
for RRS by Albrecht. Alternatively, the analysis of RHRS can also be described using the time-dependent formalism pioneered by Heller and coworkers. The time-dependent formalism offers the advantage of recasting the explicit summation over the intermediate vibrational states into a time-integral. This makes the method computationally attractive for dealing with large systems.

Referring to Ziegler’s vibronic theory, Cameron and coworkers analyzed in solution RHRS of napthalene and substituted benzenes. Solution phase RHRS has also been performed for numerous push-pull (donor-acceptor) chromophores and zinc pthalocyanine, applying both Ziegler’s vibronic theory and the time-dependent formalism. Non-Condon effects have also been included in the time-dependent formalism to describe OPA and RRS and to a lesser degree RHRS. Shoute et al. examined RHRS of push-pull donor-acceptor complexes, using a model where the intermediate state of the two-photon excitation was assumed to be a vibrational level of the ground electronic state. A recent investigation of RHRS for the fluorescent dye rhodamine 6G illustrated that non-Condon terms can be larger than FC terms in circumstances when one- and two-photon transitions are not simultaneously strong.

In this work, we present a comprehensive derivation of the vibronic coupling model included FC and HT terms based on the time-dependent formalism. We will derive the time-dependent expression for OPA, RRS, TPA, and RHRS. Previously, expressions for the FC terms of OPA, RRS, and RHRS have been shown but are included here for consistency. As far as we are aware, the TPA expressions and the HT terms derived in the time-dependent formalism for OPA, TPA, and RHRS are shown for the first time, including the explicit vector description of all involved response properties. Inclusion of components of the transition dipole moment vector yields a more detailed description of interference effects between electronic states in linear and nonlinear Raman scattering processes.

Starting from the sum-over-states formulas for the OPA cross section, RRS transition polarizability, TPA cross section, and RHRS transition hyperpolarizability, it is demonstrated how each expression is converted to its time-domain analogue. For all methods described, the response properties (the transition dipole moment of linear response and
two-photon transition moment of quadratic response) are expanded in Taylor series around the normal modes, allowing explicit inclusion of the FC and HT effects for each spectral simulation. Following conversion to the time-dependent formalism, expressions for the wavepackets of the ground state and first excited state of the harmonic oscillator are used to define the autocorrelation functions for evaluating the lineshape functions. These are reviewed in order to define all quantities in a consistent notation, revealing typographical errors in originally derived expressions for the wavepacket autocorrelation function and lifetime function. The expressions for the autocorrelation functions used in HT terms are presented for the first time. The final section summarizes the prefactors, which include the transition dipole moment and two-photon transition moment and their nuclear dependence, in relation to the numerous terms related to each simulation.

5.2 Analysis of Spectral Types

5.2.1 One-Photon Absorbance

When the Born-Oppenheimer (BO) approximation is applied, the expression for the OPA cross section \( \sigma_{OPA} \) is given in terms of a sum over states as

\[
\sigma_{OPA}(\omega) = \frac{4\pi^2c}{3} \sum_{j,j'} \frac{\langle I_0 | \langle 0 | \mu_\rho | j \rangle | J_j \rangle \langle j | \mu_\rho | I_0 \rangle}{(E_{J_j} - E_{I_0} - \omega) - i\Gamma_j} \tag{5.1}
\]

where \( E_{J_j} = E_j + \epsilon_j \) is the energy of the final electronic state \( |j\rangle \) and final vibrational state \( |J_j\rangle \), \( E_{I_0} = E_0 + \epsilon_{I_0} \) is the energy of the initial electronic state \( |0\rangle \) and vibrational state \( |I_0\rangle \), \( \omega \) is the energy of the incident photon, \( \Gamma_j \) is the lifetime parameter for the final state, and \( \mu_\rho \) is a component of the transition dipole moment \( (\rho = x, y, \text{ or } z) \). Expanding \( \mu_\rho \) as a Taylor series, \( \mu_\rho = (\mu_\rho)^{eq} + \sum_a (\mu_\rho)^{a'} Q_a \ldots \), about the normal modes, \( Q_a \), Eq. (5.1) becomes

\[
\sigma_{OPA}(\omega) = \frac{4\pi^2c}{3} \sum_{j,j'} \frac{\langle I_0 | \langle 0 | (\mu_\rho)^{eq} + \sum_a (\mu_\rho)^{a'} Q_a | j \rangle | J_j \rangle \langle j | (\mu_\rho)^{eq} + \sum_a (\mu_\rho)^{a'} Q_a | I_0 \rangle}{(E_{J_j} - E_{I_0} - \omega) - i\Gamma_j} \tag{5.2}
\]

In this expression, the notation \( (\mu_\rho)^{eq} \) means the transition dipole moment evaluated at the ground state optimized geometry, and \( (\mu_\rho)^{a'} \) is the derivative of the transition dipole moment along normal mode \( Q_a \) at the ground state optimized geometry. Subsequently, \( \sigma_{OPA} \) may be written as a sum of a FC term, FC-HT interference term and first HT
Performing a Fourier transform allows the evaluation of the FC term in the time-dependent formalism

\[
\sigma_{OPA}(\omega) = \frac{4\pi^2\omega}{3c} \left\{ \sum_{J,j} (\mu^0_j)^{eq} (\mu_j^0)^{eq} \frac{\langle I_0|J_j\rangle \langle J_j|I_0\rangle}{(E_{J_j} - E_{I_0} - \omega - i\Gamma_j)} \right\} + \left\{ \sum_{J,j} \sum_a (\mu_j^0)^{eq} (\mu_j^0)^{eq} \frac{\langle I_0|Q_a|J_j\rangle \langle J_j|Q_a|I_0\rangle}{(E_{J_j} - E_{I_0} - \omega - i\Gamma_j)} \right\} + \left\{ \sum_{J,j} \sum_b (\mu_j^0)^{eq} (\mu_j^0)^{eq} \frac{\langle I_0|Q_b|J_j\rangle \langle J_j|Q_b|I_0\rangle}{(E_{J_j} - E_{I_0} - \omega - i\Gamma_j)} \right\} = \sigma_{FC,OPA}(\omega) + \sigma_{FC-HT,OPA}(\omega) + \sigma_{HT,OPA}(\omega)
\]

(5.3)

in which the transition strength, \((M_{0j})^2\), is defined

\[
(M_{0j})^2 = [(\mu_x^{0j})^{eq}]^2 + [(\mu_y^{0j})^{eq}]^2 + [(\mu_z^{0j})^{eq}]^2
\]

(5.5)

and \(\epsilon_{I_0}\) is the energy of vibrational state \(|I_0\rangle\). Also, \(|I_j(t)\rangle = e^{-iH_jt}|I_0\rangle\) is the wavepacket corresponding to the time-dependent nuclear wavefunction of electronic state \(j\). In Eq. (5.4) the simple homogeneous broadening parameter \(\Gamma_j\) was replaced by the general lifetime function \(g_j(t)\). For the present discussion it is sufficient to know that \(g_j(t)\) is dependent on \(\Gamma_j t\). Due to complexity of the relationship between the lifetime parameters, the specific form of the lifetime function \(g_j(t)\) will be described in a later section. The FC-HT interference term can similarly be simplified in the time-dependent formalism to give the following expression
In Eq. (5.6), $\omega_a$ is the normal mode frequency of mode $Q_a$, and the overlap integral will be described in a later section. Because the majority of molecules are in the ground state of the harmonic oscillator, even at room temperature, the second term in parentheses of Eq. (5.6) is zero unless the normal modes are allowed to populate vibrational levels above the ground state. The subscript $FC$ on the vibrational overlaps indicates that the reference state for the raising and lowering operators was the one used for the FC term. The normal coordinate dependence of the integral is accounted for using the second-quantized form of $Q_a$, i.e.

$$Q_a = \sqrt{\frac{\hbar}{2\omega_a}} (\hat{b}_a + \hat{b}_a^\dagger) \quad (5.7)$$

The derivative of the transition strength along mode $Q_a$, $[(M_{0j})^2]^{a'}$, is given as

$$[(M_{0j})^2]^{a'} = 2(\mu_0^0 j^{a'})^{eq} + 2(\mu_j^0 j^{a'})^{eq} + 2(\mu_0^j j^{a'})^{eq} \quad (5.8)$$

Finally, the HT term is defined

$$\sigma_{OPA}^{HT}(\omega) = \frac{4\pi\omega}{3c} \sum_j \sum_a \sum_b \sqrt{\frac{\hbar}{2\omega_a}} \sqrt{\frac{\hbar}{2\omega_b}} (\mu_0^{0j})^{a'} (\mu_0^{0j})^{b'} \times \text{Re} \int_0^\infty \left( \sqrt{I_a + 1} \sqrt{I_b + 1} \langle (I_a + 1)_0 | (I_b + 1)_j(t) \rangle_{FC} + \sqrt{I_a} \sqrt{I_b + 1} \langle (I_a - 1)_0 | (I_b + 1)_j(t) \rangle_{FC} + \sqrt{I_a} \sqrt{I_b} \langle (I_a - 1)_0 | (I_b - 1)_j(t) \rangle_{FC} \right) e^{i(\epsilon_{I_0} + \omega)t - g_j(t)} dt \quad (5.9)$$

The summation indices $a$ and $b$ in Eq. (5.9) run through the normal modes, with no restriction on their values. As such, it is possible to observe contributions when $a = b$ that differ from contributions when $a \neq b$. The latter three terms inside parentheses of
Eq. (5.9) are zero unless vibrational levels above the ground state are populated.

5.2.2 Resonance Raman Scattering

Assuming that the incident photon energy is on resonance with an electronic transition, the RRS transition polarizability for normal mode \( Q_p \) may be written as

\[
\alpha_{\alpha\beta}^p = \sum_{J,j} \frac{\langle F_0 | \langle 0 | \mu_\alpha | j \rangle \langle j | \mu_\beta | 0 \rangle | I_0 \rangle}{E_{J_j} - E_{I_0} - \omega - i\Gamma_j} \tag{5.10}
\]

Expanding the transition dipole moment components \( \mu_\alpha \) and \( \mu_\beta \) as a Taylor series on normal mode \( Q_a \), the RRS polarizability can be expressed as a sum of terms

\[
\alpha_{\alpha\beta}^p = \sum_{J,j} \left\{ \langle \mu^0_\alpha \rangle_{eq} \langle \mu^0_\beta \rangle_{eq} \frac{\langle F_0 | J_j | I_0 \rangle}{E_{J_j} - E_{I_0} - \omega - i\Gamma_j} \right\} \\
+ \sum_a \left\{ \langle \mu^0_\alpha \rangle_{eq} \langle \mu^0_\beta \rangle_{eq} \frac{\langle F_0 | J_j | Q_a | I_0 \rangle}{E_{J_j} - E_{I_0} - \omega - i\Gamma_j} + \langle \mu^0_\alpha \rangle_{eq} \langle \mu^0_\beta \rangle_{eq} \frac{\langle F_0 | Q_a | J_j | I_0 \rangle}{E_{J_j} - E_{I_0} - \omega - i\Gamma_j} \right\} \\
= A^p + B^p \tag{5.11}
\]

The first term after the sum in Eq. (5.11) is the A term (FC), while the term after the sum over normal modes is the B term (HT).\(^{134,357}\) Previous works\(^{93,359,405}\) have shown that the A term may be written

\[
A^p = (A)_{\alpha\beta}^p = \sum_j \langle \mu^0_\alpha \rangle_{eq} \langle \mu^0_\beta \rangle_{eq} i \int_0^\infty \langle F_0 | J_j(t) \rangle e^{i(\epsilon_{I_0} + \omega) t - g_j(t)} dt \tag{5.12}
\]

Applying the same relationship (Eq. (5.7)) for the normal mode, the B term in RRS can be recast in the time-dependent formalism as
Here, the reference vibrational states for the B term, \(|I_0⟩\) and \(|F_0⟩\), come from the states used for calculating the A term, as indicated by the subscript \(A_p\). Summation of Eqs. (5.12) and (5.13) gives the total transition polarizability for RRS. One must be cautious when evaluating the time-dependent vibrational overlap integrals for the B term, being mindful that the lineshape function and the transition dipole moment derivative cause coupling between the normal modes.

Determination of the differential Raman scattering cross section, in terms of the molecular transition polarizability \(\alpha^{p}_{\alpha\beta}\) given above, is carried out as shown in Ref. 4. A measurement of RRS perpendicular to the incident radiation path yields a differential Raman scattering cross section is calculated as

\[
\frac{d\sigma}{d\Omega} = \frac{\pi^2}{\epsilon_0^2} \sum_l N_{p'\ell} (\omega - \omega_{p_0})^4 \left( \frac{45a_{p'\ell}^2 + 7\gamma_{p'\ell}^2}{45} \right)
\]

where \(N_{p'\ell}\) defines the Boltzmann population of mode \(Q_p\) for initial vibrational state \(|I_0⟩\),

\[
N_{p'\ell} = \frac{g_{p'\ell} \exp \left[-\epsilon_{p'\ell}/k_B T\right]}{\sum_l g_{p'\ell} \exp \left[-\epsilon_{p'\ell}/k_B T\right]}
\]

where \(g_{p'\ell}\) is the degeneracy of the vibrational state, and \(\epsilon_{p'\ell}\) is the vibrational energy of the molecule in the state \(I\) for mode \(Q_{p'}\). Typically, it is assumed that only the lowest vibrational state is significantly populated and the sum in Eq. (5.14) is reduced to a single term. For situations where multiple important vibrational transitions \(I \rightarrow F\) exist at the same wavenumber, it is necessary to sum the contributions of each transition weighted by its Boltzmann population in Eq. (5.14). This is shown, for example, in Ref. 107. The isotropic polarizability average, \(a_{p'\ell}\), is defined as
\[ a_{pI} = \frac{1}{3} \left\{ (\alpha_{xx})_{pI} + (\alpha_{yy})_{pI} + (\alpha_{zz})_{pI} \right\} \] (5.16)

and the anisotropic polarizability average, \( \gamma_{pI} \), is defined using

\[ \gamma_{pI}^2 = \frac{1}{2} \left\{ \left[ (\alpha_{xx})_{pI} - (\alpha_{yy})_{pI} \right]^2 + \left[ (\alpha_{yy})_{pI} - (\alpha_{zz})_{pI} \right]^2 \\
+ \left[ (\alpha_{zz})_{pI} - (\alpha_{xx})_{pI} \right]^2 + 6 \left[ (\alpha_{xy})_{pI} + (\alpha_{yz})_{pI} + (\alpha_{zx})_{pI} \right]^2 \right\} \] (5.17)

Orientational averaging illustrated above is performed in order to account for the various molecular orientations in solution when a measurement is taken. This facilitates the translation between the molecular fixed-frame to a laboratory fixed-frame.

### 5.2.3 Two-Photon Absorbance

Assuming degenerate linearly polarized photons, the TPA cross section \( \sigma_{TPA} \) can be written as

\[ \sigma_{TPA}(\omega) = \frac{2\pi^3 \alpha^2 \omega^2 \hbar^3}{15e^4} 2 \sum_{\alpha,\beta} \text{Im} \left[ \gamma_{\alpha\alpha\beta\beta}(-\omega;\omega,\omega,-\omega) + \gamma_{\alpha\beta\beta\alpha}(-\omega;\omega,\omega,-\omega) \right. \\
+ \left. \gamma_{\alpha\beta\alpha\beta}(-\omega;\omega,\omega,-\omega) \right] \] (5.18)

in which \( \alpha \) is a fine structure constant and the \( \gamma_{ijkl}(-\omega;\omega,\omega,-\omega) \) are the second-hyperpolarizability tensor elements. For instance, \( \gamma_{\alpha\alpha\beta\beta}(-\omega;\omega,\omega,-\omega) \) is defined

\[ \gamma_{\alpha\alpha\beta\beta}(-\omega;\omega,\omega,-\omega) = \sum_{K,k,L,l} \left( \langle I_0 | \langle 0 | \mu_\alpha | l \rangle | L_l \rangle | l | \mu_\alpha | k \rangle | K_k \rangle + \langle I_0 | \langle 0 | \mu_\alpha | l \rangle | L_l \rangle | l | \mu_\alpha | k \rangle | K_k \rangle \right) \times \\
\times \left( (K_k | \langle k | \mu_\beta | l \rangle | L_l \rangle | l | \mu_\beta | 0 \rangle | I_0 \rangle + \langle K_k | \langle k | \mu_\beta | l \rangle | L_l \rangle | l | \mu_\beta | 0 \rangle | I_0 \rangle \right) \times \\
\times \left( [(E_{K_k} - E_{I_0} - 2\omega) - i\Gamma_{k}](E_{L_l} - E_{I_0} - \omega)^2 \right)^{-1} \] (5.19)

Because the incident photon is far from resonance with intermediate vibrational states, it is possible to write \( E_{L_l} - E_{I_0} \approx E_l - E_0 \) and perform closure over the intermediate
vibrational state $|I_l\rangle$. In doing so, and performing the BO approximation, the second hyperpolarizability becomes

$$\gamma_{\alpha\alpha\beta\beta}(-\omega;\omega,\omega,-\omega) = \sum_{K,k} \frac{(\langle I_0|S^{0k}_{\alpha\alpha}|K_k\rangle) (\langle K_k|S^{0k}_{\beta\beta}|I_0\rangle)}{[(E_{K_k} - E_{I_0} - 2\omega) - i\Gamma_k]} \quad (5.20)$$

where the two-photon transition moments are defined

$$S^{k0}_{\beta\gamma} = \sum_l \left\{ \mu_{l\beta}^{k\Gamma} \mu_{\gamma}^{l0} + \mu_{l\beta}^{k\Gamma} \mu_{\gamma}^{l0} \right\} \quad (5.21)$$

The same procedure may be used for the other second-hyperpolarizability terms as well.

Rather than expanding each transition dipole moment as a Taylor series about the normal modes, it is less algebraically tedious to work with the two-photon transition moment ($S^{k0}_{\beta\gamma}$, defined in Eq. (5.21)). This is given by $S^{k0}_{\beta\gamma} = (S^{k0}_{\beta\gamma})^{eq} + \sum_a (S^{k0}_{\beta\gamma}) a Q_a \ldots$ (where $\beta$ and $\gamma$ are Cartesian components). To reduce repetition we will focus on the end result of the derivation of the FC, interference and first HT terms of $\sigma_{TPA}$, where $\sigma_{TPA} = \sigma_{TPA}^{FC} + \sigma_{TPA}^{FC-HT} + \sigma_{TPA}^{HT}$. It is assumed in the derivation that each individual photon is not near resonant with an electronic excited state, but a resonance exists with a two-photon excited state.

The FC term in TPA is defined in the time-dependent formalism as

$$\sigma_{TPA}^{FC}(\omega) = \frac{4\pi^3 \alpha^2 \omega^2 \hbar^3}{e^4} \sum_k \delta^{0k}_{TPA} Re \int_0^\infty \langle I_0|I_k(t)\rangle e^{i(\epsilon_{I_0} + 2\omega) t - \phi_k(t)} dt \quad (5.22)$$

The two-photon transition strength (sometimes referred to as the two-photon cross section), $\delta^{0k}_{TPA}$, is given by

$$\delta^{0k}_{TPA} = 2 \sum_{\alpha,\beta} \frac{1}{30} \left[ (S^{0k}_{\alpha\alpha})^{eq} (S^{k0}_{\beta\beta})^{eq} + (S^{0k}_{\beta\beta})^{eq} (S^{k0}_{\alpha\alpha})^{eq} + (S^{0k}_{\alpha\beta})^{eq} (S^{k0}_{\alpha\beta})^{eq} \right] \quad (5.23)$$

In general, $\delta^0_G = \delta^0_H$ so only one of the two values is reported. The FC-HT interference term can be derived as
\[ \sigma_{TPA}^{FC-HT}(\omega) = \frac{4\pi^3\alpha^2\omega^2\hbar^3}{e^4} \sum_k \sum_a (\delta_{TPA}^{0k})^{a^f} \sqrt{\frac{\hbar}{2\omega_a}} \times \text{Re} \int_0^\infty \left( \sqrt{I_a + 1} \langle (I_a + 1)_0 | I_k(t) \rangle_{FC} + \sqrt{I_b} \langle (I_b - 1)_0 | I_k(t) \rangle_{FC} \right) e^{i(\epsilon I_0 + 2\omega t - g_k(t))} dt \] (5.24)

Like the OPA case, the subscript FC on the vibrational overlap integral indicates that the reference state for the raising and lowering operators is that of the FC term. The derivative of the two-photon transition strength along mode \( Q_a \), denoted \( (\delta_{TPA}^{0k})^{a^f} \), is given as

\[ (\delta_{TPA}^{0k})^{a^f} = 2 \sum_{\alpha,\beta} \frac{1}{30} \left[ (S^{0k}_{\alpha\alpha})^{a^f} (S^{0k}_{\beta\beta})^{eq} + (S^{0k}_{\alpha\beta})^{a^f} (S^{0k}_{\beta\alpha})^{eq} + (S^{0k}_{\alpha\beta})^{a^f} (S^{0k}_{\beta\alpha})^{eq} + (S^{0k}_{\alpha\beta})^{a^f} (S^{0k}_{\beta\alpha})^{eq} \right] \] (5.25)

The value of the two-photon transition moment at the ground state optimized geometry is given by \( (S_{\beta\gamma})^{eq} \) and its derivative along normal mode \( Q_a \) is \( (S_{\beta\gamma})^{a^f} \). For the HT term, the derivation leads to the following form

\[ \sigma_{TPA}^{HT}(\omega) = \frac{4\pi^3\alpha^2\omega^2\hbar^3}{e^4} \sum_k \sum_a \sum_b (\delta_{TPA}^{0k})^{ab^f} \sqrt{\frac{\hbar}{2\omega_a}} \sqrt{\frac{\hbar}{2\omega_b}} \times \text{Re} \int_0^\infty \left( \sqrt{I_a + 1} \sqrt{I_b} \langle (I_a + 1)_0 | (I_b + 1)_k(t) \rangle_{FC} + \sqrt{I_a} \sqrt{I_b} \langle (I_a - 1)_0 | (I_b + 1)_k(t) \rangle_{FC} + \sqrt{I_a} \sqrt{I_b} \langle (I_a + 1)_0 | (I_b - 1)_k(t) \rangle_{FC} + \sqrt{I_a} \sqrt{I_b} \langle (I_a - 1)_0 | (I_b - 1)_k(t) \rangle_{FC} \right) e^{i(\epsilon I_0 + 2\omega t - g_k(t))} dt \] (5.26)

The prefactor \( (\delta_{TPA}^{0k})^{ab^f} \) is defined

\[ (\delta_{TPA}^{0k})^{ab^f} = 2 \sum_{\alpha,\beta} \frac{1}{30} \left[ (S^{0k}_{\alpha\alpha})^{a^f} (S^{0k}_{\beta\beta})^{b^f} + (S^{0k}_{\alpha\beta})^{a^f} (S^{0k}_{\beta\alpha})^{b^f} + (S^{0k}_{\alpha\beta})^{a^f} (S^{0k}_{\beta\alpha})^{b^f} \right] \] (5.27)
As before for the OPA spectra, there are distinguishable contributions for the cases when $a = b$ and $a \neq b$. The second term in Eq. (5.24) and final three terms in Eq. (5.26) are zero unless a population of excited vibrational levels are accounted for.

5.2.4 Resonance Hyper-Raman Scattering

The decomposition of the RHRS hyperpolarizability in terms of a Taylor series expansion of the transition dipole moment in terms of the derivatives along normal modes was applied by Chung et al. to examine the RHRS spectra of small molecules. It was shown by those authors that the hyperpolarizability could be written in terms of an A term (FC), B term (first HT), and C term (second HT) analogous to Albrecht’s analysis of the polarizability. This same procedure has been applied to analyze data for napthalene, where it was shown that the B term should be written as a sum of terms arising from vibronic coupling to dipole-allowed one- and two-photon transitions. Indeed, as will be shown here, such a separation of the B term is convenient for analyzing the contributions to the RHRS hyperpolarizability.

For two degenerate photons on resonance with an electronic transition the RHRS hyperpolarizability for normal mode $Q_p$ is

$$\beta_{\alpha\beta\gamma}^p(-2\omega; \omega, \omega) = \sum_{K,k,L,l} \frac{\langle F_0 | \mu^{0k}_\alpha | K_k \rangle \langle K_k | \mu^{l0}_\beta | L_l \rangle \langle L_l | \mu^{00}_\gamma | I_0 \rangle}{(E_{K_k} - E_{I_0} - 2\omega) - i\Gamma_k (E_{L_l} - E_{I_0} - \omega)}$$

$$+ \frac{\langle F_0 | \mu^{0k}_\alpha | K_k \rangle \langle K_k | \mu^{l0}_\gamma | L_l \rangle \langle L_l | \mu^{00}_\beta | I_0 \rangle}{(E_{K_k} - E_{I_0} - 2\omega) - i\Gamma_k (E_{L_l} - E_{I_0} - \omega)}$$

(5.28)

Because the incident frequency used is assumed far from resonance with any intermediate vibrational states, it is possible to write that $E_{L_l} - E_{I_0} \approx E_l - E_0$. This allows for a closure over intermediate vibrational state $|L_l\rangle$, such that the expression for the transition hyperpolarizability may be simplified. Like the TPA derivation above we assume that a single photon is not near resonant with an electronic excited state, but a resonance exists with a two-photon excited state. The hyperpolarizability is then

$$\beta_{\alpha\beta\gamma}^p(-2\omega; \omega, \omega) = \sum_{K,k} \frac{\langle F_0 | \mu^{0k}_\alpha | K_k \rangle \langle K_k | S^{k0}_{\beta\gamma} | I_0 \rangle}{(E_{K_k} - E_{I_0} - 2\omega) - i\Gamma_k}$$

(5.29)

The transition dipole moment $\mu^{0k}_\alpha$ and two-photon moment $S^{k0}_{\beta\gamma}$ can then be written by series expansion to include the nuclear coordinate dependence of each quantity.
The $B_1$ term given here contains information about vibronic coupling to dipole allowed two-photon transitions. Similarly, the $B_2$ term contains information about vibronic coupling to dipole allowed one-photon transitions. This distinction can be applied to determine the relative importance of the individual $B$ terms. In the article by Bonang et al. referenced above,\textsuperscript{201} it was first illustrated that the RHRS B term could be written as a sum of a $B_1$ and $B_2$ term. Their notation reverses the association of the derivatives $(\mu_0^k)_{\alpha}^{\alpha'}$ and $(S_{\beta\gamma}^{k0})_{\beta}^{\beta'}$ with the $B_1$ and $B_2$ terms in comparison to the present article. That difference in notation is arbitrary, but is noted here to avoid confusion. The time-dependent expressions for the $A$, $B_1$, and $B_2$ terms are written below.

$$A^p = (A^p)_{\alpha\beta\gamma} = \sum_k (\mu_0^k)_{\alpha}^{\alpha'} (S_{\beta\gamma}^{k0})_{\beta}^{\beta'} i \int_0^\infty \langle F_0 \mid I_k(t) \rangle e^{i(\epsilon_{I_0} + 2\omega)t - g_k(t)} dt$$  \hspace{1cm} (5.31)

$$B_1^p = (B_1^p)_{\alpha\beta\gamma} = \sum_k \sum_a \sqrt{\frac{\hbar}{2\omega_a}} (\mu_0^k)_{\alpha}^{\alpha'} (S_{\beta\gamma}^{k0})_{\beta}^{\beta'}$$
$$\times i \int_0^\infty \left( \sqrt{F_a} \langle (F_a - 1)_0 \mid I_k(t) \rangle_{A^p} + \sqrt{F_a + 1} \langle (F_a + 1)_0 \mid I_k(t) \rangle_{A^p} \right) e^{i(\epsilon_{I_0} + 2\omega)t - g_k(t)} dt$$ \hspace{1cm} (5.32)
\[ B_2^p = (B_2)^p_{\alpha\beta\gamma} = \sum_k \sum_b \sqrt{\frac{\hbar}{2\omega_b}} (\mu_{\alpha k}^{0k})^\text{eq} (S_{\beta\gamma}^{k0})^{b'} \]

\[ \times i \int_0^\infty \left( \sqrt{I_b + 1} \langle F_0 | (I_b + 1)_k(t) \rangle_{\text{Ap}} + \sqrt{I_b} \langle F_0 | (I_b - 1)_k(t) \rangle_{\text{Ap}} \right) e^{i(\epsilon_{t_0} + 2\omega)t - g_k(t)} dt \]

(5.33)

Similar to the RRS case, the subscript \( \text{Ap} \) on the vibrational overlap integrals indicates that raising and lowering operators are employed using the A term vibrational state as a reference. Explanation of the evaluation of wavepacket autocorrelation functions is left to the sections following this one. Note that in Eq. (5.33) the second term in parentheses is zero when only the ground vibrational state is populated.

Calculation of the differential hyper-Raman scattering cross sections (for 90 degree collection angle)

\[
\frac{d\sigma}{d\Omega} = \frac{16\pi^2\hbar^3\alpha^3(2\omega - \omega_{p_0})^4}{c^2e^\delta} \sum L \sum_{\alpha\beta} \langle \beta_{\alpha\beta\beta}(\omega, Q_p) \rangle^2 \]

(5.34)

The hyper-Raman intensity activity coefficient can be calculated assuming that the scattered light is measured perpendicular to the incident radiation path. \( N_{p'} \) is the Boltzmann population defined in Eq. (5.15). For normal mode \( Q_p \), this is evaluated as

\[
\sum_{\alpha\beta} (\langle \beta_{\alpha\beta\beta}(\omega, Q_p) \rangle^2) = (\langle \beta_{\alpha\alpha\alpha} \rangle^2) + (\langle \beta_{\alpha\beta} \rangle^2) \]

(5.35)

where
\begin{equation}
\langle (\beta_{a\alpha\alpha}^{\prime})^2 \rangle = \frac{1}{7} \sum_{\alpha} (\beta_{a\alpha\alpha}^{\prime})^2 + \frac{4}{35} \sum_{\alpha \neq \beta} (\beta_{a\alpha\beta}^{\prime})^2 + \frac{2}{35} \sum_{\alpha \neq \beta} (\beta_{a\alpha\alpha}^{\prime})(\beta_{a\beta\beta}^{\prime})
\end{equation}

\begin{equation}
+ \frac{4}{35} \sum_{\alpha \neq \beta} (\beta_{a\beta\beta}^{\prime})(\beta_{a\alpha\alpha}^{\prime}) + \frac{4}{35} \sum_{\alpha \neq \beta} (\beta_{a\alpha\alpha}^{\prime})(\beta_{a\beta\alpha}^{\prime}) + \frac{1}{35} \sum_{\alpha \neq \beta} (\beta_{a\beta\alpha}^{\prime})^2
\end{equation}

\begin{equation}
+ \frac{4}{105} \sum_{\alpha \neq \beta \neq \gamma} (\beta_{a\beta\beta}^{\prime})(\beta_{a\alpha\gamma}^{\prime}) + \frac{1}{105} \sum_{\alpha \neq \beta \neq \gamma} (\beta_{a\alpha\alpha}^{\prime})(\beta_{a\beta\gamma}^{\prime})
\end{equation}

and

\begin{equation}
\langle (\beta_{a\beta\beta}^{\prime})^2 \rangle = \frac{1}{35} \sum_{\alpha} (\beta_{a\alpha\alpha}^{\prime})^2 + \frac{4}{105} \sum_{\alpha \neq \beta} (\beta_{a\alpha\alpha}^{\prime})(\beta_{a\beta\beta}^{\prime})
\end{equation}

\begin{equation}
- \frac{4}{70} \sum_{\alpha \neq \beta} (\beta_{a\alpha\alpha}^{\prime})(\beta_{a\beta\alpha}^{\prime}) + \frac{8}{105} \sum_{\alpha \neq \beta} (\beta_{a\alpha\beta}^{\prime})^2 + \frac{3}{35} \sum_{\alpha \neq \beta} (\beta_{a\beta\beta}^{\prime})^2
\end{equation}

\begin{equation}
- \frac{4}{210} \sum_{\alpha \neq \beta \neq \gamma} (\beta_{a\alpha\alpha}^{\prime})(\beta_{a\beta\gamma}^{\prime}) - \frac{4}{210} \sum_{\alpha \neq \beta \neq \gamma} (\beta_{a\beta\alpha}^{\prime})(\beta_{a\gamma\gamma}^{\prime})
\end{equation}

Orientational averaging allows for the calculation of differential hyper-Raman scattering cross sections for an assembly of randomly oriented molecules, based on the conversion between the molecular fixed-frame to a laboratory fixed-frame. Like RRS, if multiple important vibrational transitions \((I \rightarrow F)\) exist at the same wavenumber, it is necessary to include the Boltzmann population weighted sum of all contributing transitions in Eq. (5.34).

### 5.2.5 Models Accounting for Spectral Broadening

The explicit form of the lifetime function \(g_j(t)\) is described in this section. Because inclusion of inhomogeneous broadening is a significant focus of the literature, the present
section does not seek to review all methods that have been developed in the literature. The focus is instead on two models. In order to understand the spectral broadening, it is necessary to distinguish the homogeneous broadening effects, which result from mechanisms that broaden a spectrum for a single molecule, \(^5,409,410\) and inhomogeneous broadening effects that account for variations in the solvent microenvironment and the initial states of every molecule in an ensemble. \(^409–411\) The inhomogeneous broadening is associated with a distribution of electronic zero-zero energies in the absorption spectrum.

For the first model, it is assumed that the dominant effect of inhomogeneous broadening comes from the distribution of the electronic energies. \(^100,359,411\) In this circumstance, the lifetime function is given by \(g_j(t) = \Gamma_j t\), where \(\Gamma_j\) is the homogeneous broadening parameter. Inclusion of inhomogeneous broadening proceeds by assuming a Gaussian distribution of electronic zero-zero energies. For absorbance spectra, it is possible to convolute the Gaussian distribution with the Lorentzian form of \(g_j(t)\) in the time-domain (see, for instance, Eq. 31 of Ref. 359). This model is advantageous because it requires little additional computational effort compared to only incorporating homogeneous broadening. Additional parameters representing the mean value and variations in the excitation energies are required for resonance Raman and resonance hyper-Raman scattering, along with performing an integral of the Gaussian distribution of excitation energies. \(^91,107\) This is a consequence of the dependence of resonance Raman scattering intensities on the absolute square of the transition polarizability and the dependence of resonance hyper-Raman scattering intensities on the absolute square of the transition hyperpolarizability. Another disadvantage of the model is that the inhomogeneous broadening parameter (associated with the variations in the excitation energies) cannot be used to obtain physical intuition with respect to solute-bath interactions, and therefore it is not possible to quantify the solvent contribution to the reorganization energy (sometimes referred to as the outer sphere reorganization energy). \(^6,122,353,412,413\)

A more advanced model was proposed by Mukamel and coworkers, where the bath degrees of freedom are incorporated using a density matrix formalism and the bath is represented using an overdamped Brownian oscillator. \(^406,407,414\) The detailed derivation of \(g_j(t)\) in this stochastic representation is shown in Ref. 407. The total reorganization energy of the system is defined

\[
\lambda_{\text{tot}} = \lambda_v + \lambda_s
\]

(5.38)

where \(\lambda_v = \sum_a \lambda_a = \sum_a \frac{\omega_a \Delta^2_a}{2}\) is the vibrational (or internal) contribution to the reorganization energy, and \(\lambda_s\) is the solvent contribution to the reorganization energy. In
contrast to Refs. 407, 406, and 415, in this paper \( \Delta_a \) refers to the dimensionless displacement of mode \( Q_a \) with frequency \( \omega_a \) and \( D_j \) refers to the strength of the coupling between the solvent motion and electronic transition \( j \leftarrow 0 \). The coupling strength \( D_j \) can be partitioned into a vibrational and solvent contribution also (ignoring Duschinsky rotations)

\[
D_j^2 = D_{v,j}^2 + D_{s,j}^2 = \sum_a \left\{ \lambda_{a,j} \omega_a \left( \frac{2}{e^{\hbar \omega_a/k_B T} - 1} + 1 \right) \right\} + \left\{ \lambda_{s,j} \omega_{B,j} \left( \frac{2}{e^{\hbar \omega_{B,j}/k_B T} - 1} + 1 \right) \right\} \quad (5.39)
\]

For the solvent contribution to \( D_j \), \( \lambda_{s,j} = \frac{\omega_{B,j} \Delta_{B,j}^2}{2} \) with \( \omega_{B,j} \) defining the bath frequency and \( \Delta_{B,j} \) is the dimensionless displacement of the bath. The dependence of the solvent contribution on the electronic state is implicitly defined via a combination of the homogeneous full-width at half maximum (\( \Gamma_{FWHM}^j = 2 \Gamma_j \)) and the dimensionless lineshape parameter, \( \kappa_j \), defined as

\[
\kappa_j = \frac{\Lambda_j}{D_{s,j}} \quad (5.40)
\]

where \( \Lambda_j^{-1} \) defines the solvent correlation time (timescale of solvent fluctuations). The lineshape parameter can be continuously varied to interpolate between a Lorentzian lineshape and Gaussian lineshape.\(^{415}\)

In the high-temperature limit \( (\hbar \omega_B \ll k_B T) \), the expression for the coupling strength is \( D_{s,j} = 2 \lambda_{s,j} k_B T / \hbar \) and \( g_j(t) \) is given by\(^{407}\)

\[
g_j(t) = \left( \frac{D_{s,j}}{\Lambda_j} \right)^2 \left[ e^{-\Lambda_j t} + \Lambda_j t - 1 \right] - i \left( \frac{\lambda_{s,j}}{\Lambda_j} \right) \left[ e^{-\Lambda_j t} + \Lambda_j t - 1 \right] \quad (5.41)
\]

The corresponding expression in Ref. 406, Eq. 18, is missing the \( \Lambda_j t \) term for the imaginary part of \( g_j(t) \) in the square brackets of Eq. (5.41) although the implementation and analysis presented in that reference are correct. It was shown by plotting \( \Gamma_{FWHM}^j/D_{s,j} \) versus \( \kappa_j \) that the value of the lineshape parameter can be employed to define \( D_{s,j} \) using a Padé approximant\(^ {407,415}\)

\[
\frac{\Gamma_{FWHM}^j}{D_{s,j}} = \frac{2.355 + 1.76\kappa_j}{1 + 0.85\kappa_j + 0.88\kappa_j^2} \quad (5.42)
\]

Because \( \Gamma_{FWHM}^j \) is dependent on the excited state being studied, both the coupling
strength and lineshape parameter (related through Eq. (5.40)) must be state dependent also. Using Eq. (5.42) requires knowledge of the homogeneous full-width at half maximum and lineshape parameter, from which $D_{s,j}$ and subsequently $\lambda_{s,j}$ may be calculated.

The overdamped Brownian oscillator model can also be used in the general temperature limit, where

$$g_j(t) = g_{R,j}(t) - ig_{I,j}(t)$$

(5.43)

$$g_{R,j}(t) = \left( \frac{\lambda_{s,j}}{\Lambda_j} \right) \cot \left( \frac{\hbar \Lambda_j}{2k_B T} \right) \left[ e^{-\Lambda_j t} + \Lambda_j t - 1 \right] + \frac{4\lambda_{s,j} \Lambda_j k_B T}{\hbar} \sum_{n=1}^{\infty} \frac{e^{-\nu_n t} + \nu_n t - 1}{\nu_n (\nu_n^2 - \Lambda_j^2)}$$

(5.44)

$$g_{I,j}(t) = \left( \frac{\lambda_{s,j}}{\Lambda_j} \right) \left[ e^{-\Lambda_j t} + \Lambda_j t - 1 \right]$$

(5.45)

Specifically for the real part of the lifetime function, $\nu_n = \frac{2\pi k_B T_n}{\hbar}$ are the Matsubara frequencies. For the general temperature limit, $D_{s,j}$ is defined in Eq. (5.39). There are two approaches for determining the coupling strength. First, if the Padé approximant is used, the solvent reorganization energy can be calculated if $\omega_{B,j}$ is defined. The second approach requires that both $\Delta_{B,j}$ and $\omega_{B,j}$ are defined, and therefore the solvent reorganization energy may be calculated directly from its definition. The coupling strength may then be directly computed. The disadvantage of the latter approach is that $\Delta_{B,j}$ and $\omega_{B,j}$ cannot be determined experimentally, and thus two parameters are defined arbitrarily.

In the simple model, it is advantageous that few parameters are used to define the lineshape when first principles calculations are used. The small number of parameters is also a disadvantage because inhomogeneous broadening is more complicated than a simple convolution with a Gaussian lineshape. This disadvantage is compensated by the overdamped Brownian oscillator, where physical parameters are used to account for the strength of coupling between the solvent and electronic transition, and the solvent correlation time. The physically meaningful parameters allow for estimates of the solvent reorganization energy. The temperature dependence in $g_j(t)$ means that the calculated polarizability, hyperpolarizability, and cross sections are temperature dependent. This allows for more consistency with experimental data where the zero-temperature approximation of the simple model is avoided. A disadvantage of the Brownian oscillator is the inclusion of more parameters. As described above, in the general
temperature limit the determination of the solvent reorganization energy is impeded by requiring that \( \omega_{B,j} \) (and possibly \( \Delta_{B,j} \)) are known. Representing the broadening as purely homogeneous for spectra where vibronic features are important is normally adequate, although inhomogeneous broadening is also important for correctly describing the red-edge of the absorbance maximum, so completely neglecting this feature may reduce the quality of the simulation compared to experiment.  

5.3 Time-Dependent Wavepacket Approach

5.3.1 Franck-Condon Terms

For a multidimensional harmonic oscillator, Ref. 132 demonstrates the derivation of expressions for simulating the lineshape in RRS and OPA. In particular, we want to solve the equation for \( I_n = \langle \phi_{f,n} | \phi_{k,0}(t) \rangle \), where \( n \) is the quantum number of the final vibrational level in the final electronic state \( |f\rangle \) and 0 is the ground state of the harmonic oscillator in electronic state \( |k\rangle \). Herein we use the same notation that was applied in Ref. 132 such that the equations may be easily compared. Based on Eq. B1 in Ref. 132, this integral is

\[
I_n \equiv \frac{1}{\sqrt{2^n n!}} \left( \frac{\det \alpha}{\pi} \right)^{1/2} \int H_n(x - x_0) \exp \left[ -(q - q_0)^T \cdot A_0^* \cdot (q - q_0) \right] \\
\times \exp \left[ -i p_0^T \cdot (q - q_0) \right] \exp[-i \gamma_0] \exp \left[ -(q - q_t)^T \cdot A_t \cdot (q - q_t) \right] \\
\times \exp \left[ ip_t^T \cdot (q - q_t) \right] \exp[i \gamma_t] \, dq
\]

(5.46)

The variable \( \alpha \) is used for converting between dimensionless and Cartesian coordinates of the ground state. Integration is performed with respect to dimensionless normal coordinates \( q \), where the expectation value of the position \( (q_t) \) and momentum \( (p_t) \) for the wavepacket are evaluated with respect to time. For the definitions of the other variables in the equation, the reader is referred to Section B and Appendix A of Ref. 132 and other works as well.  

In order to analytically evaluate the integral, it is suggested that the generating function for the Hermite polynomial \( \sum_{n=0}^{\infty} H_n(x - x_0) \frac{z}{m}^n = \exp \left[ 2(x - x_0)^T \cdot z - z^2 \right] \) be applied. Applying the generating function allows the problem to be written in terms of a multidimensional Gaussian integral, which has the solution
\[ I \equiv \int_{-\infty}^{\infty} \exp \left[ -q^T \cdot A \cdot q \right] \exp \left[ i p^T \cdot q \right] \exp \left[ i \gamma \right] dq \]

\[ = \sqrt{\frac{\pi^N}{\det A}} \exp \left[ -\frac{p^T \cdot A^{-1} \cdot p}{4} \right] \exp \left[ i \gamma \right] \quad (5.47) \]

The variables are defined

\[ A = A_0^* + A_t \]

\[ p = (p_t - p_0) - 2iz - 2i (A_t \cdot q_t + A_0^* \cdot q_0) \quad (5.49) \]

\[ \gamma = (\gamma_t - \gamma_0^*) - (p_t^T \cdot q_t - p_0^T \cdot q_0) + i \left( z^2 + q_0^T \cdot A_0^* \cdot q_0 + q_t^T \cdot A_t \cdot q_t + 2q_0^T \cdot z \right) \quad (5.50) \]

Eq. 5.47 may be written in an alternative form that allows the generating function to be applied in reverse, with a change of variables

\[ I = \sqrt{\frac{\pi^N}{\det A}} \exp \left[ -\frac{p^T \cdot A^{-1} \cdot p'}{4} \right] \exp \left[ ip^T \cdot A^{-1} \cdot z + A^{-1} z^2 - 2q_0^T \cdot z - z^2 \right] \exp \left[ i \gamma \right] \]

\[ = \sqrt{\frac{\pi^N}{\det A}} \exp \left[ -\frac{p^T \cdot A^{-1} \cdot p'}{4} \right] \exp \left[ i \gamma' \right] \sum_{n=0}^{\infty} H_n(\gamma') \frac{z^n}{n!} \left[ 1 - (A^{-1})_{xx} \right]^{n/2} \quad (5.54) \]

In this case, the subscript \( x \) means the x-component of a vector, and \( xx \) means the
xx-element of a matrix. The variable \( x' \) is defined

\[
x' = \frac{(iA^{-1} \cdot p' - 2q_0)x}{2[1 - (A^{-1})_{xx}^{1/2}]}
\]

Since the solutions to the original integral \( I_n \) are factors of \( \frac{z^n}{n!} \), the solution to the integral is

\[
I_n = \frac{1}{\sqrt{2^n n!}} \sqrt{\frac{\pi^N}{\det A}} \exp \left[ -\frac{p'^T \cdot A^{-1} \cdot p'}{4} \right] \exp \left[ i\gamma' \right] H_n(x')[1 - (A^{-1})_{xx}^{n/2}] (5.55)
\]

In comparison to Ref. 132, there are a few important differences with the equations presented in this section. In Eq. B9 of that work, there is a typo that eventually causes the definition of \( x' \) to have an opposite sign compared with Eq. (5.55). A well-known identity involving Hermite polynomials is:

\[
H_n(\bar{x}) = (-1)^n H_n(x),
\]

where \( n \) is the order of the Hermite polynomial (the difference in vibrational quantum number). The relevance of this sign difference will become apparent in the following discussion.

For OPA or TPA, in the FC approximation the integral \( I_0 = \langle \phi_f | \phi_0(t) \rangle \) is used to calculate the lineshape. We will now switch to a more convenient notation, where the integral is written \( I_n = \langle F_0 | I_k(t) \rangle \). In this circumstance, the final state \( |F_0 \rangle \) is associated through its subscript with the ground electronic state, and the time-dependent wavepacket is defined as: \( |I_k(t) \rangle = e^{-i\hat{H}_k t} |I_0 \rangle \). The integral is evaluated when \( F = I = 0 \), which in the absence of Duschinsky rotations, has the form

\[
\langle I_0 | I_k(t) \rangle = \langle 0_0 | 0_k(t) \rangle = e^{-\sum_j s^k_j (1 - e^{-i\omega_j t}) - i(\epsilon_{I_0} + E_{0k}) t} (5.57)
\]

In this equation, \( \omega_j \) is the vibrational frequency of mode \( j \), \( \epsilon_{I_0} \) is the energy of state \( |I_0 \rangle \), \( E_{0k} \) is the excitation energy between electronic states \( 0 \) and \( k \), and \( s^k_j = \frac{(\Delta^k_j)^2}{2} \) are the Huang-Rhys factors that depend on the dimensionless displacements \( \Delta^k_j \).

For RRS and RHRS, the respective transition polarizability and hyperpolarizability derived in the FC approximation are commonly referred to as the A term.\(^{134,208,357}\) The A term depends on the integral \( I_n = \langle F_0 | I_k(t) \rangle \), where \( n \) and therefore \( F \) may be any integer greater than zero. Again, when Duschinsky rotations are ignored, this integral has the form

\[
\langle F_0 | I_k(t) \rangle = \prod_m \left\{ \frac{(\Delta^k_m)^{r_m}}{(2^{r_m} r_m !)^{1/2}} \right\} e^{-\sum_j s^k_j (1 - e^{-i\omega_j t}) - i(\epsilon_{I_0} + E_{0k}) t} (5.58)
\]
Eq. (5.58) is also used to evaluate the FC-HT interference terms in absorbance spectra, in the case where \( F = I + 1 = 1 \). In addition to the definitions of variables outlined above, this expression also includes the excitation numbers \( r_m \) that are defined as the difference between \( F \) and \( I \) for mode \( Q_m \). Eq. (5.58) is a very general expression allowing for treatment of fundamentals, overtones, and combination bands in RRS and RHRS, depending on which of the modes in the product over \( m \) are excited. Eq. (5.58) is also employed in evaluation of the B terms in RRS and RHRS, where \( F_a + 1 = 1 \) or 2 and \( I_a + 1 = 1 \) (see Eqs. (5.13), (5.32) and (5.33), for instance). Typically this equation also includes a factor of \((-1)^{r_m}\) when reported in the literature. The reason that this factor does not appear in Eq. (5.58) is due to the sign difference in the definition of \( x' \) compared to the original derivation.

In general, Eq. (5.58) has included a negative sign on \( \Delta_k^m \) in previous publications. Fortunately, this has no effect on the simulated spectra in the FC approximation. Because OPA and TPA use Eq. (5.57) to determine the lineshape, the negative sign does not change the simulation of the cross sections. Intensity in RRS depends on the absolute square of the transition polarizability, which depends on Eq. (5.58), and therefore the negative sign is also unimportant. This point is also true for RHRS which is related to the absolute square of the transition hyperpolarizability. For multiple excited states, where interference effects can be important in RRS and RHRS, this sign difference is unimportant in the FC approximation as long as every excited state is subject to the same sign convention. However, the sign is important when non-Condon effects are included.

5.3.2 Herzberg-Teller Terms

In the previous section, the time-dependent formalism was applied when all normal modes are in their ground state. Using the independent mode, displaced harmonic oscillator (IMDHO) model, that circumstance yields the following expression for the wavepacket when Duschinsky rotations are ignored:

\[
I_k(t) = 0_k(t) = e^{-iE_0 t} \prod_m^{N} \frac{1}{\pi^{1/4}} \exp \left[ -\frac{1}{2} (q - q_{t,km})^2 + ip_{t,km}(q - q_{t,km}) + i\gamma_{t,km} \right]
\]

(5.59)

where the expectation values for the position \((q_{t,km})\) and momentum \((p_{t,km})\) of the wavepacket are defined.
\[ p_{t,km} = \Delta_m^k \sin(\omega_m^k t) \] (5.60)

\[ q_{t,km} = \Delta_m^k \left( 1 - \cos(\omega_m^k t) \right) \] (5.61)

and the final term \( \gamma_{t,km} \) involving the energy of each harmonic oscillator and classical Lagrangian is defined

\[ \gamma_{t,km} = -\frac{\omega_m^k}{2} + \frac{1}{2} p_{t,km} \left( q_{t,km} - \Delta_m^k \right) \] (5.62)

As shown in previous sections, the derivation of the HT terms, the dipole operator is first expanded in a series about the normal modes \( \mu_\rho = (\mu_\rho)^{eq} + \sum_a (\mu_\rho)^a Q_a \ldots \) (here \( \rho \) is one of the Cartesian components of the vector, x, y, or z). In that expression, the transition dipole moment evaluated at the ground state optimized structure is denoted \( (\mu_\rho)^{eq} \), and the derivative along normal mode \( Q_a \) of the transition dipole moment at the ground state optimized structure is \( (\mu_\rho)^a \). The first term in the series corresponds to the FC or A term. For absorbance type processes, the second term in the series corresponds to the interference term between the FC and HT terms and also yields the HT term. For the Raman scattering processes, the second term in the series leads to the HT or B term.

Extending the time-dependent formalism to HT terms requires overlap integrals that involve the nuclear coordinate \( Q_a \) for each normal mode. Evaluation of those integrals is facilitated by writing the normal coordinates in terms of the creation and annihilation operators, via Eq. (5.7). For the multidimensional wavefunctions considered here, the creation and annihilation operators \( \hat{b}_a^\dagger \) and \( \hat{b}_a \) increase and decrease the excitation level of mode \( Q_a \) by one. The multiplicative factor in the square root amounts to 0.388 to 0.183 Bohr amu\(^{1/2}\) for respective frequencies between 400 and 1800 cm\(^{-1}\). Explicitly, for a molecule with \( k \) modes with excitation levels \( n_i \) in the state \( |n_1 n_2 \ldots n_a-1 n_a n_{a+1} \ldots n_k-1 n_k\rangle \), those operators yield

\[ \hat{b}_a^\dagger |n_1 n_2 \ldots n_a-1 n_a n_{a+1} \ldots n_k-1 n_k\rangle = \sqrt{n_a + 1} |n_1 n_2 \ldots n_a-1 (n_a + 1) n_{a+1} \ldots n_k-1 n_k\rangle \] (5.63)

\[ \hat{b}_a |n_1 n_2 \ldots n_a-1 n_a n_{a+1} \ldots n_k-1 n_k\rangle = \sqrt{n_a} |n_1 n_2 \ldots n_a-1 (n_a - 1) n_{a+1} \ldots n_k-1 n_k\rangle \] (5.64)
Because we assume in our current model that all modes begin in their ground vibrational state, the annihilation operator causes zero contribution when operated on the initial state.

Following from the same ansatz for the expression for the wavepacket in Eq. (5.59), it is possible to find expressions when the starting point of the derivation is the first harmonic oscillator excited state.\(^{416,417}\) In this circumstance, the initial state is denoted \((I_a + 1)_k(t)\), indicating that the mode \(Q_a\) is in its first excited state. This wavepacket has the form

\[
(I_a + 1)_k(t) = e^{-i\Delta_k t} \frac{4}{\pi^{1/4}} (q - q_{t,ka}) \exp \left[ -\frac{1}{2} (q - q_{t,ka})^2 + ip_{t,ka}(q - q_{t,ka}) + i\gamma_{t,ka} \right] \\
\times \prod_{m \neq a}^{N} \frac{1}{\pi^{1/4}} \exp \left[ -\frac{1}{2} (q - q_{t,km})^2 + ip_{t,km}(q - q_{t,km}) + i\gamma_{t,km} \right]
\]

(5.65)

The definitions of the variables follow from Eqs. (5.60) and (5.61), and \(\gamma_{t,ka} = -\frac{3\omega_{ka}^2}{2} + \frac{1}{2}p_{t,ka}(q_{t,ka} - \Delta_k)\) where it is explicit that \(\gamma_{t,ka}\) carries the energy of the first excited state of the harmonic oscillator. This is important because the energy of the initial state (prior to applying the creation/annihilation operators) is a sum of the zero-point energies of every normal mode. Whereas the overlap integral involving the wavepacket results in the cancellation of the zero-point energy in FC terms, there is a leftover vibrational frequency contribution from the “raised” mode in HT terms that can result in a noticeable shift in the location of the absorbance maximum. This may also cause a different behavior in the wavelength dependence of RRS and RHRS spectra.

As demonstrated in the previous sections, several types of overlap integrals result from applying this wavepacket for HT terms. In absorbance spectra, integrals that have the form

\[
\langle (I_a + 1)_0 | I_k(t) \rangle
\]

are evaluated from Eq. (5.58) for the FC-HT interference terms. HT terms for absorbance spectra come from situations where the dipole operators \(\mu\) and two-photon transition moment operators \(S\) are all expanded in a series through first order. In effect, this causes the overlap integrals to contain two normal modes \(Q_a\) and \(Q_b\). Because there is no restriction on the summations in the series expansion, it is possible to obtain diagonal HT term contributions where \(a = b\) and off-diagonal HT term contributions where \(a \neq b\). These are given below.
\[
\langle (I_a + 1)_0 | (I_a + 1)_k(t) \rangle = \left[ 1 - (\Delta^k_a)^2 + (\Delta^k_a)^2 \cos(\omega_a t) \right] e^{-\sum s_j^k (1-e^{-i\omega_j t}) - i(\epsilon_{1a} + E_{0k})t}
\]

\[
(5.66)
\]

\[
\langle (I_a + 1)_0 | (I_b + 1)_k(t) \rangle = \left\{ \frac{\Delta^k_a}{(2)^{1/2}} (1-e^{-i\omega_a t}) \right\} \left\{ \frac{\Delta^k_b}{(2)^{1/2}} (1-e^{-i\omega_b t}) \right\} e^{-\sum s_j^k (1-e^{-i\omega_j t}) - i(\epsilon_{1a} + E_{0k})t}
\]

\[
(5.67)
\]

In Eq. (5.66), the notation \(\epsilon_{1a}\) indicates the sum of the first harmonic oscillator excited state energy for mode \(Q_a\) with the zero point energies of every other normal mode. This form is also used in evaluating the integrals in RRS B term and RHRS B\(_2\) term when \((I_a + 1)_0 = F_0\) (see Eqs. (5.13) and (5.33)). When combined with the time-dependent expressions in prior sections, that additional vibrational energy term causes a shift in the absorbance maximum for the HT term. Eq. (5.66) is used to evaluate the B term in RRS and RHRS, and also when \(a = b\) for HT terms in OPA and TPA. Eq. (5.67) is used when \(a \neq b\) in HT terms for all spectral simulations.

### 5.3.3 Dimensionless Displacements and Property Derivatives

Evaluation of all of the time-dependent overlap integrals used for OPA, RRS, TPA, and RHRS simulations requires the calculation of dimensionless excited state displacements \((\Delta^k_p)\). For harmonic potential energy surfaces, \(\Delta^k_p\) is related to the partial derivative of the excited state electronic energy with respect to a ground state normal mode at the ground state equilibrium position,

\[
\left( \frac{\partial E^k}{\partial q_p} \right)_{q_p=0} = -\omega_p \Delta^k_p
\]

\[
(5.68)
\]

The excited state electronic energy gradients in Eq. (5.68) are calculated using a three-point central differences formula around the ground state equilibrium geometry. For convenience, the derivatives are initially determined in mass-weighted normal coordinates, \(Q_p\), not the dimensionless normal coordinates \(q_p\). However, a simple relationship allows the conversion between the two.
Table 5.1. Summary of prefactors to integrals for FC and HT terms. Subscripts $\alpha$ and $\beta$ are one of the x, y, or z components of the transition dipole moment or two-photon moment. The notation $(A)^{eq}$ means that the property $A$ is evaluated at the ground state optimized structure, and $(A)^{a'}$ indicates the derivative of the property along normal mode $Q_a$.

<table>
<thead>
<tr>
<th>Prefactor</th>
<th>OPA</th>
<th>RRS</th>
<th>TPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\mu_\alpha)^{eq}$</td>
<td>FC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\mu_\alpha)^{a'}$</td>
<td>HT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(S_{\alpha\beta})^{eq}$</td>
<td></td>
<td>FC</td>
<td></td>
</tr>
<tr>
<td>$(S_{\alpha\beta})^{a'}$</td>
<td></td>
<td>HT</td>
<td></td>
</tr>
</tbody>
</table>

$$\frac{\partial E^k}{\partial q_p} = \left( \frac{dQ_p}{dq_p} \right) \frac{\partial E^k}{\partial Q_p} = \sqrt{\frac{\hbar}{2\pi c\nu_0}} \frac{\partial E^k}{\partial Q_p}$$  \hspace{1cm} (5.69)

Excited state electronic energy gradients in terms of mass-weighted normal coordinates were evaluated using a numerical procedure similar to that presented by Reiher et al. for the polarizability tensor elements, with the electronic energy replacing the polarizability.

For the derivatives of the transition dipole moment $\mu_\alpha$ and two-photon transition moment $S_{\beta\gamma}$, the derivative of the excitation energy is replaced by the appropriate property. However, the conversion between mass-weighted and dimensionless normal coordinates is incorporated into the equation with the additional factor in the square root (see Eq. (5.7)) that cancels the denominator of the derivative.

5.4 Summary of Prefactors

The contributions of each term to the total intensity of absorbance and Raman spectra is largely determined by the prefactor in this method. It is important to examine the magnitude of the prefactor when analyzing the relative intensity of spectral features. In order to aid this understanding, Table 5.1 relates the type of prefactor to the spectrum being simulated and also the term it is related to. The intersection of each row and column yields a single prefactor for one of the terms.

For OPA, the FC term intensity is derived from the square of the transition dipole moment. This is also true for the A term in RRS. However, previous sections highlight that the lineshape functions are key in distinguishing the two spectra. Previous articles of HT coupling schemes indicate that the HT terms in OPA involve the product
of the transition dipole moment derivatives. The intermediate term between the FC and HT term in OPA is the FC-HT interference term. In the present model, this interference is rationalized by the signs of the transition dipole moment and its derivative not being identical, and also that the lineshape contributes asymmetrically about the horizontal axis. The analogous term to the FC-HT interference term based on the prefactors is the B term in RRS, which even in the absence of multiple excited states in the simulation may result in interference with the A term.

The nonlinear optical processes have similar features to the linear optical processes. Terms in the TPA spectrum can be seen to result from the two-photon transition moment and its derivatives. Instead of individually expanding each of the transition dipole moments in the second-hyperpolarizability (e.g. Eq. (5.19)), it is much simpler to consider the Taylor series expansion about the normal modes using the two-photon transition moment much like what was done in Ref. 388. Similar behavior to the OPA spectrum, where the FC and HT terms are positive and the FC-HT interference term has positive and negative contributions, is observed for the TPA spectrum. This is partially the consequence of the similarities of the lineshape functions in the FC-HT terms of OPA and TPA spectra.

In RHRS, the transition hyperpolarizability is separated into contributions from the A, B$_1$, and B$_2$ terms. It is particularly interesting that these terms involve products of the transition dipole moment and two-photon transition moment. This can have consequences on the intensity of different states in a RHRS spectrum if multiple excited states are included in the calculation. Only when the transition dipole moment is large and the two-photon transition moment is large is it expected that the A term dominates the spectrum. For cases where either the transition dipole moment or two-photon transition moment are small (weakly allowed states), it is possible that the B terms may contribute significantly. It is particularly important that two competing mechanisms exist for the HT terms to gain intensity. If either the transition dipole moment derivative ($\mu^\alpha$) or two-photon moment derivative ($S_{\alpha\beta}$) are large, the B$_1$ or B$_2$ terms can give significant intensity. This can result in the model capturing the differences in the selection rules between RRS and RHRS.\textsuperscript{205,206} Interference between A terms, B terms, and cross terms from different excited states may also be quantified,\textsuperscript{404} along with interference between the different terms of the same excited state.
5.5 Conclusions

A comprehensive vibronic coupling model incorporating both Condon and non-Condon effects is derived in this work. Applications of this model include both the linear optical processes OPA and RRS and also nonlinear optical processes TPA and RHRS. Simulations of linear and nonlinear optical processes has not been attempted using the same model. Although the basic framework of the model involves similar lineshapes for each spectral simulation, a clear distinction exists when comparing the prefactors of each type of spectrum. Resulting from those differences it is possible that each spectrum behaves differently. A future publication will apply the theory in this work to a set of small molecules including NH$_3$, CS$_2$, CH$_2$O, and para-nitroaniline.
Chapter 6

Vibronic Coupling Simulations for Linear and Nonlinear Optical Processes: Simulation Results


Abstract

A vibronic coupling model based on the time-dependent wavepacket approach is applied to simulate linear optical processes, such as one-photon absorbance and resonance Raman scattering, and nonlinear optical processes, such as two-photon absorbance and resonance hyper-Raman scattering, on a series of small molecules. Simulations employing both the long-range corrected approach in density functional theory and coupled cluster are compared and also examined based on available experimental data. Although many of the small molecules are prone to anharmonicity in their potential energy surfaces, the harmonic approach performs adequately. A detailed discussion of the non-Condon effects is illustrated by the molecules presented in this work. Linear and nonlinear Raman scattering simulations allow for the quantification of interference between the Franck-Condon and Herzberg-Teller terms for different molecules.
6.1 Introduction

Vibronic coupling simulations are an important tool for understanding the relationship between molecular vibrations and electronic motion. Applications of such simulations enable detailed characterization of molecular electron transfer, temperature-induced broadening of absorbance and fluorescence, aggregation of chromophores, and the importance of non-Condon effects. A general formulation for vibronic coupling simulations was developed by Heller et al. that uses a time-dependent wavepacket approach. The time-dependent formalism has been applied in numerous situations and good agreement with experimental data has been observed for a variety of molecules, both when simulation parameters are based on experimental resonance Raman scattering (RRS) spectra and first principles calculations.

Nonlinear optical processes involving the simultaneous absorption of two-photons, such as two-photon absorbance (TPA) and resonance hyper-Raman scattering (RHRS), have seen applications in 3D optical memory storage, studying IR and Raman inactive normal modes and one-photon forbidden electronic states, biological imaging, and two-photon phototherapy. Widespread use of nonlinear optical processes has been impeded by their lower cross sections in comparison to linear optical processes, although several advantages exist for nonlinear optical processes in comparison to their linear optical counterparts. For example, nonlinear optical processes are more selective, have less risk of photodamage to the sample, and the photons used can generally penetrate deeper into the sample. Consequently, significant effort has focused on amplifying the measured signal, either by synthesizing molecules with appropriate electron-donating and accepting functional groups or enhancing the measured signal using metal surfaces.

This study seeks to illustrate the difference between vibronic coupling simulations for one-photon absorbance (OPA), RRS, TPA, and RHRS based on the same level of theory. In particular, the method allows for detailed analysis of each spectrum via the Franck-Condon (FC) approximation and also incorporating non-Condon effects via Herzberg-Teller (HT) terms. Spectral simulations of the small molecules NH\textsubscript{3}, CS\textsubscript{2}, CH\textsubscript{2}O, and p-nitroaniline (PNA) are performed in the frameworks of density functional theory (DFT) and coupled cluster with single and double excitations (CCSD), and accuracy is tested when possible by comparison to experimental data. Simulation results for each molecule emphasize the capabilities of our program for modeling linear and nonlinear optical processes...
optical processes.

Analysis also details the interference effects between Franck-Condon (A term) and Herzberg-Teller (B term) terms in RRS and RHRS. Interference between the A and B terms has been investigated in RRS of metalloporphyrins, although absolute units were not used and the magnitude of the interference was not quantified. A recent study compared simulated RHRS spectra with measured surface-enhanced hyper-Raman scattering spectra for rhodamine 6G, illustrating strong B term scattering. Interference between the first two excited states accounted for a significant 34% of the observed intensity of RHRS in that molecule, which is surprising because both states are well separated energetically. To our knowledge the current study presents the first quantification of A and B term interference for both RRS and RHRS for a single excited state.

6.2 Computational Details

Application of the long-range corrected (LC-) method in DFT yields a partitioning of the interelectronic repulsion, which is given for electronic separation \( r_{12} \) as

\[
\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta \cdot \text{erf}(\omega r_{12})]}{r_{12}} + \frac{\alpha + \beta \cdot \text{erf}(\omega r_{12})}{r_{12}} \tag{6.1}
\]

where \( \omega \) is the attenuation parameter and the terms on the right side of Eq. (6.1) are the short- and long-range part of the exchange, respectively. Applying the approach outlined by Hirao and co-workers, we implemented the LC-PBE functional into Dalton 2.0 based on the general approach produced by constructing the short-range GGA exchange-correlation (XC) functional. In the present paper, LC-PBE using \( \alpha = 0.00, \beta = 1.00, \) and \( \omega = 0.30 \text{ a}_0^{-1} \) was employed for every calculation.

The ground state equilibrium geometry and vibrational normal modes for CS\(_2\), NH\(_3\), and CH\(_2\)O were determined using the B3LYP functional and aug-cc-pVDZ basis set in NWChem. For PNA, the equilibrium structure and normal modes were determined using the cc-pVDZ basis set. A study by Paterson et al. indicated that the aug-cc-pVDZ basis set gives consistent values with larger correlation consistent basis sets for estimates of the two-photon transition moments using both DFT and several models from the coupled cluster hierarchy. Due to the volume of calculations required to simulate nonresonant Raman scattering (NRS), nonresonant hyper-Raman scattering (NHRS), OPA, RRS, TPA, and RHRS, the aug-cc-pVDZ basis set used here for response properties is advantageous because it offers consistency in two-photon properties without prohibitive calculation times. Normal mode frequencies were scaled by 0.98 from the
B3LYP values to obtain better agreement with experimental frequencies.

The static polarizability and static hyperpolarizability, used for respective NRS and NHRS spectral simulations (not shown), were evaluated using the linear and quadratic response modules implemented in Dalton 2.0. Nonresonant spectra are useful for determining the resonance enhancement based on first principles calculations. Response properties, including the excitation energy, transition dipole moment, and two-photon transition moment were evaluated using CCSD, B3LYP, and LC-PBE. Calculating those properties allows for the determination of dimensionless displacements, derivatives of the transition dipole moment and derivatives of the two-photon transition moment to obtain the Herzberg-Teller contributions to each process. The expressions for the OPA and TPA cross sections and RRS transition polarizability and RHRS transition hyperpolarizability we derived previously are implemented into a standalone program, TDSPEC.

The sign of the transition moments is dependent on the phase of the ground state wavefunction, so the numerical derivatives were evaluated using a single sign convention. This convention is based on the signs determined when calculating the properties at the ground state equilibrium structure. In order to preserve orientation of the molecule for each calculation, no symmetry was used in the calculation of the response properties. For dipole allowed states, the signs are chosen for steps in the plus/minus direction along every mode such that the signs match that of the reference calculation before performing the differentiation. In dipole forbidden states, a “linear” approximation is adopted where stepping in the plus direction along a mode yields a positive sign and stepping in the negative direction gives a negative sign.

For this paper, all spectra for the smaller molecules are assumed to be taken in the gas-phase and thus no solvent effects are accounted for. Typically, the time-dependent method is applied using first principles calculations where the homogeneous broadening, accounting for the lifetime of the excited state, and inhomogeneous broadening, accounting for the effects of microsolvation environment, are treated as fitting parameters. This is dependent on the availability of experimental absorbance spectra that can be used to determine those parameters.

With the exception of CS$_2$, simulated OPA, TPA, RRS, and RHRS spectra for smaller molecules were performed using a two-state approximation. For NH$_3$ and CH$_2$O, the excited state investigated was the lowest energy singlet excitation. For CS$_2$, the fourth and fifth singlet excited states were investigated. Except for CS$_2$, the difference in energy between the excited state studied and the next closest excited state was at least 1.50
eV, which justifies a two-state approximation. For CS$_2$, the one-photon forbidden/two-photon allowed fifth excited state was found to be $\sim$0.40 eV higher in energy, and it’s neglect may have serious consequences on the intensities of the simulated spectra. As such, a three-state approximation was used for this molecule. Both CS$_2$ and CH$_2$O have at least one dipole forbidden transition and the numerical differentiation is performed as described above.

For PNA, experimental data is available for the OPA, nonresonant Raman, and RRS spectra.$^{424}$ For this molecule calculations were performed only at the DFT level. The C$_{2v}$ structure was used in all calculations, although there exists a more stable C$_s$ structure. However, in solution PNA tends to become more planar$^{440}$ and, therefore, we chose to use the C$_{2v}$ structure in this work. A single imaginary frequency (-327 cm$^{-1}$), associated with pyramidalization of the -NH$_2$ group, was therefore observed when the normal mode frequencies were calculated. OPA spectra were simulated by performing a fit to the experimental OPA spectrum including inhomogeneous broadening. For this molecule only the second excited state was included in the simulations. Linear dependencies were observed with the aug-cc-pVDZ basis set for this molecule. Experimental estimates for the differential Raman cross section of PNA are available for comparison in Ref. 424.

In this work, some conventions will be used for discussing spectra. The OPA and TPA spectra will include labels identifying what component of the cross section is shown. For simplicity, the total spectrum will be labeled “T” and includes the sum of three terms: Franck-Condon, Interference, and Herzberg-Teller. The spectrum including only the Franck-Condon term is labeled “FC”. Spectra including both the Interference term and Herzberg-Teller term and labeled “HT”. RRS and RHRS spectra are labeled “T” for the total spectrum (A+B terms), “A” for the A term only, “B$_1$” for the RHRS B$_1$ term, and “B” for the total B term. Specifically to OPA and TPA, the horizontal axis is labeled “Excitation Energy” throughout this work. For OPA, the wavelength shown on the axis is the incident light wavelength. For TPA, where two photons are used in the excitation, the wavelength shown is half of the incident light wavelength (twice the energy). This means it corresponds to the sum of two photons, each with twice the given wavelength. In RHRS, the wavelength given corresponds to the wavelength of each photon shone on the molecule.

The paper focuses on comparing spectra simulated with CCSD and LC-PBE. Except for PNA, the simulations use no inhomogeneous broadening. It is possible to simulate each type of spectrum for any molecule, but only the most interesting ones are shown in this work. Spectra not shown in this work, including OPA, TPA, RRS, and RHRS
for LC-PBE and CCSD, are given in Appendix C. In addition, spectra using B3LYP (PNA excluded) and simulation parameters including dimensionless displacements and averaged response property derivatives for both functionals and CCSD are available in the Appendix C.

6.3 Results and Discussion

6.3.1 Ammonia

The RRS spectrum of NH$_3$ was investigated by Ziegler and Hudson, illustrating the first RRS spectrum measured on resonance with a Rydberg state.\textsuperscript{441} The authors show a gas phase NRS spectrum, containing the intense symmetric N–H stretch ($\nu_1$) and weak pyramidalization mode ($\nu_2$). The RRS spectrum is highly structured and had numerous lines resulting from the $\nu_1$ and $\nu_2$ fundamentals, overtones, combination bands, and hot bands. It was also noticeable that $\nu_2$ was significantly more resonance enhanced than $\nu_1$, because the relative intensity of the fundamentals was reversed compared to the NRS spectrum.

The first reported gas phase RHRS spectra were shown for NH$_3$ and its isotopologue ND$_3$ by Ziegler\textit{ et al.}\textsuperscript{197} A few years later, Chung and Ziegler illustrated A and B term scattering in both RRS and RHRS for gas phase NH$_3$, CH$_3$I, and CS$_2$.\textsuperscript{208} It was discussed that CH$_3$I was an A term scatterer in RRS and RHRS, while NH$_3$ and CS$_2$ were determined to be B term scatterers in RHRS and A term scatterers in RRS. The basis for those assignments was the symmetry of each molecule in its ground state compared to the excited state.

In Table 6.1, data for the excitation to the S$_1$ state of NH$_3$ are collected. The S$_1$ state of NH$_3$ is a known Rydberg state, involving the excitation of an electron from the N(2p$_z$) to N(3s) orbital. For the energetic placement of the excited state, both B3LYP and LC-PBE underestimate its location by 4–8% compared to CCSD. Transition strengths using both XC-functionals are underestimated by around 5–8% with respect to CCSD. However, the experimental value for the oscillator strength is 0.079,\textsuperscript{442} which is in best agreement with the LC-PBE result (0.079). Two-photon transition strengths show a less consistent trend, where B3LYP overestimates the CCSD value by 25% and LC-PBE underestimates it by 27%. The work by Paterson\textit{ et al.} indicated that increasing the basis set cardinality (i.e. going from aug-cc-pVDZ to aug-cc-pVTZ) results in a decrease in the two-photon transition strength for CCSD, whereas both B3LYP and CAM-B3LYP functionals saw an increase in that quantity.\textsuperscript{438} It may therefore be possible to improve
Table 6.1. Vertical electronic excitation energies, transition strengths, and two-photon transition strengths for the S₁ (1¹A₂′′) state of NH₃ for B3LYP, LC-PBE, and CCSD.

<table>
<thead>
<tr>
<th>Method</th>
<th>E₀¹ (eV)</th>
<th>(M₀¹)² (a.u.)</th>
<th>δ₀¹TPA (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>5.89</td>
<td>0.515</td>
<td>33.363</td>
</tr>
<tr>
<td>LC-PBE</td>
<td>6.12</td>
<td>0.528</td>
<td>19.572</td>
</tr>
<tr>
<td>CCSD</td>
<td>6.40</td>
<td>0.558</td>
<td>26.753</td>
</tr>
</tbody>
</table>

the agreement between LC-PBE and CCSD for the two-photon properties of NH₃ by increasing the basis set size, without significantly changing the excitation energy or transition dipole moment.

It is not surprising that LC-PBE improves the description of this transition in terms of the one-photon properties because it is a Rydberg transition. However, even the B3LYP calculation gives reasonable agreement with CCSD. Both DFT functionals yield significant errors in the two-photon properties compared to CCSD, possibly resulting from the ~5% double excitation character predicted for this excited state by the latter method. In that respect, the LC-DFT approach, including 100% exact exchange at long-range, only slightly improves on a traditional global hybrid.

OPA spectra are plotted for CCSD and LC-PBE in Fig. 6.1 showing highly structured vibronic features. The spacing of those features is ~1000 cm⁻¹ indicating that the progression results from ν₂ (980 cm⁻¹). Comparing FC terms from each method, the spectra are similar in appearance. This is unsurprising because each method yields a very similar transition strength (Table 6.1) and although there are variations in the dimensionless displacements, they are difficult to resolve using the OPA spectra.

The bottom plot in Fig. 6.1 shows the experimentally measured OPA spectrum. Note that the simulated and measured spectra are plotted over different wavelength regions to align them. For the red edge of the spectrum, there is good agreement between the harmonic model and the measured spectrum, independent of whether CCSD or DFT is used. However, the harmonic model does not capture the full progression of the spectrum. This is expected because the dimensionless displacements for ν₂ determined by CCSD and LC-PBE, 3.60 and 3.16 respectively, are very large and indicate the breakdown of the harmonic model. Inclusion of anharmonic corrections would likely aid the reproduction of all spectral features.

Based on the simulation parameters, each method yields a similar description of the curvature of the excited state because the derivatives of the excitation energy and response properties reflect the molecule’s potential energy surface. With this in mind, the
HT term for each method is very similar. A two-peaked progression is observed for both methods. This doubled progression results from having both the FC-HT interference term and HT term plotted on the same graph. The progressions from LC-PBE and CCSD are comparable where both peaks are similar in intensity. It may be surprising that the graph labeled “HT” can be both positive and negative. The FC-HT interference term has an asymmetric lineshape around the horizontal axis that causes a wave-like shape, whereas the HT term has a symmetric lineshape around the horizontal axis. When the FC-HT interference and HT terms are on the same order of magnitude the sum of those terms results in a lineshape from both terms. Because both the FC and FC-HT interference terms derive intensity from the transition dipole moment, both terms contribute only for dipole-allowed transitions. Although the FC-HT interference term can be negative, the OPA cross section (and TPA as well) cannot be unphysically negative in the present model because the FC term is significantly larger.

The experimental RRS spectrum for NH$_3$ was measured on the red edge of the absorbance maximum.$^{441}$ In order to effectively compare RRS spectra from each method with experiment, RRS simulations were performed assuming a wavelength on the red edge of the simulated absorption maximum (see Fig. 6.2). The simulated RRS spectra, including overtones and combination bands, are shown in Fig. 6.2 for CCSD and LC-PBE.

Examining the RRS spectrum from CCSD (Fig. 6.2(a)), the most noticeable feature is that the simulated spectrum contains all of the experimentally observed peaks for transitions starting from the vibrational ground state. In the present implementation

---

**Figure 6.1.** Simulated NH$_3$ OPA spectra using CCSD and LC-PBE applying a 200 cm$^{-1}$ lifetime. The experimental spectrum is adapted from Ref. 442.
Simulated NH$_3$ RRS spectra using CCSD and LC-PBE applying a 200 cm$^{-1}$ lifetime. The experimental RRS spectrum (at 212.8 nm) is adapted from Ref. 441. We do not allow for hot band transitions (those marked by asterisks in Ref. 441, where the initial state has one mode that is thermally excited) nor does the model include rotational transitions. The intensities of fundamentals and overtones are reproduced well, but combination bands are underestimated significantly using a 200 cm$^{-1}$ lifetime. Overall the agreement is good, especially when considering that small molecules like NH$_3$ are prone to anharmonic effects.

The simulated RRS spectrum from LC-PBE is shown in Fig. 6.2(b). Using a 200 cm$^{-1}$ lifetime gives good agreement with experiment for fundamentals and overtones. Like CCSD the intensity of combination bands is underestimated. Tests on this molecule indicated that the relative peak intensities are very sensitive to the incident wavelength, especially for overtones and combination bands. A likely reason for the difficulties in describing the intensity of combination bands is that those features involve products of dimensionless displacements. Although the dimensionless displacements for each method are similar, the values are different enough that the relative intensities of combination bands are significantly altered.

For each method, the full RRS spectrum derives significant intensity from the A term. Comparing the contributions from the A term to those of the B term (see Appendix C), the A term is approximately 100-200 times larger than the B term for a 200 cm$^{-1}$ lifetime parameter. Both of the asymmetric modes ($\nu_3$, the asymmetric stretch, and $\nu_4$, the asymmetric bending) are observed in the B term spectrum. It appears that the B
term is insensitive to the choice of lifetime parameters because the relative and absolute intensities on the RRS spectrum are very similar when those parameters are changed. Ammonia is an A term scatterer according to the vibronic theory for RRS, in agreement with previous studies, with a resonance enhancement of approximately four orders of magnitude.

Figure 6.3. Simulated NH₃ RHRS spectra using CCSD and LC-PBE applying a 200 cm⁻¹ lifetime.

In RHRS spectra (Fig. 6.3), NH₃ is clearly an A term scatterer similar to RRS. However, the B term has a non-negligible intensity and clearly causes destructive interference with the A term. This is evident for the entire spectrum. For instance, the first overtone of ν₂ is reduced in intensity by \(\sim 50000 \times 10^{-64} \text{ cm}^4 \text{ s photon}^{-1} \text{ sr}^{-1}\) on the total spectrum compared to the A term spectrum. Consequently, the interference between the A and B term hyperpolarizabilities can have significant impact on the total intensity of peaks on a RHRS spectrum. This interference was negligible in RRS because the modes with strong A term activity (ν₁ and ν₂) have small derivatives of their transition dipole moment. Both modes have significant derivatives of the two-photon transition moment, allowing for interference via the B₂ term.

The full B term, in comparison to the B₁ term, is approximately 3-5 times more intense. This shows that the B₂ term, which depends on the derivatives of the two-photon transition moment, is more intense than the B₁ term, which depends on the derivatives of the transition dipole moment. It is important to include both terms when simulating a RHRS spectrum if one wants to consider the size of the first HT term.
relative to the FC term.

Because the two-photon transition is not dipole forbidden as was thought in Ref. 208, NH$_3$ is not a B term scatterer in RHRS. Inspection of the vibrational structure in RRS and RHRS spectra in Fig. 2 of Ref. 208, which highlights the overtones and combination bands of NH$_3$, demonstrated that both spectra almost look identical. Only the $\nu_1 + \nu_2$ and $\nu_1 + 4\nu_2$ combination bands have slightly different intensity in the spectra presented in that work, which may be an artifact of the different pressures used in measuring the RHRS and RRS spectra.\textsuperscript{443,444} Based on the observations of strong A/B term interference discussed above, the B term in RHRS may cause observed differences in the relative peak intensities due to interference.

Since NH$_3$ is predicted to be an A term scatterer in RRS, and the measured RHRS spectrum is nearly identical to the measured RRS spectrum, NH$_3$ must be an A term scatterer in RHRS as well. The simulations predict NH$_3$ is an A term scatterer in RHRS in agreement with this analysis. For RHRS in comparison to NHRS, NH$_3$ has a resonance enhancement of three to four orders of magnitude.

### 6.3.2 Formaldehyde

The transition to the $1^1A_2$ (or $\pi^* \leftarrow n$) state in CH$_2$O is dipole forbidden for one-photon absorption. Resulting from this feature, CH$_2$O allows one to study the HT terms. Thus, by considering the expressions for the OPA and RRS spectra,\textsuperscript{435} one can see that the FC/A term and FC-HT interference/B term must be zero for this transition. In fact, the A term in RHRS is zero for this molecule because it too involves the transition dipole moment. Inclusion of higher order terms (the second HT term in OPA or C term in RHRS) might further refine the spectra in this circumstance. That effect should be weak and therefore is likely to be negligible even for a molecule like CH$_2$O.

With the previous paragraph in mind, Table 6.2 summarizes the response properties for CH$_2$O. Looking at the vertical excitation energies, B3LYP positions the excited state 3% lower than CCSD, while LC-PBE has a larger 7% error for this quantity. This is interesting and contrasts the findings for NH$_3$ in which LC-PBE gave improved positioning of the excited state. Each method correctly predicts that the transition is one-photon dipole forbidden. LC-PBE improves the agreement with CCSD (6% error) compared to B3LYP (80% error) in the two-photon transition strength.

Dimensionless displacements are reproduced well by LC-PBE compared to CCSD. This illustrates a similarity in the curvature of the excited states for LC-PBE and CCSD. Derivatives of the transition dipole moment are in agreement between each method.
Overall, LC-PBE yields better agreement for the derivatives of the two-photon transition moment in comparison to CCSD than B3LYP.

Table 6.2. Unshifted vertical electronic excitation energies and two-photon transition strengths for the $S_1$ ($1^1A_2$, or $\pi^* \leftarrow n$) state of CH$_2$O for B3LYP, LC-PBE, and CCSD. Transition strengths are 0.00 a.u. for this excitation for each method.

<table>
<thead>
<tr>
<th>Method</th>
<th>$E^{01}$ (eV)</th>
<th>$\delta_{TPA}^{01}$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>3.91</td>
<td>0.378</td>
</tr>
<tr>
<td>LC-PBE</td>
<td>3.76</td>
<td>0.197</td>
</tr>
<tr>
<td>CCSD</td>
<td>4.03</td>
<td>0.210</td>
</tr>
</tbody>
</table>

TPA spectra are shown in Fig. 6.4. Experimental TPA spectra are unavailable for CH$_2$O, so the comparison between DFT and CCSD will serve to evaluate the accuracy of the method. Similar appearance is observed for the spectra derived from DFT and CCSD. The third peak in the progression is more intense, however, in the CCSD spectrum than the LC-PBE spectrum. The B3LYP spectrum has an overestimated FC term so the agreement with CCSD is slightly worse for the features resulting from the HT term. Resulting from the two-photon transition strengths shown in Table 6.2, the peak intensity is overestimated even though the dimensionless displacements dictate that B3LYP yields a similar bandshape to CCSD. Every method also illustrates that there is interference between the FC and HT term because the first peak in the progression has reduced intensity compared to the FC term spectrum. Furthermore, the spectra show that it is possible to examine weakly allowed transitions, and that features for those states may result from both the FC and HT terms.

The OPA and TPA spectra illustrate an interesting feature of the FC and HT terms (see Appendix C for OPA spectra). Examining the CCSD OPA spectrum, the first peak of the progression begins at $\sim 299$ nm. The CCSD TPA spectrum (Fig. 6.4(a)) progression begins at $\sim 309$ nm, which is clearly redshifted from the OPA spectrum onset. This also occurs for both of the DFT functionals. This observation results from the HT term activity of the TPA spectrum, where the HT term for absorbance spectra includes an extra vibrational frequency in the exponential. Effectively the vibrational frequency is added to the ground state electronic energy, reducing the energetic spacing with the excited state electronic energy (analogous to a zero-point energy correction). The observed shifts are indeed on the order of the $\nu_1$ or $\nu_2$ vibrational frequency. TPA spectra from each method have a very featured appearance resulting from this shift and also the similar magnitude of the FC and HT terms.
Simulated CH$_2$O TPA spectra using CCSD and LC-PBE applying a 200 cm$^{-1}$
lifetime.

Simulated RHRS spectra are shown in Fig. 6.5. The most striking feature of the
RHRS spectra is the very small intensity of the peaks. Whereas NHRS was predicted on
the order of $100 \times 10^{-64} \text{ cm}^4 \text{s photon}^{-1} \text{ sr}^{-1}$, RHRS spectra are shown to be one order of
magnitude smaller. When no excitation has a large transition dipole moment, intensity
is gained from the sum over states formalism where all intermediate vibrational states
are included in the summation. A large discrepancy in the predicted NHRS and RHRS
Table 6.3. Unshifted vertical electronic excitation energies, transition strengths, and two-photon transition strengths for the $S_4 \left( ^1B_2 \left( ^3\Sigma_u^+ \right) \right)$ and $S_5$ states of CS$_2$ for B3LYP, LC-PBE, and CCSD.

<table>
<thead>
<tr>
<th>Excited State</th>
<th>Method</th>
<th>$E^0n$ (eV)</th>
<th>$(M^0n)^2$ (a.u.)</th>
<th>$\delta^0n_{TPA}$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_4$</td>
<td>B3LYP</td>
<td>6.55</td>
<td>6.289</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>LC-PBE</td>
<td>6.60</td>
<td>6.718</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>CCSD</td>
<td>6.45</td>
<td>7.385</td>
<td>0.000</td>
</tr>
<tr>
<td>$S_5$</td>
<td>B3LYP</td>
<td>6.74</td>
<td>0.000</td>
<td>151.005</td>
</tr>
<tr>
<td></td>
<td>LC-PBE</td>
<td>7.14</td>
<td>0.000</td>
<td>119.265</td>
</tr>
<tr>
<td></td>
<td>CCSD</td>
<td>6.89</td>
<td>0.000</td>
<td>164.421</td>
</tr>
</tbody>
</table>

is thus unsurprising. LC-PBE and CCSD give similar RHRS spectra which is explained by the agreement of the parameters determined by both methods.

6.3.3 Carbon Disulfide

The data for CS$_2$ presented in this section highlight important selection rules for centrosymmetric molecules. For molecules like CS$_2$, excitations cannot simultaneously be one-photon allowed (transition dipole moment is nonzero) and two-photon allowed (two-photon transition moment is nonzero). The fourth and fifth excitations of CS$_2$ illustrate this point (see Table 6.3). For this molecule, the $S_4$ state is a $\pi^* \leftarrow \pi$ transition, and the $S_5$ state is a $\sigma^* \leftarrow \pi$ transition. Although experimental data are available for RHRS, it cannot be ignored that these high lying excited states are dissociative and that the experimental spectrum includes features derived from hot bands. These features are not included in the present simulations.

Data shown in Table 6.3 indicate that B3LYP yields more comparable excitation energies with CCSD. The transition strengths are large for the $S_4$ state, but both XC-functionals underestimate this quantity by 9-15%. The two-photon transition moments of the $S_4$ state are observed to be zero. The $S_5$ state is one-photon forbidden, while it is a bright state in two-photon absorbance. B3LYP in this case compares better with CCSD for the two-photon transition strength.

Simulation parameters corresponding to the fourth and fifth excitations predicted by each method show only one normal mode with activity in the FC approximation for both excited states. This has important consequences on the simulated RRS and RHRS spectra because no combination bands can occur if only one normal mode has a nonzero displacement in the harmonic model. The fourth excitation has small derivatives of the transition dipole moment and two-photon moment. However, there is significant
improvement in the description of the derivatives when LC-PBE is used instead of B3LYP in comparison to CCSD.

The fifth excited state again has only one mode active in the FC approximation. LC-PBE results in derivatives of the transition dipole moment that are in better agreement with CCSD than B3LYP. For the derivatives of the two-photon transition moment, the DFT functionals deviate from CCSD. This is particularly apparent for B3LYP where the degenerate $\nu_2$ bending modes have very different two-photon moment derivatives. It may not be surprising that the derivatives are very different because the high-lying states in this molecule are likely anharmonic, and it is plausible that the derivatives of the response properties are overestimated. However, as will be shown below the derivatives demonstrate a few concepts when comparing FC and HT terms.

OPA spectra are shown in Fig. 6.6 including both excited states. Both LC-PBE and CCSD predict that the OPA spectrum is very featured, resulting from a progression in the symmetric stretch $\nu_1$. A large $\sigma_{OPA}$ value is observed for CS$_2$ in the fourth excitation in the simulations which is caused by the large transition dipole moment. It is also interesting that each method predicts the fifth excitation, which is dipole forbidden, gains some intensity based on the nonzero transition dipole moment derivatives. The close positioning of both states causes the progression from the fourth state to overlap with the onset of the dipole forbidden fifth state.

![Simulated CS$_2$ OPA spectra using CCSD and LC-PBE applying a 100 cm$^{-1}$ lifetime. The experimental spectrum is adapted from Ref. 445.](image)

**Figure 6.6.** Simulated CS$_2$ OPA spectra using CCSD and LC-PBE applying a 100 cm$^{-1}$ lifetime. The experimental spectrum is adapted from Ref. 445.

For comparison, the gas-phase experimental OPA spectrum is included in the bottom
plot in Fig. 6.6. Like the discussion of NH$_3$ above, the wavelength regions of the simulated and experimental spectra are different to facilitate comparison. In general, the agreement between the measured and simulated spectra is poor. Progression features on the red edge of the absorbance maximum and noticeably missing in the simulated spectra. Also, the intensity of the simulated spectrum is 40-50% larger than the measured spectrum, and the features of the progression in the simulation are still broader than the measured spectrum. In contrast to the NH$_3$ discussion, the blue edge of the progression is better reproduced in the harmonic model. Anharmonic corrections to the harmonic model$^{445}$ have previously been employed to improve agreement with measured RRS spectra, so it is likely that they would improve agreement in OPA also. The progression is known to result from contributions of the symmetric stretch $\nu_1$ and degenerate bending $\nu_2$, based on high-resolution jet-cooled spectra.$^{446}$ Only $\nu_1$ is active in the harmonic approach so observing the full progression is not possible without accounting for anharmonicity in the simulations.

The emphasis of the present work is illustrating the types of spectra that can be simulated with TDSPEC. CS$_2$ results indicate that spectra obtained in the harmonic model must be carefully compared with experiment to gauge reliability. Dimensionless displacements for $\nu_1$ of CS$_2$ are 1.75 from CCSD and 1.58 from LC-PBE ($\sim$3.90 is estimated experimentally in cyclohexane$^{445}$). These large displacements serve as an indicator of the importance of anharmonicity in obtaining the correct shape of spectra.

Based on the simulation parameters, the relative order of magnitude required for the FC and HT terms to have similar intensity can be understood. In previous sections, the transition dipole moment derivatives were only on the order of 0.10 a.u. amu$^{-1/2}$ Bohr$^{-1}$, which was clearly too small for the HT term to be observed except in the special case of CH$_2$O. The fifth excited state of CS$_2$ has derivatives of that property of $\sim$1.60 a.u. amu$^{-1/2}$ Bohr$^{-1}$. Increasing the order of magnitude of the transition dipole moment derivative allows the HT term to be observed. Based on the anharmonic effects on the fourth and fifth excited states, it is likely that the harmonic approach is not adequate for accurately determining the derivatives of the transition properties. Again, the spectra presented here illustrate the magnitudes of different prefactors required to simultaneously observe the FC term and HT term.

### 6.3.4 para-Nitroaniline

PNA is known for its large first hyperpolarizability resulting from its electron donating -NH$_2$ and electron accepting -NO$_2$ groups. It has been used as the prototype for developing
Table 6.4. Unshifted vertical electronic excitation energies, transition strengths, two-photon transition strengths, electronic homogeneous FWHM, lineshape parameters, and reorganization energies. Simulation parameters for the experimental spectra are included also, for PNA in a cyclohexane solvent.  

<table>
<thead>
<tr>
<th></th>
<th>B3LYP</th>
<th>LC-PBE</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0^0$ (eV)</td>
<td>3.87</td>
<td>4.39</td>
<td>3.85</td>
</tr>
<tr>
<td>$(M_0^0)^2$ (a.u.)</td>
<td>3.486</td>
<td>3.699</td>
<td>4.360</td>
</tr>
<tr>
<td>$\delta_{TPA}$ (a.u.)</td>
<td>2029.152</td>
<td>1860.338</td>
<td>-</td>
</tr>
<tr>
<td>$\Gamma_{FWHM}^2$ (cm$^{-1}$)</td>
<td>3200</td>
<td>2800</td>
<td>2045</td>
</tr>
<tr>
<td>Lineshape parameter, $\kappa$</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Solvent reorg. energy (cm$^{-1}$)</td>
<td>4586</td>
<td>3511</td>
<td>1890</td>
</tr>
<tr>
<td>Total vib. reorg. energy (cm$^{-1}$)</td>
<td>863</td>
<td>1703</td>
<td>2058</td>
</tr>
</tbody>
</table>

molecules with large nonlinear optical response, and has been examined using OPA, NRS, and RRS and also using TPA. Using theory, research has focused on diverse topics like investigating second harmonic generation using DFT, enhancement of the first and second hyperpolarizability for PNA near Au clusters, solvatochromic shifts of the PNA charge-transfer (CT) state, solvation shifts of the first hyperpolarizability, and CT states of PNA aggregates.

Simulated OPA spectra for PNA using DFT are shown in Fig. 6.7 in comparison to the experimentally measured OPA spectrum in cyclohexane. Table 6.4 presents the simulation parameters used in this section. The CT band is peaked at around 322 nm, and is very broad and featureless. To facilitate the simulations of the OPA spectra the theoretically obtained excitation energies for the CT band is shifted (0.10 eV for B3LYP, and 0.68 eV for LC-PBE) so as to match the experimental result. It was noted in Ref. that the measured OPA spectrum is slightly asymmetric. This makes simulating the bandshape difficult which is observed in this study also. Using the simulation parameters from experiment a very good fit to the measured spectrum is obtained. Both functionals give a good fit, but underestimate the onset of the absorbance and also the blue edge of the absorbance maximum. Using the experimental parameters results in similar underestimation in comparison to the measured OPA spectrum in cyclohexane (see Fig. 3 of Ref.). The HT contributions to the OPA spectra are very small (peak values of 0.007 and 0.035 Å$^2$/molecule for B3LYP and LC-PBE, respectively), but a redshift of ~2 nm is observed for the total spectrum for LC-PBE compared to the FC term simulation. This is caused by the asymmetric FC-HT interference term, which adds to the red edge and subtracts from the blue edge of the absorbance maximum.
The calculated vibrational reorganization energies in Table 6.4 give quantitative evidence that LC-PBE better describes the vibronic coupling in PNA than B3LYP. In comparison to the experimental value (2058 cm\(^{-1}\)), displacements along the potential energy surface from LC-PBE yield a vibrational reorganization energy of 1703 cm\(^{-1}\). The B3LYP displacements give a vibrational reorganization energy of 863 cm\(^{-1}\), which is in significant error compared to the experimental value. The LC-DFT approach is therefore important for determining the vibrational reorganization energy of molecules with CT states, which has been indicated previously.\(^{405}\)

The solvent reorganization energies in Table 6.4 show a less clear trend because the calculated values are highly sensitive to the value of \(\Gamma_{FWHM}^2\), and it is possible that several values of that parameter can give a good fit to an absorbance spectrum.

The experimentally determined dimensionless displacements\(^{424}\) indicate that there are only a few modes from PNA that are resonantly enhanced. The dominant mode according to the experimental RRS spectrum is the -NO\(_2\) symmetric stretch at 1338 cm\(^{-1}\). In addition to that mode, a ring-breathing/-NO\(_2\) scissors (859 cm\(^{-1}\)), phenyl-NO\(_2\) stretch (1112 cm\(^{-1}\)), C-H wagging/-NH\(_2\) scissors (1498 cm\(^{-1}\)), and C-C stretch/-NH\(_2\) scissors (1599 cm\(^{-1}\)) are also observed experimentally. LC-PBE overall agrees with the experimental estimates for the displacements, although it overestimates the displacement at 859 cm\(^{-1}\) and underestimates it at 1338 cm\(^{-1}\). The only significant deviation in the mode assignments is the mode at 1599 cm\(^{-1}\). Although the calculated mode at 1593 cm\(^{-1}\), dominated by the scissoring of the -NH\(_2\) group, is close to the experimental wavenumber, the calculated displacement is around 60% too small. The mode at 1632 cm\(^{-1}\), involving strong C-C stretching and -NH\(_2\) group scissoring, yields a displacement (0.48) that is nearly identical to the experimental value (0.496) but is 30 cm\(^{-1}\) too high in energy. With the displacements in mind it seems that the latter mode is correct to assign with the experimental spectrum.

B3LYP displacements agree well with experiment for modes below 1300 cm\(^{-1}\), but are in poor agreement for all of the higher wavenumber modes. This is surprising because the intramolecular charge transfer state studied here is short range, but the observation is in line with a previous work by our group comparing long-range corrected DFT to B3LYP for donor-acceptor complexes.\(^{405}\) One must consider that the DFT displacements are based on gas-phase calculations, so directly comparing the displacements to experiment must be done cautiously. For medium and large molecules the superposition of several normal modes can yield an apparent single peak, such that the displacements are overestimated from the experimental RRS spectra. As discussed below, it is also possible for the A and
B terms to interfere constructively and destructively with a non-negligible contribution. Larger displacements based on fitting to experimental RRS spectra may result if the B term is neglected.

Figure 6.7. Simulated PNA OPA spectra using parameters from Table 6.4, compared with measured experimental OPA spectra in cyclohexane and DMSO solvents. The intensities of simulated spectra were scaled to fit the cyclohexane spectrum as follows: B3LYP = 0.775, LC-PBE = 0.802. The DMSO spectrum was blueshifted by 65 nm, and the peak height (in normalized absorbance) was scaled by 0.554 to coincide with the height of the cyclohexane spectrum.

Simulated RRS spectra are shown in Fig. 6.8 along with the simulated RRS spectrum using experimental parameters. The simulation based on experimental parameters looks very similar to the NRS spectrum, with the dominant feature attributed to the -NO$_2$ symmetric stretching. Examining the RRS spectrum from B3LYP, there are several prominent features with the largest located at 861 cm$^{-1}$. B3LYP predicts that the correct modes are active in the RRS spectrum, but the incorrectly describes the relative intensities of every peak. This results from a well known failure of traditional XC-functionals in DFT, in which the curvature of the potential energy surface for CT states is incorrectly described. From LC-PBE, the correct peak at 1359 cm$^{-1}$ is predicted to be the largest. The peak intensities at 861 and 1632 cm$^{-1}$ are still overestimated by LC-PBE, but there is substantially improved agreement with experiment nonetheless. Simulations with both functionals result in a smaller differential RRS cross section by a factor of $\sim$2 to 3 compared to the simulation with experimental parameters.

Interestingly, B3LYP predicts that there is significant activity in the B term above 1500 cm$^{-1}$ resulting in several features that are not observed when only the A term is used in the simulation. In contrast, LC-PBE predicts all of the observed features result
Figure 6.8. Simulated PNA RRS spectra using parameters from Table 6.4 with an incident wavelength of 322 nm. The experimental spectrum is simulated using parameters given in Ref. 424. Peak intensities were scaled as performed in the OPA spectra, and spectra were broadened using a Lorentzian function with 20 cm$^{-1}$ width.

mostly from A term activity. Significant A/B term constructive interference is observed for both functionals, ranging from 7% for B3LYP to 14% for LC-PBE when looking at the peak at 1359 cm$^{-1}$. Interference is also observed at 861, 1106, and 1632 cm$^{-1}$ when comparing the total spectrum and A term spectrum. Regardless of the functional, it is predicted that PNA is an A term scatterer in RRS. However, inspection of the simulation parameters implies that the functional is very important in describing the curvature of the potential energy surface, which is reflected in the displacements and the derivatives of the response properties.

Estimates of the peak RRS cross section in Ref. 424 are on the order of $10^{-24}$ cm$^2$ sr$^{-1}$ at 309 nm for the mode at 1328 cm$^{-1}$. By comparison, the simulations in this work imply that the peak cross section for the same mode is $10^{-26}$ to $10^{-27}$ cm$^2$ sr$^{-1}$. Neglect of solvent effects contributes to this underestimation, and it is also clear that both functionals underestimate the transition strength by 15-20%. This underestimation is unexpected because a previous work by our group showed good agreement when simulated RRS cross sections were compared to experimental results from the same group. Reduction of the inhomogeneous and homogeneous broadening can increase the RRS cross sections by at least a factor of ten, at the cost of poorer agreement between the simulated and measured OPA spectrum. In any case, the enhancement of Raman
scattering from resonance is predicted from simulations to be on the order of $10^3$ to $10^4$ for PNA.

Simulated TPA spectra are shown in Fig. 6.9. An estimate for the peak measured $\sigma_{TPA}$ based on the data in Ref. 447 is $12 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ in DMSO (data was not measured at the absorbance peak). Based on calculations of the TPA cross section for the lowest excited states of PNA, it is expected that the CT state (excited state 2) is most intense. The maximum of TPA is therefore expected to coincide with the maximum of OPA. Unfortunately, measured TPA data for PNA in cyclohexane is unavailable, so the experimental data in DMSO was used as a reference. Comparison of the measured OPA spectra in Fig. 6.7 indicates that the spectrum in DMSO is broader than the spectrum in cyclohexane. Based on Ref. 424, where solvents of varying polarity were used and the shape of the OPA spectrum was almost identical in each for the same PNA concentration, changing to DMSO solvent is not likely to cause significant additional broadening compared to an aprotic solvent of similar polarity, such as acetonitrile. However, some additional broadening due to differences in microsolvation environment (inhomogeneous broadening) when comparing a nonpolar solvent like cyclohexane and a polar aprotic solvent like DMSO is expected. In Fig. 6.9, the simulations were carried out using the parameters in Table 6.4 and therefore fit the cyclohexane OPA spectrum. Because the first principles calculations were carried out in the gas phase, the simulations are best compared to the spectra measured in a nonpolar solvent like cyclohexane.

The measured OPA and TPA spectra of PNA in DMSO illustrate that the shape and width of the spectra are unchanged when comparing the linear and nonlinear optical processes. This implies that if a TPA spectrum were measured in cyclohexane for PNA, the spectral shape would be similar to the OPA spectrum. It is justified to use the same homogeneous and inhomogeneous broadening for the simulations of the PNA OPA and TPA spectra as a result.

The simulations indicate that $\sigma_{TPA}$ is on the order of $14-17 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$ molecule$^{-1}$, which is on the correct order of magnitude considering the difficulty in measuring $\sigma_{TPA}$ experimentally. Because the same parameters used for simulating the OPA spectrum were applied to the TPA spectrum, the band shapes are identical to what was shown in Fig. 6.7. Agreement with the experimental intensity may be improved by using larger homogeneous/inhomogeneous broadening, but this is not physically correct in comparison to the experimental evidence described above because those changes alter the bandshape. Based on the magnitude of the derivatives of the two-photon transition
moment, the simulations show that the B3LYP HT term dominates while for LC-PBE the FC-HT interference term is larger when the HT term is plotted. Neither functional indicates that the contributions from HT terms are significant in TPA for PNA.

Figure 6.9. Simulated PNA TPA spectra using parameters from Table 6.4. The experimental TPA spectrum in DMSO \(^{447}\) includes error bars of \(\pm 1.7 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}\), and was blueshifted by 65 nm.

RHRS simulated using DFT are shown in Fig. 6.10. Measured RHRS spectra are not available for PNA. Several interesting features are observed for both XC-functionals. Comparing the total and A term spectra, evidence for constructive and destructive interference exists for several peaks. For instance, at 1106 cm\(^{-1}\) on the B3LYP total spectrum there is a significant intensity reduction compared to the A term spectrum. For LC-PBE, the behavior is much more similar to the RRS spectra where peaks at 1106, 1359, and 1632 cm\(^{-1}\) have increased intensity in the total spectrum compared with the A term alone. The total constructive interference for the mode at 1359 cm\(^{-1}\) is 11% for LC-PBE and 20% for B3LYP. Although the B term is smaller than the A term by an order of magnitude, the RHRS spectra (and RRS spectra discussed above) indicate that the B term may be important for finding relative peak intensities.

Along with A/B term interference, it is also possible to observe B\(_1\)/B\(_2\) term interference (referred to as B term interference in the following discussion). This B term interference is dependent on the XC-functional, and also the normal mode being examined. For instance, the mode at 1359 cm\(^{-1}\) has destructive interference for B3LYP and constructive interference for LC-PBE when the B\(_1\) and B\(_2\) terms are added. Analogous to the B term in RRS, the B3LYP and LC-PBE B terms look very different in RHRS.
This is reasonable because both functionals yield different derivatives of the transition dipole moment and two-photon transition moments along each normal mode. Examining the mode at 1632 cm\(^{-1}\) instead yields constructive interference for both functionals. For B3LYP this illustrates that the type of interference observed for a particular wavelength is mode dependent.

Based on the discussion above dealing with the RRS spectra, it is apparent that LC-PBE is giving a more realistic description of the RHRS spectrum than B3LYP for PNA. In comparison to the NHRS spectra, the enhancement due to resonance for PNA is only two orders of magnitude. This is significantly smaller than the enhancement for RRS for the same molecule. Because the transition is allowed in both one-photon and two-photon excitation, it is not surprising that PNA is considered an A term scatterer in both RRS and RHRS. To obtain RRS spectra comparable with experiment, it is necessary to use XC-functionals with the correct asymptotic behavior of the potential for describing CT states. This is likely true for RHRS as well.

### 6.4 Conclusions

The present work illustrates the theory derived in Ref. 435, which allows for simulations of linear and nonlinear optical processes using the time-dependent wavepacket approach.
Although many of the molecules presented contain significant anharmonicity in their potential energy surfaces, the model is capable of capturing the correct spectral shape and intensities for absorbance and Raman scattering processes. In particular, NH$_3$ illustrated that anharmonicity through the intensities of combination bands on the Raman spectra. Simulations of spectra for CS$_2$ and CH$_2$O demonstrate a technique for handling dipole forbidden transitions, although data obtained using the prescribed technique must be analyzed cautiously and it is helpful having experimental data as a guide. Finally, the PNA results show the importance of choosing an appropriate XC-functional for describing charge transfer states if the curvature of the potential energy surface is to be accurately reproduced.

Some surprising behavior is obtained in this model, with respect to interference between the A and B terms in Raman/hyper-Raman scattering. Although it is popular to discuss the relative magnitude of the A and B terms in relation to their importance, it is possible that a significantly weaker B term can modulate the intensity of peaks on a Raman/hyper-Raman spectrum via intensity borrowing from the A term. This indicates that it may not be fully correct to describe the relative importance of the B term without considering its multiplication with the larger A term. Further investigation of the model is underway for larger systems where the importance of anharmonic effects is reduced.
Part IV

Hyper-Raman scattering of rhodamine 6G
Probing One-Photon Inaccessible Electronic States with High Sensitivity: Wavelength Scanned Surface Enhanced Hyper-Raman Scattering


Abstract

How exciting! A combined experimental and theoretical study of the surface-enhanced hyper-Raman scattering (SEHRS) provides a detailed picture of the electronic excited state of the benchmark Rhodamine 6G molecule (see picture). These results demonstrate the ability of SEHRS to explore excited states that are not easily accessible via one-photon excitation using nonlinear spectroscopy at very low (1010m) concentrations.
Electronic excited states play an essential role in a wide range of molecular processes from biology to molecular electronics. For example, charge separation and its subsequent transport in organic photovoltaics occurs through molecular excited states. Traditionally, experimental characterization of the topology of molecular excited states is achieved through spectroscopic techniques such as resonance Raman scattering. The sensitivity of resonance Raman to details of the excited state potential energy landscape is clearly elucidated in the theory of inelastic light scattering, although ab initio calculations of electronic excited states remain quite challenging.

In some cases, one photon transitions to the electronic state of interest are either weak or forbidden and thus the methods available for probing these “dark” states are severely restricted. These dark states, however, are often coupled to the bright states and can play a major role in the electronic and nuclear dynamics. Indeed, a recent study of excited-state intermolecular proton transfer demonstrated that dark states can directly affect electronic relaxation kinetics, which subsequently alters the product branching ratios.

Herein we report a method utilizing surface enhanced hyper-Raman scattering (SEHRS) to probe these one-photon inaccessible electronic states for analytes at low concentration (∼10−10 m). We also demonstrate that a close coupling of time-dependent density functional theory (TDDFT) simulations of the two-photon absorption spectrum and off-resonance hyper-Raman spectra yield important insights into the nature of the probed electronic states.

Hyper-Raman scattering is a type of nonlinear light scattering in which a photon at $\omega = 2\omega_0 - \omega_{\text{vib}}$ is incoherently scattered, where $\omega_0$ is the laser frequency and $\omega_{\text{vib}}$ is a vibration characteristic of the material. Hyper-Raman scattering provides information that is complementary to that obtained from IR and Raman; further resonance hyper-Raman provides access to electronic states that are not one-photon allowed. While hyper-Raman scattering is an inherently weak process, the signal originating from molecules located near the surface of a plasmonic nanostructure can be enhanced by many orders of magnitude. SEHRS also contains unique information about surface symmetry and can be applied to biological imaging.

SEHRS spectra of Rhodamine 6G (R6G) adsorbed on aggregated silver colloids were recorded for excitation wavelengths between 750-1045 nm in increments of ∼15 nm. This range spans the two-photon absorption spectrum of R6G and selected (4 of 20) spectra are shown in Figure 7.1. All spectra are reported without baseline or background corrections and typical laser powers were ∼5 mW (∼63 pJpulse−1) at the sample. The concentration of R6G was 10−7 M for the wavelength scanned experiments but we have...
obtained spectra with \([R6G]=10^{-10} \text{ M}\).

**Figure 7.1.** Selected (4 of 20) surface enhanced hyper-Raman spectra (SEHRS) obtained from R6G on silver colloids for wavelengths between 750 and 1050 nm. Spectra are reported without background or baseline correction.

In order to systematically explore the changes in the SEHRS spectra as a function of excitation energy, we fit each spectrum to determine peak positions and areas (see Appendix D). The fitted areas were then used to plot ratios of the 771, 1316, 1535, and 1611 bands to the 1189 band as a function of excitation wavelength. Figure 7.2 compares the experimental and theoretical, one- and two-photon absorption spectrum of R6G with our peak area ratios as a function of excitation energy. The 1189 band was chosen as a reference because it remains mostly constant over the measured range and because the large signal difference between SEHRS and normal hyper-Raman scattering makes calibration to an internal standard difficult.

The ratio 1316:1189 remains constant over the measured range, while the other ratios 771:1189, 1535:1189 and 1611:1189 correlate well with peaks in the two-photon absorption spectrum, suggesting that these bands experience a resonance enhancement. Further, 1535 peaks in a region where the one-photon absorption cross section is negligible. Our theoretically calculated absorption spectra (Figure 7.2) are in good agreement with
Figure 7.2. Theoretical (top) and experimental (middle) one- and two-photon (Ref. 458) absorption spectra for R6G compared with ratios of the 771, 1316, 1535, and 1611 bands to the 1189 band (bottom) obtained from wavelength scanned SEHRS experiments. 

experiment and yield insight into the nature of the responsible excited states. For excitation energies probed here, three excited states, $S_1$, $S_2$, and $S_3$, contribute to the absorption spectra. However, excitation to $S_2$ is not observed in the one-photon spectra. Figure 7.3 displays the frontier orbitals involved in the electronic transitions $S_1 ← S_0$, $S_2 ← S_0$, and $S_3 ← S_0$. All three states are localized on the xanthene ring region of the R6G molecule and indeed the major modes observed are vibrations whose motion is concentrated in this area.

To understand in more detail the observed SEHRS spectra we calculated the off-resonance hyper-Raman spectra by numerical differentiation of the static hyperpolarizability obtained from TDDFT. Calculations at this level of theory yield excellent agreement with experimental measurements of the absolute hyper-Raman cross section of water ($\sigma_{\text{TDDFT}} = 6 \times 10^{-64}$ cm$^4$ s photon$^{-1}$ and $\sigma_{\text{expt}} = 6 \times 10^{-63}$ cm$^4$ s photon$^{-1}$ at 840 nm$^{459}$). A comparison of the simulated off-resonance spectrum with the experimental SEHRS spectrum obtained at 1050 nm (shown in Appendix D) yields good agreement with respect to both band positions and intensities. The observed differences are likely due to the neglect of surface orientation$^{19}$ and resonance effects in the simulations.

Resonance hyper-Raman scattering can be characterized in terms of Franck-Condon
Figure 7.3. Frontier orbitals involved in the electronic transitions responsible for the features in the one- and two-photon absorption spectra in Figure 7.1. Normal mode coordinates and frequencies for the vibrations that experience strong resonance enhancement: 772 for $S_1$, 1535 for $S_2$, 1621 for $S_3$. Frequencies given here are from our DFT calculations (scaled by 0.98).

scattering (A-term) and Herzberg-Teller scattering (B-term).\textsuperscript{208} If we assume only A-term scattering, the absolute resonance hyper-Raman cross sections for the strongest band of R6G is $1 \times 10^{-59}$ cm$^4$ s photon$^{-1}$ on resonance with $S_1$, $3 \times 10^{-61}$ cm$^4$ s photon$^{-1}$ on resonance with $S_2$, and $7 \times 10^{-59}$ cm$^4$ s photon$^{-1}$ on resonance with $S_3$. Thus, the resonance enhancement for R6G arising from the A-term is comparable in magnitude to the strong off-resonance hyper-Raman cross section ($6 \times 10^{-60}$ cm$^4$ s
This feature of the scattering occurs because none of the excited states have simultaneously strong one- and two-photon absorption, as observed in the absorption spectra. Calculations of B-term scattering for a molecule the size of R6G is non-trivial and its magnitude is likely to be comparable or smaller than the cross sections obtained for the A-term.

The hyper-Raman spectrum of R6G, therefore, is dominated by a strong off-resonance spectrum for which only a few bands are selectively enhanced by resonance with the different electronic states. This also explains the good agreement between the simulated off-resonance hyper-Raman spectrum compared with the experimental SEHRS spectrum and suggests that the normal approximations made in calculating resonance hyper-Raman scattering are not applicable to the case of R6G. This is in sharp contrast to the resonance Raman spectrum of R6G, which is strongly enhanced for excitations into the $S_1$ band. The fact that the hyper-Raman spectrum is not strongly dominated by A-term resonance enhancements also explains why it appears very different from the corresponding SERS spectrum, resolving a long standing question as to the origin of the difference in the SERS and SEHRS spectra of R6G.

Herein, we have demonstrated the ability of SEHRS to probe, with high sensitivity, a molecular electronic excited state in the R6G molecule which is not accessible via one-photon excitation. Direct comparison with ab initio simulations of the one- and two-photon properties of R6G enabled a detailed understanding of the relevant electronic excited states. We believe that the complementary nature of the hyper-Raman selection rules, when combined with the large surface enhancement factors provided by plasmonic nanostructures, yields a general method to explore the potential energy landscape of “dark” electronic states.

7.1 Experimental Section

Citrate reduced Ag colloids were treated with R6G and aggregated with NaCl ($\sim10$ nm). The SEHRS measurements were carried out on an inverted microscope using a $20\times$ objective (NA=0.5). A mode-locked Ti:Sapphire (2 ps, 80 MHz) was used as the excitation source. The hyper-Raman scattered light, after passing through an appropriate filter, was dispersed in a grating spectrometer and detected using a CCD camera. All spectra are reported without baseline or background corrections. Typical laser powers were $\sim5$ mW ($\sim63$ pJ per pulse) at the sample. To check for the influence of R6G dimers, we recorded SEHRS spectra with varying concentrations of R6G (between $10^{-5}$ and
10^{-10}M). No changes in the spectral features were observed (see Appendix D). We have further checked that the spectra do not change as a function of laser power by recording spectra with excitation energies between 500 \( \mu \)W and 10 mW at the sample.
Chapter 8

Probing Two-Photon Properties of Molecules: Large Non-Condon Effects Dominate the Resonance Hyper-Raman Scattering of Rhodamine 6G


Abstract

Experimentally measured resonance hyper-Raman (RHR) spectra spanning the $S_1 \leftrightarrow S_0$, $S_2 \leftrightarrow S_0$, and $S_3 \leftrightarrow S_0$ transitions in rhodamine 6G (R6G) have been recorded. These spectra are compared to the results of first-principles calculations of the RHR intensity that include both Franck-Condon (A-term) and non-Condon (B-term) scattering effects. Good agreement between the experimental and theoretical results is observed, demonstrating that first-principles calculations of hyper-Raman intensities are now possible for large molecules such as R6G. Such agreement indicates that RHR spectroscopy will now be a routine aid for probing multiphoton processes. This work further shows that optimization of molecular properties to enhance either A- or B-term scattering might yield molecules with significantly enhanced two-photon properties.
There is significant interest in utilizing multiphoton processes for applications in all-optical switching, energy-up conversion, and biological imaging.\textsuperscript{85,175,460,461} For example, two-photon transitions can be used in optical-power-limiting materials, photodynamic therapy, optical data storage, two-photon fluorescence microscopy, and two-photon photopolymerization for three-dimensional lithographic microfabrication.\textsuperscript{85,175,461–464} Two-photon techniques also provide a method to probe dark electronic states, i.e., those that are either forbidden or only weakly allowed via one-photon excitation.\textsuperscript{29}

Hyper-Raman scattering\textsuperscript{2} is a type of nonlinear light scattering in which a photon at $\omega = 2\omega_0 - \omega_v$ is incoherently scattered, where $\omega_0$ is the laser frequency and $\omega_v$ is a vibrational frequency characteristic of the material. Resonance hyper-Raman (RHR) scattering provides detailed information about the geometry of two-photon-accessible excited states. For weakly allowed one- or two-photon transitions, RHR scattering provides additional information about non-Condon effects, i.e., the nuclear dependence of the one- or two-photon transition moments. The framework provided by the vibronic theory of RHR scattering\textsuperscript{208} interprets the observed scattering intensities in terms of vibronic coupling terms, Franck-Condon factors, and one- and two-photon dipole moments and their nuclear dependence. This rich set of information, however, is not easily interpreted because of the complex interplay of the various excited states and their topology.

In this communication, we report a detailed comparison of experimentally measured and theoretically calculated RHR intensities spanning the $S_1 \leftarrow S_0$, $S_2 \leftarrow S_0$, and $S_3 \leftarrow S_0$ transitions in rhodamine 6G (R6G). This comparison has allowed us to identify and quantify the various contributions to the RHR intensities and demonstrates that reliable calculations of RHR spectra including both Franck-Condon and non-Condon effects are now possible for large molecules such as R6G. Furthermore, we have found that the hyper-Raman scattering of R6G is dominated by non-Condon effects and that interference between the two lowest electronic states plays an essential role, even though they are separated by more than 100 nm (0.4 eV).

RHR and surface-enhanced hyper-Raman scattering (SEHRS)\textsuperscript{27,285,286,465} spectra were recorded for excitation wavelengths spanning the two-photon absorption spectrum of R6G. For some of the wavelengths in this region, the large two-photon fluorescence of R6G hinders the collection of RHR spectra. The fluorescence quenching provided by Ag nanoparticles, however, removes this limitation. The concentration of R6G was $10^{-7} \text{ M}$ for the SEHRS studies and $10^{-3} \text{ M}$ for the aqueous-solution-phase RHR measurements. The laser bandwidth was narrowed in comparison to our previous studies\textsuperscript{29} by increasing the pulse length to 6 ps.
Figure 8.1 displays the RHR (Figure 8.1a) and SEHRS spectra (Figure 8.1b) of R6G at $\lambda = 825$ nm. While there are minor differences between the RHR and SEHRS spectra, the good agreement suggests that surface effects are a minor perturbation on the spectra. Figure 8.1 also compares the experimental spectra with first-principles simulations using a time-dependent formalism for describing the RHR scattering. The molecular properties needed for simulating the hyper-Raman scattering were obtained using time-dependent density functional theory (TDDFT) at the B3LYP/6-311G* level. Details of the simulations are provided in Appendix E. Our simulations included the three lowest excited states ($S_1$, $S_2$, and $S_3$) and explored Franck-Condon (A-term) and non-Condon (B-term) scattering effects.

Figure 8.1. Comparison of experimentally measured and theoretically calculated RHR spectra of R6G at $\lambda = 825$ nm. (a) RHR spectrum of $10^{-3}$ M R6G in water. (b) SEHRS spectrum of R6G on aggregated silver colloids. (c) TDDFT calculation of the RHR spectrum including both Franck-Condon (A-term) and non-Condon (B-term) scattering. (d) Spectrum calculated including only A-term scattering. The spectra were measured and calculated on resonance with the two-photon $S_2 \leftarrow S_0$ transition.

Good agreement between theory and experiment was obtained when both A- and B-term scattering was included (Figure 8.1a-c). The spectrum calculated using only Franck-Condon effects (Figure 8.1d) did not agree with experiment. A further comparison of the experimental and theoretical spectra for wavelengths spanning the $S_1$, $S_2$, and $S_3$
transitions is displayed in Figure 8.2. To the best of our knowledge, this represents the first first-principles calculation of RHR intensities that includes non-Condon effects for a molecule as large as R6G.

**Figure 8.2.** Comparison of (top) experimentally measured and (bottom) theoretically calculated hyper-Raman spectra of R6G for excitation wavelengths between 750 and 1050 nm.

We now interpret these effects with reference to the one- and two-photon absorption spectrum of R6G shown in Figure 8.3. In a previous study, we found that the dominant 1535 cm$^{-1}$ band is correlated with the S$_2$ ← S$_0$ transition. The S$_2$ ← S$_0$ transition is two-photon-allowed, but only weakly one-photon-allowed; therefore, the non-Condon
effects arise from the nuclear dependence of the transition dipole moment (the $B_1$ term). In contrast, the $S_1 \leftarrow S_0$ transition is strongly one-photon-allowed but only weakly two-photon-allowed; therefore, on resonance with $S_1$, the non-Condon effects arise from the nuclear dependence of the two-photon transition moments (the $B_2$ term). Figure 8.4 compares the $B_2$ and $B_1$ terms for the two states and displays the normal mode associated with the strongest vibrational band (1535 cm$^{-1}$) observed on resonance with $S_2$. From these data, we must conclude that the hyper-Raman spectrum of R6G is characterized by significant non-Condon effects for both the $S_1$ and $S_2$ states.

![Figure 8.3.](image)

Figure 8.3. Comparison of the experimentally measured one-photon (blue) and two-photon (black; Ref. 458) absorption spectra of R6G. The ratio of the 1535 and 1189 cm$^{-1}$ peaks (x) is reproduced from Ref. 29.

Non-Condon scattering is typically weak because either the two-photon or one-photon electronic transition is forbidden (or nearly so). Our simulations show, however, that R6G has a large differential hyper-Raman cross section of $7.6 \times 10^{-58}$ cm$^4$ s photon$^{-1}$ sr$^{-1}$ on resonance with the $S_2$ state. At this wavelength, the contribution from the $B$ term is 300 times stronger than the contribution from the $A$ term. For comparison, the hyper-Raman differential cross section of p-nitroaniline (PNA), a prototypical push-pull molecule with a significant hyperpolarizability, is only $4.1 \times 10^{-58}$ cm$^4$ s photon$^{-1}$ sr$^{-1}$ on resonance with a state that is both one- and two-photon-allowed. This suggests that further optimization of the molecular properties to enhance either $A$- or $B$-term scattering could yield molecules with significantly larger hyper-Raman cross sections.
Figure 8.4. Non-Condon effects in R6G. The hyper-Raman scattering resonant with the $S_1$ state is dominated by $B_2$ scattering, where the non-Condon effects arise from the nuclear dependence of the two-photon transition moment. For the $S_2$ state, the hyper-Raman scattering is dominated by $B_1$ scattering, where the non-Condon effects arise from the one-photon transition moment. Depicted for each electronic state are the normal mode of the $1535 \text{ cm}^{-1}$ vibration and the corresponding one- and two-photon transition moments.

In resonance Raman scattering, it is well-known that interference effects in the spectrum may arise when multiple excited states contribute to the scattering process. This typically requires spectral overlap between the excited states, as the Franck-Condon scattering intensity falls off rapidly with detuning from resonance. This is not the case, however, for B-term scattering, and our calculations showed significant interference between the two lowest excited states in the RHR spectra even though they are separated by more than 100 nm. On resonance with $S_2$, we found that the constructive interference between the $S_2$ and $S_1$ states amounts to roughly 34% the intensity while the contributions from only $S_2$ or $S_1$ contribute 53 and 13%, respectively. While the interference is constructive when resonant with $S_2$, we found it to be destructive when resonant with $S_1$.

The interference is caused by a combination of the detuning from resonance and the relative orientations of the one- and two-photon transition moments and their derivatives on the two excited states. The interference from the detuning was found to cause
constructive interference at $S_1$ and destructive interference at $S_2$ (see the SI). For the $S_2$ state, we found that the two-photon transition moment ($S_{20}$) and the nuclear dependence of the one-photon transition moment ($d\mu_{20}/dQ$) are almost antiparallel. However, for the $S_1$ state, the one-photon transition moment ($\mu_{10}$) and the nuclear dependence of the two-photon transition moment ($dS_{10}/dQ$) are parallel. This leads to a change in the sign of the interference. Thus, the observed interference is a result of the combined effect of the interference from detuning and the sign arising from the transition moments.

This work has demonstrated that the complex interplay of electronic excited states encountered in RHR scattering is now accessible using first-principles theory for large molecules such as R6G. This agreement was achieved only after the inclusion of non-Condon terms in the calculations, which yields important insights into the two-photon properties of the molecular chromophore. Furthermore, this work suggests that non-Condon terms and interference effects are more important in determining two-photon properties than previously expected. Future studies utilizing RHR and SEHRS will elucidate the complex interplay of electronic excited states encountered in multiphoton processes such as all-optical switching, energy up-conversion, and biological imaging.
Surface-Enhanced Hyper-Raman Scattering Elucidates the Two-Photon Absorption Spectrum of Rhodamine 6G


Abstract

The surface-enhanced hyper-Raman (SEHRS) spectra of Rhodamine 6G (R6G) are measured for two different excitation energies: ~25000 cm⁻¹ (~810 nm) and ~19000 cm⁻¹ (1030 nm). The collected spectra are compared to time-dependent density functional theory simulations of the resonance hyper-Raman spectra for the same excitation energies. The analysis of molecular orbital changes in these nonlinear transitions elucidates the mechanism of vibronic enhancement. This analysis is used to elucidate features in the two-photon absorption spectra of R6G.
9.1 Introduction

The past decade has seen an exponential increase in the exploration and utilization of multiphoton processes. Two-photon transitions, for example, play essential roles in energy up-conversion, all-optical switching, optical data storage, 3D lithography, and biological imaging. The recent availability of turn-key mode-locked lasers further promises intense future interest in nonlinear spectroscopy. The use of two-photon excited fluorescence, for example, has become routine in microscopy imaging studies, yet very little is known about the two-photon properties of even routine nonlinear chromophores, such as Rhodamine 6G (R6G).

Often, in engineering molecules suitable for two-photon fluorescence, the two-photon absorption (TPA) spectrum is used as an indicator of the relative strength of the two-photon properties of a molecule. Analyzing the TPA spectrum, however, is often difficult, and it is rarely possible to make definitive assignments to the various absorption features by relying only on TPA experiments. The inclusion of theoretical calculations can significantly improve the situation; however, accurate calculations of nonlinear molecular properties remain a formidable challenge. Given the lack of discrete information in the two-photon absorption spectra and calculations, it is necessary to use other two-photon processes, such as hyper-Raman spectroscopy (HRS), to aid in the interpretation of the spectra.

Hyper-Raman scattering is a type of nonlinear spontaneous light scattering, which gives rise to frequencies of $2\omega_E \pm \omega_v$, where $\omega_E$ is the incident frequency and $\omega_v$ is a molecular vibration frequency. The hyper-Raman effect was first reported in 1965 by Terhune, Savage, and Maker, and recent progress in the application of hyper-Raman spectroscopy was recently reviewed by Kelley. Although multiphoton processes afford advantages such as higher selectivity, decreased risk of photodamage to the sample, and higher penetration depth, the detected intensities of the processes are significantly lower. For the same laser intensity and nonresonant conditions, it has been estimated that hyper-Raman scattering intensities are 5-7 orders of magnitude weaker than Raman scattering intensities. For many molecules it is, therefore, beneficial to make use of surface and resonance enhancements to detect hyper-Raman scattering.

In previous works, we utilized both resonance and surface enhancements to show non-Condon scattering can dominate a resonant hyper-Raman (RHR) spectrum, and this information can be used to assign features in the two-photon absorption spectrum of R6G. After reviewing prior RHR studies of R6G and the theoretical framework for
RHR calculations, we make a detailed comparison between theoretical simulations and experimental measurements of RHR spectra of R6G. This combined approach provides an interpretation of the seemingly contradictory SERS and SEHRS spectra of R6G. In the process, the mechanism of the one- and two-photon electronic transitions in R6G around 19000 wavenumbers emerges, thus demonstrating the power of resonance hyper-Raman studies to elucidate the features in two-photon absorption spectra.

9.1.1 Nonlinear Spectroscopy of R6G

Rhodamine, a xanthene derivative, is one of the most popular molecules to modify as a two-photon dye. Rhodamine dyes or derivatives have recently been used as two-photon fluorescence probes for mercury ions in live cells, as multiphoton probes for exploring diffusion in vivo skin samples, and as benchmark molecules in two-photon excitation systems. The first SEHRS of R6G, reported in 1982 by Baranov and Bobovich, dates from the earliest days of surface-enhanced vibrational spectroscopy. Their pioneering study compared SEHRS and SERS of R6G at excitation wavelengths of 1064 and 532 nm, respectively, and found dramatic differences between the two. Figure 9.1 displays SEHRS spectra at 1028 nm and SERS spectra at 514 nm for R6G, illustrating these differences. Even though both spectra are measured at equivalent scattered energies, the two spectra share very few common peaks and the peak intensities are drastically different. Even 30 years after this observation, the origin of these differences has not been satisfactorily explained, despite numerous studies of the two-photon properties of R6G.

In Figure 9.2, the one- and two-photon absorption spectra of R6G between 18000 and 27000 wavenumbers are presented. A peak is observed at 19000 wavenumbers in both the one- and two-photon absorption spectra. This energy corresponds to the electronic transition from the ground state to the first excited singlet state ($S_1$). The existence of both a one- and two-photon absorption suggests that the $S_1$ transition is both one- and two-photon allowed, and therefore the $S_1 \leftarrow S_0$ electronic transition is not governed by parity of the states involved. A lack of symmetry elements for $S_1$ and $S_0$ implies that the resonance-enhanced SERS and SEHRS spectra should be identical; however, this is clearly not supported by the experimental RHR spectra. Initial theories suggested that the spectral differences resulted from a local symmetry breaking in the molecule: the molecule becomes distorted on the surface of the metal or by anions in solution, and this allows transitions of the molecule which would be otherwise forbidden. The simple picture of symmetry “allowed” or “forbidden” transitions, however, does not sufficiently explain
Figure 9.1. Comparison of SERS (top, $P = 300 \mu W$, $t_{acq} = 5$ s) and SEHRS (bottom, $P = 6$ mW, $t_{acq} = 120$ s) of R6G ($10^{-6}$ M) on aggregated Ag colloids taken at excitations of 514 and 1028 nm, respectively.

the nonlinear scattering spectrum. In particular, the $S_2$ state at 25000 wavenumbers appears to be two-photon-allowed and one-photon-forbidden, a contradiction that should not exist if the molecule has no symmetry. In fact, R6G is a relatively weak two-photon absorber at 19000 wavenumbers compared to other nonlinear chromophores in the same region.\cite{458} Understanding the mechanism of the two-photon accessible electronic transitions in such a complex molecule is almost impossible if one utilizes only two-photon fluorescence or hyper-Raman spectroscopy; however, understanding can be achieved by examining both spectroscopies.

In the past, our group utilized both theoretical simulations and hyper-Raman experiments to show that RHR calculations can contribute greatly to understanding the transitions between electronic states which are probed by nonlinear spectroscopy.\cite{29} Recently, we showed that vibronic coupling enables the one-photon allowed but two-photon forbidden state to contribute significantly to both hyper-Raman scattering and two-photon fluorescence in this region.\cite{404} However, the physical mechanism which facilitates the vibrational coupling in RHR remains unexplored and constitutes the subject of this work. Understanding of such mechanisms should also shed light on the nonlinear properties of the molecule.
Figure 9.2. One-photon absorbance and two-photon excitation spectra\textsuperscript{458} are shown for R6G. Also indicated are two transitions within the molecule: $S_1$, which is one and two-photon accessible, and $S_2$, which is only two-photon accessible.

9.1.2 Resonance Hyper-Raman Calculations

Simulations of RHR scattering require calculation of the resonant first hyperpolarizability, which is a formidable task, and one which is more computationally demanding than the calculations of the resonant polarizability for resonance Raman (RR) scattering. This challenge can be reduced by employing the vibronic theory of RHR scattering developed by Ziegler et al.\textsuperscript{208} in combination with the time-dependent wavepacket approach.\textsuperscript{131–133,358,401} The vibronic theory for RHR involves writing the hyperpolarizability of the molecule as a sum of terms: $\beta = A + B + C + \ldots$, where $A$ is the Franck-Condon (FC) term, $B$ is the first Herzberg-Teller (HT) term, $C$ is the second HT term, etc. Several studies have demonstrated the utility of the vibronic theory for analyzing experimental observations and the feasibility of RHR simulations for predicting spectra in comparison to available experimental data.\textsuperscript{1,209,211,213,215} Furthermore, it has been found that RHR scattering is sensitive to non-Condon effects, possibly more so than resonance Raman scattering.\textsuperscript{212,404} This feature is related to the selection rules of hyper-Raman scattering, which are complementary to Raman and IR, allowing forbidden IR- and Raman-active vibrations to be hyper-Raman-active.

Figure 9.3 demonstrates three important cases to consider in the discussion of reso-
Figure 9.3. Terms included in the calculation of resonance hyper-Raman spectra. In both one- and two-photon allowed transition $S_k \leftarrow S_0$, both the two-photon transition dipole ($S^{k0}$) and one-photon transition dipole ($\mu^{0k}$) are nonzero. However, in cases where the one-photon transition is forbidden/weakly allowed ($\mu^{0k}$ is zero or nearly zero) or where the two-photon transition is forbidden/weakly allowed (when $S^{k0}$ is zero or nearly zero), then vibronic coupling may produce nonzero terms ($d\mu^{0k}/dQ$ and $dS^{k0}/dQ$, respectively) that contribute to the resonant hyper-Raman calculation at these wavelengths.

The following discussion assumes an electronic transition $S_k \leftarrow S_0$, where $S_0$ is the ground electronic state and $S_k$ refers to the $k$th singlet excited electronic state. In A-term scattering the transition is allowed via both one-photon and two-photon absorption. Therefore, both the two-photon transition dipole moment ($S^{k0}$) and the one-photon transition dipole moment ($\mu^{0k}$) have nonzero values. In this case, the resonance hyper-Raman scattering is calculated using the FC overlap between the initial and final vibrational states of the molecule, and just as in resonance Raman, these overlap terms are called “A-term” contributions to the resonance hyper-Raman spectrum or A-term scattering, for short. The notation $S^{k0}$ refers to the amplitude of the two-photon excited transition $S_k \leftarrow S_0$ and should not be confused with the labeling of the singlet electronic states (e.g., $S_0$, $S_1$, ..., $S_k$, ...).

In the other two cases, the transition is allowed in either the two-photon absorption or the one-photon absorption, but is forbidden or weakly allowed, in the other absorption. For these, at least one of the transition dipole moments ($\mu^{0k}$ or $S^{k0}$) is zero or very small, which leads to weaker resonance hyper-Raman intensity via A-term scattering for that transition. In the well-known Condon approximation, it is usually assumed that $\mu^{0k}$ or $S^{k0}$ does not depend strongly on the nuclear coordinates ($Q$). Molecular
vibrations, however, can couple together nearby electronic states via the derivative of the one-photon transition dipole moment \((d\mu_{0k}/dQ)\) or the derivative of the two-photon transition dipole moment \((dS^{k0}/dQ)\). These terms provide an additional mechanism for the enhancement of the resonance hyper-Raman cross section. It is important to realize that although the two-photon transition dipole moments are calculated directly using quadratic response theory this formally contains a sum over all intermediate states. This is valid as long as the incident light is not resonant with any intermediate states. The direct calculation of the two-photon transition moments is computationally advantageous since it avoids the explicit sum; however, it also means that individual contributions from intermediate states cannot be identified. The coupling terms can be calculated by the HT approximation, and as in resonance Raman, these terms are referred to as “B-term” contributions. In RHR they are divided into two types: \(B_1\), where the two-photon transition is allowed, and the one-photon transition is vibronically coupled, and \(B_2\), where the one-photon transition is allowed, and the two-photon transition is vibronically coupled.

9.2 Experimental Methods

9.2.1 Experimental Setup
The experimental setup, similar to ones used in previous experiments,\(^{29}\) is shown in Figure 9.4. In detail, the pump laser used is capable of 15 W of continuous wave 532 nm radiation (Millenia Pro, Spectra-Physics). The oscillator is a Ti: sapphire (Tsunami, Spectra-Physics), which is equipped with broadband optics to allow the 5 ps pulse to be tuned to a selected wavelength between 690 and 1080 nm. The fundamental from the Ti:sapphire is split, using a combination half-wave plate (Thor Laboratories) and Glan polarizer (Thor Laboratories). The horizontal polarization is used to irradiate the sample, while the vertical polarization is frequency doubled via a second harmonic generator (SHG, Model 3890, Spectra-Physics). The excitation beam is directed into the back port of an inverted microscope (Ti-U, Nikon), through a 20×, NA = 0.5, objective (Nikon) which is focused on the sample. A 690 nm short-pass filter (Semrock) is used to reduce the intensity of the laser line before it is reflected to the spectrometer (Acton, Princeton Instruments). The detector is a back-illuminated CCD camera (Spec-10, Princeton Instruments) which is operated using either the commercially available Winspec (Princeton Instruments) or a home-built LabView program.
9.2.2 SERS/SEHRS Sample Preparation and Use

Collodial silver nanoparticles were synthesized using the Lee and Meisel method.\textsuperscript{480} Specifically, 200 mL of $2 \times 10^{-3}$ M silver nitrate (Sigma-Aldrich) is brought to a boil. Then, 50 mg of sodium citrate monohydrate (Sigma-Aldrich) dissolved in a small amount (5 mL) of water is added. After 30 min, the volume of the solution is less than 150 mL and has turned a light green color. The solution is then removed from the heat source and allowed to cool. This produces mostly spherical nanoparticles around 30 nm in diameter. 30 mL of this solution is then mixed with 1 mL of $10^{-5}$ M R6G (Acros). The nanoparticles almost immediately begin to crash out, as the solution turns dark. Sodium bromide (Sigma-Aldrich) is then added to this sample to produce a final concentration of $10^{-2}$ M bromide ions. The colloids are allowed to aggregate into clusters which average approximately 1-2 μm in size. For hyper-Raman measurements, 6 mW of laser power is focused on one of these aggregates. Rastering the sample prevents the ablation of the nanoparticle aggregates, due to the high laser power used. Since the hyper-Rayleigh scattering from the sample is approximately the same order of magnitude as the hyper-Raman, no filter was needed to limit its intensity. In Raman measurements, less than 1 mW of laser power is focused on an aggregate. Since the Rayleigh line is much more intense than the Raman lines, a filter must be used to limit its intensity.
9.2.3 Theoretical Methods

Geometry optimization and normal mode calculations were performed in NWChem using B3LYP/6-311G*. These calculations yield both vibrations of the molecule and IR intensities. For all simulations, the normal modes were scaled by a constant factor of 0.98. Dimensionless displacements (\( \Delta \)), transition dipole moment derivatives (\( d\mu/dQ \)), and two-photon transition moment derivatives (\( dS/dQ \)) were evaluated using finite differentiation of properties calculated with the linear and quadratic response modules in Dalton 2.0 with B3LYP/6-311G*. Empirical solvent shifts on the order of 0.20-0.56 eV were applied to each excitation to facilitate comparison with experimental data. A detailed description of the simulation procedure can be found in previous publications. However, a simplified physical description of the calculated scattering “terms” is included here.

The simulations of vibronic coupling are based on the time-dependent wavepacket approach pioneered by Heller et al. Focusing on the expression for RHR (e.g., \( \Gamma_{RHR} \propto |\beta|^2 \)), the sum-over-states expression for the molecular first hyperpolarizability is written using the Born-Oppenheimer approximation and expressed in the time domain by using a Fourier transform. The result is then simplified by employing the time-propagator for the kth excited state and closure over the corresponding intermediate vibrational states. Vibrational overlaps in this method are evaluated using the independent-mode, displaced harmonic oscillator model. The one-photon transition dipole moment (\( \mu^{0k} \)) and two-photon transition dipole moment (\( S^{k0} \)) can then be expanded in a series with respect to the normal modes:

\[
\mu^{0k} = \left( \mu^{0k} \right)^{eq} + \sum_a \frac{\partial \mu^{0k}}{\partial Q_a} Q_a + \ldots \tag{9.1}
\]

and

\[
\mu^{k0} = \left( S^{k0} \right)^{eq} + \sum_a \frac{\partial S^{k0}}{\partial Q_a} Q_a + \ldots \tag{9.2}
\]

where the superscript “eq” refers to a quantity evaluated at the ground-state equilibrium geometry. On the basis of the series expansions, we can write the first hyperpolarizability as a series: \( \beta = A + B_1 + B_2 + \ldots \), where the \( A \) term is the FC term and \( B_1/B_2 \) are the first HT terms. The final expressions are for \( A, B_1, \) and \( B_2 \) are written as a product between the transition dipole moments connecting the ground state to the kth excited state and a line shape function containing vibronic information, i.e.
\[ A = \sum_k \left( \mu_0^k \right)^{eq} \left( S^{k0} \right)^{eq} L \left[ E^{k0}, \Delta_v^{k0}, \omega_v, \omega_E, g_k(t) \right] \quad (9.3) \]

\[ B_1 = \sum_k \frac{\partial \mu_0^k}{\partial Q_a} \left( S^{k0} \right)^{eq} M_a \left[ E^{k0}, \Delta_v^{k0}, \omega_v, \omega_E, g_k(t) \right] \quad (9.4) \]

\[ B_2 = \sum_k \left( \mu_0^k \right)^{eq} \frac{\partial S^{k0}}{\partial Q_a} N_a \left[ E^{k0}, \Delta_v^{k0}, \omega_v, \omega_E, g_k(t) \right] \quad (9.5) \]

where \( E^{k0} \) is the electronic excitation energy, \( \Delta_v^{k0} \) is the vibronic coupling constant for the normal mode with frequency \( \omega_v \), \( \omega_E \) is the incident frequency, and \( g_k(t) \) is a function defining the homogeneous and inhomogeneous broadening for the kth excited state. Specific forms of the line shape functions \( L \), \( M_a \), and \( N_b \) can be found in prior publications.\(^{435,481}\)

The vibronic model described above relies on the harmonic oscillator model to evaluate overlaps between vibrational states. This means that normal modes sensitive to anharmonic effects are poorly described by the present model. Also, Duschinski rotations are neglected; i.e., ground and excited states are assumed to have identical vibrational frequencies. The determination of the vibronic coupling constants is sensitive to the description of the electronic structure in the ground and excited states in addition to the molecular geometry. Therefore, the choice of the exchange-correlation functional from density functional theory is paramount to describing the potential energy surface, excitation energies, and transition moments accurately. Furthermore, it is required that the electronic states are well separated to ensure that the numerical evaluation of the derivatives required to obtain vibronic coupling constants and the B1 and B2 terms remain valid. For R6G, the \( S_1 \) and \( S_2 \) states are separated by \( \sim 0.35 \) eV for the functional chosen here, allowing for the derivatives to be evaluated accurately.

### 9.3 Results

#### 9.3.1 Vibronic Coupling in Resonance Hyper-Raman Spectra

A comparison of the experimentally measured and theoretically simulated hyper-Raman spectrum on resonance with the \( S_1 \leftarrow S_0 \) transition (19000 cm\(^{-1}\)) is displayed in Figure 9.5. We previously showed that inclusion of the B-type scattering terms is required to achieve agreement between experiment and theory in this region.\(^{404}\) Here we expand that observation to explore the relative contributions of the \( A \), \( B_1 \), and \( B_2 \) terms. At this
energy (19000 cm\(^{-1}\), 1030 nm) a small contribution from A-term scattering is visible; however, the majority of the spectrum results from \(B_2\) term. While \(S_1 \leftarrow S_0\) is a strong one-photon transition, it has a small two-photon dipole transition moment (\(S^{10}\)); therefore, vibrations which modify the transition moment (\(dS^{10}/dQ\)) are featured prominently in the resonance hyper-Raman spectrum. Further, Figure 9.5 illustrates that the spectrum at this excitation energy is almost entirely dominated by the \(B_2\) term.

![Figure 9.5](image)

**Figure 9.5.** Comparison of experimental and calculated resonance hyper-Raman spectra at an excitation energy of \(\sim 19000\) cm\(^{-1}\) (1030 nm). The contributions to the simulated spectra from the individual resonance hyper-Raman terms are also presented: A term (FC), \(B_1\) term (HT), and \(B_2\) term (HT). At this energy the RHR scattering is dominated by \(B_2\) activity.

It is interesting to contrast the results in Figure 9.5 (\(S_1 \leftarrow S_0\)) with spectra obtained on resonance with the \(S_2 \leftarrow S_0\) (24000 cm\(^{-1}\), 820 nm), which is given in Figure 9.6. No contribution from the A-term is evident, as the \(S_2 \leftarrow S_0\) transition is only two-photon allowed (see Figure 9.2). Instead, the spectrum is dominated by \(B_1\)-term scattering. The one-photon transition dipole moment (\(\mu^{02}\)) is close to zero, and the vibrationally coupled dipole moment (\(d\mu^{02}/dQ\)) is nonzero. Interestingly, a significant portion of the hyper-Raman spectrum on resonance with \(S_2 \leftarrow S_0\) can be attributed to \(B_2\) scattering, even though the transition is two-photon-allowed and one would expect the two-photon
transition dipole moment \( S_{20} \) to be greater than its vibrationally coupled derivative \( dS_{20}/dQ \). Therefore, we must conclude that scattering at this wavelength involves significant interference between the \( S_2 \leftarrow S_0 \) and the \( S_1 \leftarrow S_0 \) transitions, even though their absorption bands do not overlap. Further theoretical and experiments investigations may reveal this to be a more common feature of RHR scattering than previously anticipated.

**Figure 9.6.** Comparison of experimental and calculated resonance hyper-Raman spectra at an excitation energy of \( \sim 24,000 \text{ cm}^{-1} \) (825 nm). The contributions to the simulated spectra from the individual resonance hyper-Raman terms are also presented: A term (FC), \( B_1 \) term (HT), and \( B_2 \) term (HT). At this energy the RHR scattering is dominated by \( B_1 \) activity. For \( S_1 \leftarrow S_0 \) and \( S_2 \leftarrow S_0 \) transitions in R6G, the magnitude of the \( B \)-term contributions to RHR scattering is unusual based on comparisons to other molecules that are A-term scatterers in RR and RHR. In RR scattering, \( B \) terms (governed by \( \mu_k^0 \) and \( d\mu_k^0/dQ \)) are expected to have low intensity because the transition must be weakly allowed. RHR scattering, in contrast, has \( B \) terms governed by the two mechanisms described in Figure 9.3 (i.e., the transition is one-photon forbidden/two-photon allowed for \( B_1 \) term scattering or one-photon allowed/two-photon forbidden for \( B_2 \) term scattering).
The structure of R6G possesses nearly $C_s$ symmetry, with a mirror plane containing the carboxyphenyl ring (see Figure 9.7). This causes the one- and two-photon transitions to be mutually exclusive because R6G is almost centrosymmetric. Therefore, the intense B-term scattering on resonance with the $S_1 ← S_0$ and $S_2 ← S_0$ transition is justified since the one- and two-photon transitions cannot simultaneously be strong.

### 9.3.2 One- and Two-Photon Absorption Spectra: Theory and Experiment Comparison

Figure 9.7 displays the transitions and associated molecular orbitals for R6G in the 18000-27000 cm$^{-1}$ energy range (center panel). Here we designate the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) ($S_1 ← S_0$) and HOMO-1 to LUMO ($S_2 ← S_0$) transitions as S1 and S2. Comparisons of the experimental one-photon absorption and two-photon absorption$^{458}$ with simulated spectra are shown in the left and right panels, respectively. The simulated results incorporate the empirical shifts described in the Theoretical Methods, and spectra obtained with and without vibronic effects are presented. When vibronic effects are included, we further compare spectra obtained with only FC couplings (green line) and those obtained with a sum of FC and HT terms (red line).

![Figure 9.7](image)

**Figure 9.7.** Comparison of one-photon absorption spectra (left) to the two-photon absorption spectra$^{458}$ (right) of R6G and the electronic transitions excited in the molecular orbitals (middle). The absorption spectra are broken into three parts: (a) the experimental absorption spectrum, (b) the theory simulated spectrum without vibronic coupling (Lorentzian broadened with 0.10 eV full width at half-maximum), and (c) the theory simulated absorption spectra, calculated with FC vibronic coupling (green) and with FC and HT vibronic coupling (red) spectra.
The molecular orbitals (Figure 9.7) illustrate that R6G has local symmetry associated with the \( S_1 \) and \( S_2 \) electronic states due to the localization of the orbitals in the xanthene ring. Assuming \( C_s \) symmetry, the HOMO is antisymmetric in the \( v \) plane, while the LUMO and HOMO-1 are symmetric in the same plane. An excitation from HOMO to LUMO must be accompanied by a change in symmetry and therefore will be one-photon allowed but not two-photon allowed. This transition \( (S_1 \leftarrow S_0) \) occurs at 19000 cm\(^{-1}\) (530 nm via one-photon transition). The transition from HOMO-1 to LUMO is not accompanied by a change in symmetry and therefore is expected to be two-photon-allowed but not one-photon-allowed. This transition, which is assigned to \( S_2 \), occurs at 24 000 cm\(^{-1}\) (405 nm). No other transitions are identified in the 18000-23000 cm\(^{-1}\) region in either experiment or theory.

The one-photon absorption spectra (Figure 9.7, left panel) follow the expectation established by the molecular orbitals: the \( S_1 \leftarrow S_0 \) transition is dominant and the \( S_2 \leftarrow S_0 \) transition is nearly zero. The simulated spectra are in good agreement with experiment and the shoulder that occurs to the red of the main \( S_1 \leftarrow S_0 \) transition (20000 cm\(^{-1}\)) does not appear in the purely electronic transition spectrum. When FC vibronic coupling is included in the absorption simulations, however, the shoulder appears in the spectrum. This shows that there is a nonzero component contribution from the FC term to the one-photon absorption spectrum. This agrees with previous simulations of one-photon absorption for the \( S_1 \leftarrow S_0 \) transition of R6G.\(^{362}\) When HT coupling is included in the one-photon absorption calculations, very little change is observed, since the HT term contribution to the one-photon absorption spectrum is very weak.

The two-photon absorbance spectra (Figure 9.7, right panel) deviate from the spectrum expected based purely on the symmetry of the molecular orbitals. While the \( S_2 \leftarrow S_0 \) transition shows a strong absorption band, as expected, \( S_1 \leftarrow S_0 \) also appears in the experimental and theoretical spectra. The most likely reason for this weakly allowed transition is that, in both HOMO and LUMO, there are portions of the electronic structure that extend into the phenyl ring. These components have a symmetric overlap that makes the \( S_1 \) transition in the two-photon absorption weakly allowed. In the FC vibronic coupling spectra, a shoulder, centered around 26000 cm\(^{-1}\), appears for the \( S_2 \) state, which mimics the shoulder in the experimental spectrum. However, the shoulder that appears in the \( S_1 \) spectrum, centered around 20000 cm\(^{-1}\), only appears when the HT vibronic coupling is included in the simulations. It is evident from this comparison that the full understanding of the two-photon absorption spectrum can only be achieved through use of HT vibronic coupling terms. We have further confidence in this assignment from the
strong B-term contribution to the RHR scattering in this region. Improvement of the intensities of the $S_1$ and $S_2$ peaks may require including a solvent model in the calculations of excited state properties or changing the exchange-correlation functional used.

### 9.3.3 Origin of the Non-Condon Scattering

Using a molecular orbital approach, it is further possible to understand why only select vibrational modes of the R6G molecule experience a strong hyper-Raman enhancement. The diagrams in Figures 9.8 and 9.9 indicate the orbitals involved in the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions, respectively, and additionally illustrate the changes in the orbitals induced by vibration along the 1535 cm$^{-1}$ coordinate. This mode was selected as it shows the greatest intensity in the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ resonance spectra. The difference orbitals are generated by subtraction of the absolute value of the original molecular orbital from the absolute value of the perturbed molecular orbital. The perturbed orbital is calculated after a 1% displacement along the vibrational coordinate. The green areas represent where the orbital increased and the red represent areas where the orbital decreased.

As can be seen for $S_1 \leftarrow S_0$ (Figure 9.8), antisymmetric modes like 1535 cm$^{-1}$ can perturb the ground-state antisymmetrically, thus creating a more symmetric orbital. This perturbed orbital then enables a stronger two-photon transition to the symmetric LUMO orbital. Once excited to the symmetric LUMO, a one-photon transition is allowed down to the antisymmetric HOMO. These theoretical studies provide an interesting physical insight into the method of Herzberg-Teller coupling in the resonance hyper-Raman spectrum. In this transition, one side of the xanthene ring in R6G, acting as an electron-donating group (Figure 9.8, upper right, red), utilizes the $\pi$ backbone of the xanthene structure to transfer electron density to the other side of the xanthene ring, which acts as an electron-accepting group (Figure 9.8, upper right, green). Therefore, the nonlinear optical properties of the molecule become enhanced as indicated by the intense resonance contribution of the mode to the hyper-Raman spectrum. In this manner, R6G behaves much like a push-pull chromophore, a molecule with donating and accepting groups which has enhanced nonlinear optical characteristics. Without the use of resonance hyper-Raman experiments and simulations, the push-pull character of R6G would not be identifiable.

In the $S_2 \leftarrow S_0$ transition (Figure 9.9), the two-photon transition from symmetric HOMO-1 to symmetric LUMO is strongly allowed. In this case, antisymmetric modes like 1535 cm$^{-1}$ can induce antisymmetry into the otherwise symmetric HOMO-1. This
Figure 9.8. Molecular orbitals involved in the $S_1 \leftarrow S_0$ transition. The transition from HOMO (upper left) to LUMO (lower) is symmetry forbidden for a two-photon transition, as it involves a transition from an asymmetric orbital to a symmetric orbital. However, vibronic coupling of the 1535 cm$^{-1}$ vibration to the HOMO yields asymmetric changes (upper right; red indicates a negative change and green a positive change) in the HOMO which allows a two-photon transition to the symmetric LUMO.

allows the one-photon transition from LUMO to the perturbed HOMO-1. The reason that both $S_2$ and $S_1$ appear to have the same resonant modes is that the modes show different activities in each hyper-Raman transition. In $S_1$, the modes are $B_2$-active, while in $S_2$, they are mostly $B_1$-active (though they exhibit some $B_2$ activity as well). Similar to the behavior observed for $S_1 \leftarrow S_0$, R6G behaves as a pushpull chromophore in this instance as well. The push-pull character, however, is utilized in this mode to enhance a single-photon transition instead of a two-photon transition.
Figure 9.9. Molecular orbitals involved in the $S_2 \leftarrow S_0$ transition. The transition from LUMO (lower) to HOMO-1 (upper left) is symmetry forbidden for a one-photon transition, as it involves a transition from a symmetric orbital to a symmetric orbital. However, vibronic coupling to the 1535 cm$^{-1}$ vibration yields asymmetric changes (upper right; red indicates a negative change and green a positive change) in the HOMO-1 which allows a two-photon transition to the symmetric LUMO.

9.4 Conclusion

R6G has served as a benchmark molecule in fields such as surface-enhanced spectroscopy and two-photon imaging. Despite its widespread use, detailed assignments of the two-photon absorption spectrum have been lacking. In this study, we find that the resonance hyper-Raman scattering of R6G demonstrates both Franck-Condon (A-term) and Herzberg-Teller (B-term) coupling, and these features are further carried into the more averaged features of its absorption spectrum. In the examination of vibronic coupling, it is evident that the reason both SERS at 532 nm and SEHRS at 1064 nm spectra of
R6G are resonant is that both experience different types of resonant scattering. Only with examining both A- and B-term scattering calculations, the two-photon properties of this rich molecule can be fully understood.
Part V

Recent research progress: implementation of methods and applications to large molecules
Investigation of Linear and Nonlinear Raman Scattering for Isotopologues of Ru(bpy)$_3^{2+}$


Abstract

Tris(2,2'-bipyridine)ruthenium(II) an important transition metal complex for its robust photochemistry, is studied using simulated resonance Raman scattering (RRS) and resonance hyper-Raman scattering (RHRS) in comparison to measured surface-enhanced Raman scattering (SERS) and surface-enhanced hyper-Raman scattering (SEHRS). Detailed examination of the simulated data shows that many of the observed features in the experiments are captured by the theory. For the metal-to-ligand charge transfer (MLCT) absorption band at 452 nm, it is demonstrated that the shoulder on the absorption band at 425 nm is not a vibronic feature and that the lineshape should be considered as coming from two separate MLCT states. We find that good agreement can be obtained by comparing simulated spectra to the SERS and SEHRS spectra on resonance with the absorption band. However, the simulations do not capture the high sensitivity of relative peak intensities observed during wavelength scanned SERS and SEHRS experiments. This result is interpreted based on discussion of the literature and the approximations made in the vibronic model, where it is concluded that the simulations underestimate interference effects. These results demonstrate the complexity of using theoretical methods for accurately describing the electronic structure of large molecules, and that commonly used exchange-correlation functionals like B3LYP and LC-PBE cannot completely describe all of the
vibronic features in the Raman scattering of Rubpy.
10.1 Introduction

There is a significant interest in understanding the linear and nonlinear optical properties of ruthenium based dyes due to their rich photochemistry and electrochemistry. These dyes have important applications in photocatalysis, luminescence and electrochemiluminescence, and in dye sensitized solar cells for harvesting solar energy. Although the ruthenium dyes typically only have modest two-photon absorbance (TPA) intensities, they have found applications in two-photon 3D thermal imaging and photodynamic therapy.

The prototypical ruthenium dye is the Tris(2,2'-bipyridine)ruthenium(II) (Rubpy) molecule, for which the linear absorption spectrum is characterized by a broad main transition at 452 nm with a unresolved shoulder at 425 nm. These features are assigned to multiple metal-to-ligand charge transfer (MLCT) transitions and their vibronic side bands. It is well established that resonance Raman scattering (RRS) can be used to investigate contributions from different excited states to the absorption spectrum. A RRS study of Rubpy has shown that two distinct MLCT transitions contribute to the absorption band and that significant interference between the two states was predicted by modeling the Raman excitation profiles. This interference depends strongly on the relative energies, the orientation of the transition dipole moments, and excited state geometry of the different excited states and provides insights into the different contributions to the otherwise unresolved absorption spectrum.

Alternatively, if the electronic transitions are both one- and two-photon allowed, resonance hyper-Raman scattering (RHRS) can be used to probe the excited states. In RHRS, the scattering at $2\omega_E - \omega_v$ due to two photons is measured where $\omega_E$ is the frequency of the incident light and $\omega_v$ is the molecular vibrational frequency. Since the RHRS scattering depends both on the one- and two-photon transition moments, it provides complementary information to RRS about the excited state properties. Prior work has demonstrated the usefulness of combined RRS and RHRS to disentangle different excited state contributions to otherwise featureless absorption spectra. A problem with hyper-Raman scattering is that the cross section is significantly lower than that for normal Raman scattering, an estimate indicates that the scattering intensities are about 5 to 7 orders weaker. Thus, it is often essential to take advantage of resonance and/or surface-enhancements for practical use of hyper-Raman scattering.

Recently, we have demonstrated the power of combined wavelength scanned surface-enhanced hyper-Raman scattering (SEHRS) and surface-enhanced Raman scattering (SERS) to provide a comprehensive understanding of the linear and nonlinear optical
properties of the rhodamine 6G (R6G) dye molecule.\textsuperscript{29,404,506} Our work has shown that non-Condon scattering dominates the RHRS of R6G and that significant interference between well separated states occur.\textsuperscript{404} This work also led to a detailed assignment of the important features of the two-photon absorption spectrum of R6G.\textsuperscript{506} Such detailed assignment of the spectroscopic signatures of a molecule the size of R6G was only possible by a combination of first-principles simulations and experiments. However, it remains a formidable challenge to accurately simulate these nonlinear spectra and thus few examples are present in the literature.

In this work, we present a combined experimental and theoretical study of wavelength scanned SEHRS and SERS of Rubpy and its isotopologue Rubpy-d24. While there have been several studies reporting SERS of Rubpy, to the best of our knowledge this is the first time SEHRS is reported for Rubpy and its isotopologue. The theoretical simulations are done using vibronic coupling models based on the time-dependent wavepacket approach.\textsuperscript{435,481} Simulated one-photon absorption (OPA) spectra allow for the characterization of the MLCT state at 452 nm, illustrating that the shoulder on the absorption band at 425 nm is not a vibronic feature. RRS and RHRS spectra are simulated on resonance with the absorption band, yielding good agreement with the SERS and SEHRS data such that a detailed assignment of the spectra is possible. However, we see that the observed wavelength dependence of the SERS and SEHRS spectra for Rubpy and Rubpy-d24 is underestimated by the theory used. Several possible explanations for this discrepancy are explored. It is concluded that the main sources of error are the approximation used in the exchange-correlation energy functional in density functional theory and the vibronic coupling model used for simulating the resonant spectra.

\subsection{10.2 Experimental Methods}

\textbf{Experimental Setup.} The experimental set-up, similar to ones used in previous experiments,\textsuperscript{29} is shown in Figure 10.1. In detail, the pump laser used is capable of 15 W of continuous wave 532 nm radiation (Millenia Pro, Spectra-Physics). The main oscillator is a Ti: sapphire (Tsunami, Spectra-Physics), which is equipped with broadband optics to allow the \(~5\) ps pulse to be tuned to a selected wavelength between 690 and 1080 nm. The fundamental from the Ti:Sapphire is split, using a combination half-wave plate (Thor Labs) and Glan polarizer (Thor Labs). The horizontal polarization used to irradiate the sample, while the vertical polarization is frequency doubled via a second harmonic generator (SHG, Model 3890, Spectra-Physics). The excitation beam is
Figure 10.1. Experimental setup for surface-enhanced and bulk Raman and hyper-Raman experiments. An Nd:YAG pumped Ti:Sapphire output is split using a half-wave plate and Glan-Polarizer (labeled GP on diagram). The vertical polarization is sent to a second harmonic generator (SHG) and the horizontal polarization is converted to vertical before entering the scope (using a periscope, not pictured).

directed into the back port of an inverted microscope (Ti-U, Nikon), through a 20×, NA = 0.5, objective (Nikon) which is focused on the sample. A 690 nm short pass filter (Semrock) is used to reduce the intensity of the laser line before it is reflected to the spectrometer (Acton, Princeton Instruments). The detector is a back-illuminated CCD camera (Spec-10, Princeton Instruments) which is operated using either the commercially available Winspec (Princeton Instruments) or a homebuilt LabView program. A separate OPO (Pico-emerald, APE) was utilized to take the 1550 nm spectrum, with an identical experimental set-up to the one in Figure 10.1. The 785 nm spectra were excited by a diode laser (Innovative Photonics Solutions) which can be inserted into the system.

SERS/SEHRS Sample Preparation and Use. Colloidal silver nanoparticles were synthesized using the Lee and Meisel method. Specifically, 200 mL of $2 \times 10^{-3}$ M silver nitrate (Sigma Aldrich) is brought to a boil. Then, 50 milligrams of sodium citrate monohydrate (Sigma Aldrich) dissolved in a small amount (5 mL) of water is added. After approximately 30 minutes, the volume of the solution is less than 150 mL, and has turned a light green in color. The solution is then removed from the heat source, and allowed to cool. This produces mostly spherical nanoparticles around 30 nm in diameter. 40 mL of this solution is then mixed with either 1 mL of $10^{-6}$ M Rubpy (Acros) or 0.1 mL of $10^{-5}$ M Rubpy-d24. Sodium bromide (Sigma Aldrich) is then added to this sample to produce a final concentration of $10^{-2}$ M bromide ions. Upon addition of the sodium bromide, the nanoparticles almost immediately begin to crash out, as the...
solution turns dark. The colloids are allowed to aggregate into clusters which average
approximately 1-2 microns in size. For hyper-Raman measurements, approximately 6
mW of laser power is focused on one of these aggregates. Rastering the sample prevents
the ablation of the nanoparticle aggregates, due to the high laser power used. Since the
hyper Rayleigh scattering from the sample is approximately the same order of magnitude
as the hyper-Raman, no filter was needed to limit its intensity. In SERS measurements,
less than 1 mW of laser power is focused on an aggregate. Since the Rayleigh line is
much more intense than the Raman lines, a filter must be used to limit its intensity.

10.3 Theory

Detailed descriptions of simulations of the Franck-Condon (FC) term for OPA and
RRS\textsuperscript{132,137,359,405,435} and TPA and RHRS\textsuperscript{211,212,435} have been discussed at length in
previous works and will not be presented here. For clarity, some of the key expressions
are included in this section. The intensity of a one-photon transition is related to the
transition strength ($M_{k0}^2$), which is given in terms of the transition dipole moment ($\mu_{A0}$)
for a transition $S_k \leftarrow S_0$

\[
(M_{k0}^2) = \left[ (\mu_{x0}^0)^{eq} \right]^2 + \left[ (\mu_{y0}^0)^{eq} \right]^2 + \left[ (\mu_{z0}^0)^{eq} \right]^2
\]

(10.1)

Here, the superscript “eq” refers to the quantity being evaluated at the ground state equi-
lbrium position. Analogously, the transition strength ($\delta_{TPA}^{0k}$) for two-photon processes,
assuming linearly polarized photons, is defined

\[
\delta_{TPA}^{0k} = 2\delta_{F}^{0k} + 4\delta_{G}^{0k}
\]

(10.2)

where $\delta_{F}^{0k}$ and $\delta_{G}^{0k}$ involve products of the two-photon transition moments ($S_{\alpha\beta}^{0k}$)

\[
\delta_{F}^{0k} = \frac{1}{30} \sum_{\alpha,\beta} (S_{\alpha\alpha}^{0k})^{eq} (S_{\beta\beta}^{0k})^{eq}
\]

(10.3)

\[
\delta_{G}^{0k} = \frac{1}{30} \sum_{\alpha,\beta} (S_{\alpha\beta}^{0k})^{eq} (S_{\alpha\beta}^{0k})^{eq}
\]

(10.4)

where $\alpha, \beta \in \{x, y, z\}$ and the two-photon transition moment is defined

\[
S_{\alpha\beta}^{k0} = \sum_{l} \left\{ \frac{\mu_{l\beta}^{k0} \mu_{l\gamma}^{00} + \mu_{l\gamma}^{k0} \mu_{l\beta}^{00}}{(E_l - E_0 - \omega)} \right\}
\]

(10.5)
For the absorption type processes OPA and TPA, the vibronic expression using the Born-Oppenheimer (BO) and FC approximations is given by

\[ \sigma_{\text{FC}}(\omega) \propto \sum_k N^{k0} \text{Re} \int_0^\infty \langle I_0 | I_k(t) \rangle e^{i(\epsilon_{I_0} + \omega)t - g_k(t)} dt \] (10.6)

In this expression, \(|I_k(t)\rangle\) corresponds to the time-dependent wavepacket propagating on electronic state \(k\), \(\epsilon_{I_0}\) is the energy of vibrational state \(|I_0\rangle\), \(\omega\) is the incident frequency, and \(g_k(t)\) is a generalized lifetime function for overdamped Brownian oscillator model.\(^91,406,407\) \(N^{k0}\) is \((M^{k0})^2\) for OPA, while it is \(\delta^{k0}_{TPA}\) for TPA. Also, for TPA \(2\omega\) is inserted into the exponential term to account for both photons interacting with the molecule.

For RRS and RHRS, the resonant (hyper)polarizability \(\chi\) can be written: \(\chi = A + B + C + \ldots\), where A is the FC term, B is the first Herzberg-Teller (HT) term, etc.\(^134,208\) Specifically looking at the resonant first hyperpolarizability for RHRS, \(\beta_{\alpha\beta\gamma}\), we find the following expression

\[ \beta^p_{\alpha\beta\gamma} = \sum_k (\mu^0_{\alpha k})eq (S^k_{\beta\gamma})eq i \int_0^\infty dt \langle F_0 | I_k(t) \rangle e^{i(\epsilon_{I_0} + 2\omega)t - g_k(t)} \] (10.7)

The intensity of RHRS is proportional to the square of the transition hyperpolarizability.\(^287,408\) The expression for the resonant polarizability for RRS \((\alpha^p_{\alpha\beta})\) is identical to Eq. 10.7, with \((\mu^0_{\beta})eq\) substituted for \((S^k_{\beta\gamma})eq\) and \(\omega\) replacing \(2\omega\) in the exponential term. For further details on the derivation of these expressions, and the equations for the time-dependent overlap integrals, the reader is referred to Ref. 435.

### 10.4 Computational Details

Simulations of the OPA, TPA, RRS, and RHRS were performed using results calculated using the B3LYP and LC-PBE exchange-correlation functionals using TDSPEC.\(^435,439,481\) For this work, the LC-PBE functional was implemented in Dalton 2.0.\(^436\) Data for the linear response properties, such as vertical excitation energies and one-photon transition dipole moments, and quadratic response properties, including two-photon transition dipole moments, were taken from the Dalton program. Values for these parameters are listed in the Supporting Information. Calculations were performed using the optimized structure and normal modes from the global hybrid B3LYP functional\(^339\) using the Stuttgart RECP and basis set for Ru and 6-311G* basis set for all other atoms, using the NWChem program.\(^437\) Normal mode frequencies in this work are scaled by a constant shift of 0.98 from value obtained by B3LYP. All simulated spectra
are convoluted with a Lorentzian lineshape with 10 cm$^{-1}$ width.

The dimensionless displacements from the independent-mode displaced harmonic oscillator method that are used in the time-dependent formalism were calculated using NWChem. A fit to the experimental OPA spectrum was performed, obtaining spectral parameters for the dimensionless lineshape parameter $\kappa_k$ and homogeneous broadening parameter ($\Gamma_k$), which are the only required parameters needed for determining the lifetime function $g_k(t)$. The parameters from the OPA spectrum were also used for the TPA spectrum, since the experimental TPA spectrum for Rubpy is not available. For simulating RRS spectra, the fit to the OPA spectrum was used. The simulated RHRS spectra used the fitting parameters from the OPA spectrum also. OPA and TPA spectra can have very different spectral appearance, so the parameters used for the TPA spectrum should be treated as effective values in this work.

### 10.5 Results and Discussion

#### 10.5.1 One-photon and Two-photon absorption spectra

A comparison between the experimental absorption spectra and simulated absorption spectra based on B3LYP and LC-PBE calculations for Rubpy and Rubpy-d24 are shown in Figure 10.2. The ten lowest excited states were included in the simulations, and

**Figure 10.2.** Simulated OPA spectra (blue line) for (a) B3LYP and (b) LC-PBE in comparison to the experimental OPA spectrum (black line). For B3LYP, the intensity is scaled by 0.68 for Rubpy and 1.04 for Rubpy-d24. For LC-PBE, the intensity is scaled by 0.80 for Rubpy and 1.24 for Rubpy-d24. OPA spectra for the low (orange dashed line) and high (green line) MLCT states are also shown. See the Supporting Information for simulation parameters.
their one-photon and two-photon transition moments calculated using B3LYP and LC-PBE are shown in the Supporting Information. Both B3LYP and LC-PBE indicate that states 5 through 8 are important for OPA. Excited states 5 through 8 from both functionals involve transitions between Ru d-orbitals and ligand orbitals (MLCT). See the Supporting Information for assignments of the transitions and the plots of the orbitals involved. This assignment is in consensus with the literature that the absorbance band on the experimental OPA spectrum peaking at 452 nm is a MLCT state. Empirical solvent shifts were used to position all electronic states for comparison with the experimental measurements. The shifts used for B3LYP and LC-PBE are 0.24 and 0.82 eV, respectively. Recent electronic structure calculations employing the polarizable continuum model for solvation$^{507}$ have indicated that solvent shifts in water are between 0.30 to 1.05 eV for Ru(NH$_3$)$_4$bpy$^{2+}$,$^{105}$ which is comparable to the results shown here. The simulations show that the degenerate pairs S$_5$/S$_6$ and S$_7$/S$_8$ are responsible for the absorption band around 452 nm. For B3LYP, the same degenerate pairs are important. However, the S$_7$/S$_8$ pair is significantly stronger than S$_5$/S$_6$, in contrast to LC-PBE. Lineshape parameters used for simulating the OPA spectrum of Rubpy and Rubpy-d$_{24}$ can be found in the Supporting Information. Identical simulation parameters are used for Rubpy and Rubpy-d$_{24}$. This is justified because the experimental OPA spectra for both molecules have identical bandshapes. Also, in Ref. 105 the full-width at half-maximum for the various Ru$^{2+}$ complexes were determined to be approximately 1800 to 2800 cm$^{-1}$. These ranges correspond well to the values determined in the present work.

Examining the OPA spectra (Figure 10.2), some trends are observable. Although both functionals yield a strong absorption peak, corresponding to the bright MLCT states, the shoulder observed at 425 nm in the experimental spectra is weak or absent in the simulations. It has been suggested previously$^{105}$ that the shoulder resulted from a high energy MLCT state. However, the B3LYP calculations in Ref. 105, in agreement with the results presented here, indicate that the calculated shoulder for Rubpy is on the red-edge of the absorbance maximum, even when solvent models were used to simulate the absorption spectrum. For LC-PBE, the “low” (S$_5$/S$_6$) and “high” (S$_7$/S$_8$) MLCT states are ordered similarly to experiment, but the separation between the states is too small (0.03 eV). Solvation including the conductor-like screening model (COSMO)$^{508}$ was attempted in NWChem, but this had no significant impact on the positioning of the electronic states. This may be attributed to the implementation of COSMO in NWChem neglecting the response from the polarizable medium when determining the excitations (i.e. only the ground state density is perturbed). Calculations with COSMO
in which the response of the medium is included (not shown) were performed using
B3LYP with the TZP basis set in a local version of the Amsterdam Density Functional
(ADF) program. These indicated that inclusion of a polarizable medium can change
the relative intensities of the “low” and “high” MLCT states, but the incorrect ordering
of the states from B3LYP remained unchanged.

Another possible explanation of the shoulder is that it is a vibronic effect. The
energetic separation between the absorption maximum and the shoulder is approximately
1300 cm\(^{-1}\) for both isotopologues. Clearly, however, the shoulder of the absorption
spectrum is absent for both functionals even with the vibronic model used here. This is
important evidence that the shoulder is not vibronic, and likely results from the presence
of multiple bright electronic states in the absorption manifold.

Attempts were made to improve the simulation results. For instance, it may be
thought that the broadening of the peak is too large for both functionals. Using smaller
values of \(\Gamma_{k}^{FWHM}\) leads to the appearance of a low intensity shoulder (\(\sim\)20-30\% of
the absorption maximum intensity). However, we find that this is not a satisfactory
explanation of the shoulder in the experimental spectrum. Instead of using the Brownian
oscillator model to account for homogeneous and inhomogeneous broadening, we tried the
simpler solvent model with \(g_{k}(t) = \Gamma_{k}t + \frac{1}{2}\Theta t^{2}\), where \(\Gamma_{k}\) is the excited state lifetime and
\(\Theta\) is an inhomogeneous broadening parameter used to account for the distribution of the
electronic 0-0 energies. This does not improve or worsen the agreement with experiment,
so the results are not shown. It was determined that the only method for improving the
fit to the experimental absorption spectra was to increase the separation between the
“low” and “high” MLCT states for the LC-PBE calculations. This allows the absorption
spectrum to be fit very well with a modest increase in the separation (going from 0.03 eV
to \(\sim\)0.23 eV), but the same approach is less reasonable for the B3LYP simulations where
the MLCT states are incorrectly ordered. Therefore, for consistency we will only apply a
universal solvent shift to all states and leave the separation between the states identical
to what was determined in the electronic structure calculations when comparing with
experiment.

Although no experimental TPA spectrum exists in the literature for Rubpy, several
efforts have indicated the measured order of magnitude of the TPA cross section for
Rubpy and analogous systems. Using two-photon excited fluorescence, the two-photon
excitation cross section \(\sigma_{TPE} = \phi_{f}\sigma_{TPA}\), where \(\phi_{f}\) is the fluorescence quantum yield
and \(\sigma_{TPA}\) is the TPA cross section was determined for Rubpy as 4.3 GM (1 GM =
\(1 \times 10^{-50}\) cm\(^{4}\) s photon\(^{-1}\)) with rhodamine B as an internal reference. Different
groups have estimated $\sigma_{TPA}$ for molecules similar to Rubpy, but with more conjugated and functionalized ligands, at various wavelengths. Coe et al. determined $\sigma_{TPA}$ for Ruthenium(II) trischelate complexes involving quaterpyridinium ligands, finding values between 60 and 180 GM at 750 nm excitation.\textsuperscript{497} Nag et al. studied the two-photon induced fluorescence of cis-Ru(bpy)$_2$Cl$_2$, and estimated $\sigma_{TPA}$ for that molecule to be between 120 and 130 GM at 810 nm excitation.\textsuperscript{500} Giradot et al. used phenanthroline (Phen) ligands in place of bipyridine ligands, observing a small $\sigma_{TPA}$ value of 10 GM for the MLCT states of Ru(Phen)$_3^{2+}$.\textsuperscript{499} A recent study of Rubpy and dumbbell-shaped ruthenium complexes indicated that $\sigma_{TPA}$ is 85 GM at 575 nm.\textsuperscript{510} This value is likely overestimated because it was determined using the z-scan technique,\textsuperscript{175} but gives a possible upper limit to $\sigma_{TPA}$ for Rubpy.

In TPA, the most important states are identical to the strongest states in OPA for LC-PBE. Using the B3LYP functional it is found that the OPA forbidden S$_9$ state is strongly allowed in TPA as well. The simulated TPA spectra for Rubpy indicate that $\sigma_{TPA}$ at the absorption maximum (452 nm) is 14.5 GM with B3LYP and 9.9 GM with LC-PBE. These are reasonable values compared with the experimental data. Based on other reports of TPA cross sections for organic molecules,\textsuperscript{175,184} our simulations are on the correct order of magnitude for these molecules, which are highly symmetric and contain no terminal electron donating or accepting groups that typically enhance the nonlinear optical response. Improved agreement with the experimental $\sigma_{TPA}$ estimates may require the inclusion of solvent models in the simulations, which have been demonstrated to be important for TPA chromophores.\textsuperscript{399}

### 10.5.2 SERS and SEHRS at 470 nm

A comparison between the RRS spectra simulated using B3LYP and LC-PBE with the SERS spectra obtained for an incident light of 470 nm is shown in Figure 10.3 for Rubpy and Rubpy-d24. The assignment of the character of the most important modes are summarized in Table 10.1 based on the theoretical simulations. The SERS spectrum of Rubpy is dominated by the C-C stretching modes at 1320, 1492, 1565, 1609 cm$^{-1}$ but weaker C-H wagging modes are found at 1272 and 1174 cm$^{-1}$ and Ru-H stretching modes at 673 and 1027 cm$^{-1}$. Similar modes are found to be strong for Rubpy-d24 with the addition of a C-H wagging mode at 849 cm$^{-1}$. For Rubpy, the strongest mode is found at 1492 cm$^{-1}$ whereas for Rubpy-d24, the modes at 1426 and 1527 cm$^{-1}$ are equally strong. We see that there is good agreement between the experimental SERS spectrum and simulated RRS spectrum for both isotopologues.
Three of the modes, 673, 1565, and 1609 cm\(^{-1}\), appear to be sensitive to the exchange-correlation functional. For the mode at 673 cm\(^{-1}\), the peak intensity is best described by LC-PBE. This indicates that the coupling of that mode, which involves significant stretching in the Ru–N bonds and ring breathing in the ligands, is sensitive to the charge-transfer (CT) character of the excited states involved. It is known from previous studies on RRS\(^{405}\) and cluster models for SERS\(^{511}\) that correct description of CT states is important for simulating such Raman spectra accurately. Thus, the fact that the mode at 673 cm\(^{-1}\) is overestimated by B3LYP may not be surprising based on its assignment. Interestingly, however, the modes at 1565 and 1609 cm\(^{-1}\) are best described by B3LYP. These modes are characterized by ligand-centered C–C stretching and C–H wagging motion, and these may not be as sensitive to the MLCT character of the excited states. It is probable that the LC-PBE functional, which includes 100% exact exchange at large interelectronic separation, makes the excited state potential energy surfaces too Hartree-Fock like to accurately capture the peak intensities in RRS spectra.

In Figure 10.4 we compare the simulated RHRS spectra and the experimental SEHRS data at 940 nm for Rubpy and Rubpy-d24. A comparison of the SEHRS spectra at 940 nm (Figure 10.4) with the corresponding SERS spectra at 470 nm (Figure 10.3 for the
Table 10.1. Experimental and theoretical normal mode frequencies in cm\(^{-1}\) (scaled by 0.98 from B3LYP values) for Rubpy and Rubpy-d24 with mode assignments. Data is shown only for the most intense peaks on the RRS spectrum (8 modes for Rubpy, 9 modes for Rubpy-d24).

<table>
<thead>
<tr>
<th>Rubpy Freq.</th>
<th>Rubpy-d24 Freq.</th>
<th>Mode Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. B3LYP</td>
<td>Exp. B3LYP</td>
<td></td>
</tr>
<tr>
<td>673</td>
<td>664</td>
<td>643</td>
</tr>
<tr>
<td>1027</td>
<td>1030</td>
<td>1005</td>
</tr>
<tr>
<td>1174</td>
<td>1183</td>
<td>849</td>
</tr>
<tr>
<td>1272</td>
<td>1284</td>
<td>–</td>
</tr>
<tr>
<td>1320</td>
<td>1310</td>
<td>–</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>1259</td>
</tr>
<tr>
<td>1492</td>
<td>1491</td>
<td>1426</td>
</tr>
<tr>
<td>1565</td>
<td>1571</td>
<td>1527</td>
</tr>
<tr>
<td>1609</td>
<td>1608</td>
<td>1573</td>
</tr>
</tbody>
</table>

The reason for this is that the lineshape function determining the spectral features become identical for RRS and RHRS when only a single allowed transition contributes to the scattering. This is also found in the simulations using an A-term scattering mechanism where the RRS and RHRS spectra for the two isotopologues becomes identical. The simulations presented here rationalize the similar SERS and SEHRS spectra because the same electronic states are intense in OPA and TPA. Previous work by our group has shown that B-term scattering leads to different spectral features for a single state due to the importance of non-Condon terms when either the one-photon or two-photon transition is (nearly) forbidden. \(^{404,506}\)

The nonresonant Raman and hyper-Raman spectra of Rubpy are plotted in Figure 10.5. In contrast to the RRS spectra showing identical features on resonance with the MLCT transition, we find that there are significant differences in the nonresonant scattering spectra. We see that B3LYP and LC-PBE predict very similar Raman spectra whereas the hyper-Raman spectra differ. This is especially true for the mode at 1609 cm\(^{-1}\) which is much stronger that any other mode in the B3LYP spectrum. Comparing the nonresonant Raman spectrum with the RRS spectrum at 470 nm we see that the modes around 1000, 1300, and 1600 cm\(^{-1}\) are strong in the nonresonant Raman scattering. For the nonresonant hyper-Raman spectrum, it is the modes around 600, 1000, and 1600 cm\(^{-1}\) that are strong compared with the RHRS spectrum. The calculation predicts
Figure 10.4. Simulated resonance hyper-Raman spectra and experimental SEHRS spectra of Rubpy and Rubpy-d24 at 940 nm. See the Supporting Information for simulation parameters.

that the resonance enhancements are around $10^3$ for Raman and $10^4$ for hyper-Raman scattering, which indicates that resonance effects are more important in hyper-Raman scattering. Also, the fact that the Raman and hyper-Raman spectra are different off-resonance but become similar on-resonance indicate an A-term scattering mechanism dominated by a single electronic transition.

10.5.3 Wavelength-scanned SERS and SEHRS

In Figure 10.6 we present the experimental SERS spectra for Rubpy and Rubpy-d24 obtained at 410, 440, 470, and 515 nm. We see from the figure that the SERS spectra only show a modest wavelength dependence in this wavelength region. The main spectral changes occur for the relative intensities of the modes at 1565 and 1609 cm$^{-1}$ for Rubpy and the corresponding modes at 1523 and 1573 cm$^{-1}$ for Rubpy-d24. Also, we see that the modes around 1000 and 1300 cm$^{-1}$ become stronger for laser wavelengths around the pre-resonance region at 515 nm. These modes are strong in the nonresonant Raman spectrum and it is likely that the large intensity results from detuning from resonance. The increasing intensity of the 1609 cm$^{-1}$ mode with higher laser energy has been shown in RRS of Rubpy,\textsuperscript{104} SERS of 2,2’-bipyridine on Ag surfaces,\textsuperscript{22} and SERS of Rubpy on
Ag nanotriangles.\textsuperscript{512} This indicates that the observed changes in the SERS spectra are not related to the surface, and can be attributed to the ligands. This observed large intensity of the mode at 1609 cm\textsuperscript{-1} as the wavelength is detuned from resonance at 410 nm could be related to a blue-edge preresonance Raman like effect, since this mode is strong in the nonresonant Raman spectrum\textsuperscript{22} (see Figure 10.5).

Wavelength-scanned SEHRS data is shown for Rubpy and Rubpy-d24 in Figure 10.7. The SEHRS spectra show very different behaviors for the isotopologues. For Rubpy, the peaks at 1565 and 1609 cm\textsuperscript{-1} gradually increase in relative intensity compared to the peak at 1492 cm\textsuperscript{-1}. This is similar to what was observed using SERS in Figure 10.6(a). However, it is noticeable for the SERS of Rubpy at 410 nm that the peak at 1609 cm\textsuperscript{-1} becomes taller than the peak at 1565 cm\textsuperscript{-1}. This never occurs for the SEHRS measurements. This may indicate the presence of a strong interference effect in SERS that is not observed for the wavelengths studied with SEHRS. The loss of interference in SEHRS may result from changes in the relative contributions of different electronic states, which could be observed by comparing OPA and TPA measurements. In the following we will discuss the possibility that interference effects are responsible for the observed changes in peak intensity during the wavelength scan.
Figure 10.6. Experimental SERS spectra for (a) Rubpy and (b) Rubpy-d24 at four wavelengths. The modes at 1565 and 1609 cm$^{-1}$ (Rubpy) and 1527 and 1573 cm$^{-1}$ (Rubpy-d24) are highlighted to emphasize the significant change in relative peak intensity during wavelength scanning.

10.5.4 Peak Ratio Changes in SERS and SEHRS

In Ref. 104 it was discussed that the significant increase in relative intensity of the modes at 1565 and 1609 cm$^{-1}$ is related to interference between the “low” and “high” MLCT states on the blue edge of the absorption maximum. The best agreement for matching the results of a vibronic model with experimental RRS excitation profiles involved having two MLCT states, where the vibronic coupling constants of both states had opposite signs. In Ref. 22, the SERS spectra of 2,2'-bipyridine ligands are shown at several wavelengths and behave similarly to the SERS of Rubpy. This observation was rationalized using the CT mechanism in SERS, where it was thought that electrons were transferred from the Ag surface to the 2,2'-bipyridine ligands. Comparable behavior of the 1565 and 1609 cm$^{-1}$ peaks is observed for RRS experiments on Ru(bpy)$_3$Cl$_2$ on the blue edge of the MLCT band. However, if vibronic coupling to a CT state was responsible for the increased intensity of specific modes in the RHRS spectra, a more substantial effect should be observed for both Rubpy and Rubpy-d24, yet the results in this work only show a strong change going from the SERS to SEHRS of Rubpy-d24. The cause of the peak ratio changes must therefore be inherent to the electronic structure of bipyridine ligands in Rubpy.
Figure 10.7. Experimental SEHRS spectra for (a) Rubpy and (b) Rubpy-d24 at four wavelengths. The modes at 1565 and 1609 cm$^{-1}$ (Rubpy) and 1527 and 1573 cm$^{-1}$ (Rubpy-d24) are highlighted to emphasize the significant change in relative peak intensity during wavelength scanning.

In the following we will quantify the interference between the two MLCT states by considering the intensities of the modes at 1609 and 1565 cm$^{-1}$, relative to the mode 1492 cm$^{-1}$ for Rubpy and for Rubpy-d24 we consider the modes at 1573 and 1527 cm$^{-1}$ relative to 1425 cm$^{-1}$. The intensity ratios as a function of wavelength are shown in Figure 10.8 for both Raman and hyper-Raman scattering. From the intensity ratios several trends are apparent. The modes at 1609 cm$^{-1}$ for Rubpy and 1576 cm$^{-1}$ for Rubpy-d24 show the strongest wavelength dependence for SERS and SEHRS. The wavelength dependence of the intensity ratios is similar between the two isotopologues for SERS and SEHRS. Both modes are characterized by reaching the largest ratio at 410 nm and appear to track with excitation into the MLCT band. The mode at 1527 cm$^{-1}$ reaches a minimum at 440 nm for SERS and SEHRS of Rubpy-d24, whereas all other modes have increasing ratios when wavelength-scanning to higher energy. These differing wavelength dependences are likely indicators of interference effects from multiple transitions contributing the MLCT band.

In Figure 10.8, we also plot the ratios determined from the simulations. The wavelength-scanned simulations of RRS and RHRS using B3LYP and LC-PBE do not
Figure 10.8. Intensity ratios $I_{1565}/I_{1492}$ and $I_{1609}/I_{1492}$ for Rubpy, and $I_{1527}/I_{1426}$ and $I_{1573}/I_{1426}$ for Rubpy-d24. (a) and (b) show the ratios in SERS for Rubpy and Rubpy-d24. (c) and (d) show the ratios in SEHRS for Rubpy and Rubpy-d24.

identify the cause of the increase in the $I_{1609}/I_{1492}$ ratio for Rubpy (see Figure 10.8). While the B3LYP results show a small increase in the ratio with increasing wavelength, LC-PBE yields an almost constant ratio across all wavelengths studied. The LC-PBE results are unsurprising based on the discussion in the previous section where we showed the simulated RRS and RHRS spectra are less consistent with experiment than the B3LYP results for the ligand-centered modes (see Figure 10.3(a)). In general, we find that the wavelength dependence in the simulations are only modest compared to those observed experimentally, indicating that the simulated results are not fully capturing the physical nature of the scattering occurring in Rubpy and its isotopologue. Some possible reasons for this discrepancy are the approximations made in exchange-correlation func-
tionals and neglect of solvation effects, which can be important for accurately simulating RRS.362

The simulations show that two pairs of degenerate states contribute to the RRS and RHRS spectra. Because the states overlap, it is possible in the Franck-Condon approximation that they interfere with each other. Interference results from many factors, including the signs of the dimensionless displacements, energetic positioning of the electronic states, and detuning from resonance on the red or blue edge of the absorption maximum.106,123,405 Because degenerate states have perpendicular transition dipole moments, it is not possible to observe interference between them. The interference should be traced to non-degenerate states as a result. For RRS, B3LYP finds for the 1491 cm\(^{-1}\) mode at 470 nm that the \(S_5/S_6\) contributes \(\sim 5\)% of the intensity whereas the \(S_7/S_8\) pair contributes 89% of the total intensity. The small amount of interference (\(\sim 6\)% ) is the expected behavior because the \(S_5/S_6\) pair is very weak while the \(S_7/S_8\) pair is strongly allowed. In contrast, the RRS results obtained from LC-PBE indicate a significant constructive interference effect with around \(\sim 51\)% of the total intensity coming from the \(S_5/S_6\) pair and \(\sim 9\)% from the \(S_7/S_8\) pair, meaning 40% of the total intensity results from interference. In RHRS at 940 nm for the same mode, B3LYP predicts negligible interference with 94% of the intensity comes from the \(S_7/S_8\) pair and 6% form the \(S_5/S_6\) pair. LC-PBE finds a small amount of destructive interference with 90% of the intensity coming from the \(S_5/S_6\) pair and 12% of the intensity from the \(S_7/S_8\) pair.

The discussion above illustrates that interference is important for RRS and negligible in RHRS simulations. While LC-PBE predicts a significant interference effect for RRS in agreement with the experiments, the wavelength dependence of the spectra does not reflect the interference. The negligible wavelength dependence of the peak ratios for LC-PBE implies that the coupling between the ligand centered vibrations and the two pairs of electronic transitions is poorly described. B3LYP improves the description of vibronic coupling for the ligand centered modes. This allows B3LYP to better capture the wavelength dependence in the normal modes. Based on the interference effect described in Ref. 104, it was demonstrated that the best agreement between theory and experiment occurs when the dimensionless displacements for the “low” and “high” MLCT states have opposite sign and different magnitudes. We attempted to improve the LC-PBE results by scaling \(\Delta_{1565}\) and \(\Delta_{1608}\) by integers. It was determined that \(\Delta_{1565}\) needed a scale factor larger than 2 and \(\Delta_{1608}\) needed a scale factor larger than 8 for the peaks at 1565 and 1608 cm\(^{-1}\) to grow substantially. Based on our experience, it is unusual that displacements are \(\sim 1.00\) for normal modes above 1000 cm\(^{-1}\) for large molecules.
This makes it difficult to confirm or refute the interference effect using simulations solely based on linear optical processes within the limitations of model.

The SEHRS intensity ratios indicate that the state(s) leading to the significant changes in peak ratios observed in SERS are stronger in the two-photon process. There are no large changes in the peak ratios for Rubpy or Rubpy-d24 during RHRS simulations at different wavelengths. Because environmental effects like the solvent and surface can change the transition dipole moments of electronic states, these factors may need to be included in the simulations to correctly describe RHRS and SEHRS of Rubpy. We have also considered that the observed effects may be due to a non-Condon (Herzberg-Teller) mechanism. In recent studies of the fluorescent dye rhodamine 6G, RHRS and SEHRS were demonstrated to be capable of examining these effects. The TPA cross section of Rubpy is similar to the $S_1$ state of rhodamine 6G, which may indicate it is possible to observe B term scattering in Rubpy. However, the lack of a center of inversion in Rubpy and the observed similarity between SERS and SEHRS for Rubpy limits this rationale from being conclusive.

Contrary to the results from both exchange-correlation functionals, the feature at 1609 cm$^{-1}$ is observed to be consistently strong in SEHRS. Based on the simulations, that mode is strong in the nonresonant hyper-Raman spectrum, but the nonresonant hyper-Raman spectrum of Rubpy is approximately 4 orders of magnitude weaker than the RHRS spectrum. It is possible that the vibronic model used here, where many of the intermediate pathways to get from the ground state to the excited state are neglected, cannot correctly capture the cause of the large intensity of the modes at 1565 and 1609 cm$^{-1}$ for Rubpy. This seems to be a possible reason for the underestimated intensity of those modes, but the calculation of the resonant first hyperpolarizability using response theory remains difficult for large molecules.

### 10.6 Conclusions

Rubpy is an important molecule for examining photochemistry, having been employed in a variety of applications including catalysis, photodynamic therapy, and two-photon imaging. The detailed discussion presented here compares simulations to experimental SERS and SEHRS measurements, illustrating that it is possible to assign the experimental observations for large, complicated systems. The shoulder of the Rubpy one-photon absorption spectrum is not assigned to a vibronic effect, but is present because of multiple metal-to-ligand charge transfer states in the absorption manifold. However, deficiencies
in the simulation approach, including the exchange-correlation functionals and vibronic model used, demonstrate the difficulty in describing changes in intensity ratios during wavelength scanning for many modes observed in both SERS and SEHRS for Rubpy and its isotopologue. This indicates a need for further investigation with improved theoretical methods to fully explain the experimental observation.
Chapter 11

Efficient calculations of optical processes: analytical excited state energy gradients with time-dependent density functional theory


Abstract

An implementation of analytical excited state energy gradients is presented for the quantum chemistry program NWChem. Using the Lagrangian approach developed by Furche and Ahlrichs, it is possible to efficiently calculate excited state properties. This method is applied to calculating one-photon absorption and resonance Raman scattering spectra using a diverse set of exchange-correlation functionals. It is shown, using the optimized structure and normal modes from B3LYP, that one-photon absorption spectra can be simulated with good accuracy for many functionals. However, resonance Raman scattering simulations clearly demonstrate the B3LYP gives the best description of the potential energy surface. By comparing vibronic parameters from analytical and numerical gradients, we gain insight on similarities and differences between the approaches.
11.1 Introduction

The excited state properties of molecules lead to diverse applications, including solution phase detection of molecular binding events, photodynamic therapy, and biological imaging. Since its introduction and first development for molecules, time-dependent density functional theory (TDDFT) has become the method of choice for studying excited state properties efficiently and accurately. A particularly appealing application of TDDFT is the calculation of analytical gradients, which allow for the efficient determination of excited state geometries, dipole moments, and vibronic features for one-photon absorption (OPA) and resonance Raman scattering (RRS) spectra.

Raman scattering is an inelastic light scattering process, where radiation with frequency $\omega_L$ is absorbed and then radiation is scattered with frequency $\omega_s = \omega_L - \omega_v$ with $\omega_v$ corresponding to a vibrational frequency of the molecule. When $\omega_L$ is tuned to an electronic excitation energy, resonance enhancement is observed and the process is called RRS. Vibrational information that is coupled to an electronic transition is therefore obtained by this method. RRS has been demonstrated as a valuable technique in characterizing fluorescent dyes, biomolecules, and electron transfer processes.

The fluorescent dye rhodamine 6G (R6G) has been the center of many recent Raman scattering studies. TDDFT calculations of static and frequency-dependent polarizabilities were used to simulation nonresonant Raman and RRS, allowing the resonance enhancement ($\sim 10^5$) to be quantified. It has been demonstrated that vibronic effects are important for capturing the correct relative peak intensities with RRS for R6G also. TDDFT simulations with vibronic coupling have also been instrumental in understanding the complicated nature of resonance hyper-Raman scattering and surface-enhanced hyper-Raman scattering in R6G.

In this work we show our implementation of analytical TDDFT excitation energy gradients based on the Lagrangian formalism of Furche and Ahlrichs into the quantum chemistry program NWChem. By combining the excitation energy gradients with the time-dependent wavepacket formalism, it has been demonstrated that OPA and RRS can be simulated efficiently. We present an application of TDDFT excitation energy gradients to the OPA and RRS to R6G. In Section 11.2, we outline the theory involved in obtaining dimensionless displacements from excitation energy gradients. Section 11.4 shows the results of the simulations of optical properties of molecules from several exchange-correlation functionals. Finally, we conclude this work...
and discuss future applications in Section 11.5.

11.2 Theory

11.2.1 Analytical Excitation Energy Gradients with TDDFT

This section presents the key expressions in the derivation of gradients of the excitation energy using TDDFT. The detailed derivation of all expressions is given in Appendix H. A review of the TDDFT equations is given in Appendix G.

Based on Ref. 64, we can write the TDDFT equations in the form

\[
G[\vec{X}, \vec{Y}, \omega] = \frac{1}{2} \left[ (\vec{X} + \vec{Y})^T (A + B)(\vec{X} + \vec{Y}) + (\vec{X} - \vec{Y})^T (A - B)(\vec{X} - \vec{Y}) \right] \\
- \omega \left[ (\vec{X} + \vec{Y})^T (\vec{X} - \vec{Y}) - 1 \right] \\
= \frac{1}{2} \sum_{ia\sigma jbr} \left[ (X + Y)_{ia\sigma} (A + B)_{ia\sigma jbr} (X + Y)_{jbr} \right] \\
+ (X - Y)_{ia\sigma} (A - B)_{ia\sigma jbr} (X - Y)_{jbr} \\
- \omega \left[ \sum_{ia\sigma} (X + Y)_{ia\sigma} (X - Y)_{ia\sigma} - 1 \right]
\]  \hspace{1cm} (11.1)

In Eq. 11.1, the matrices \((A + B)\) and \((A - B)\), which are sometimes called orbital rotation Hessians, have the following matrix representation

\[
(A + B)_{ia\sigma jbr} = \delta_{\sigma\tau} \delta_{ab} \delta_{ij} (\epsilon_{a\sigma} - \epsilon_{i\sigma}) + 2 (ia\sigma | jbr) + 2 f_{ia\sigma jbr}^{xc} \\
- c_x \delta_{\sigma\tau} [(ab\sigma | ij\sigma) + (ja\sigma | ib\sigma)]
\]  \hspace{1cm} (11.2)

and

\[
(A - B)_{ia\sigma jbr} = \delta_{\sigma\tau} \delta_{ab} \delta_{ij} (\epsilon_{a\sigma} - \epsilon_{i\sigma}) + c_x \delta_{\sigma\tau} [(ja\sigma | ib\sigma) - (ab\sigma | ij\sigma)]
\]  \hspace{1cm} (11.3)

In Eqs. 11.2 and 11.3, \(f_{\sigma\tau}^{xc}\) is the exchange-correlation (XC) kernel

\[
f_{\sigma\tau}^{xc} = \frac{\delta^2 E^{xc}}{\delta \rho_{\sigma}(r') \delta \rho_{\tau}(r)}
\]  \hspace{1cm} (11.4)
For all quantities, indices $i, j, k, l, \ldots$ indicate occupied orbitals, $a, b, c, d, \ldots$ are virtual (unoccupied) orbitals, $\sigma, \tau, \upsilon$ are spin indices, and $p, q, r, s, \ldots$ are arbitrary orbitals. The molecular orbital energies are $\epsilon_{p\sigma}$, ratio of exact (Hartree-Fock) exchange is $c_x$, and the two-electron integrals are written in Mulliken notation. Upon solving the TDDFT equations, the excitation energy $\omega$ and excitation vectors (sometimes called configuration interaction vectors) $\vec{X}$ and $\vec{Y}$ are obtained.

The derivation of TDDFT gradients depends on the evaluation of the Lagrangian functional

$$L[\vec{X}, \vec{Y}, \omega, \vec{C}, \vec{Z}, \vec{W}] =$$

$$\frac{1}{2} \sum_{i\alpha j\beta} [(X + Y)_{i\alpha}(A + B)_{i\alpha j\beta}(X + Y)_{j\beta} + (X - Y)_{i\alpha}(A - B)_{i\alpha j\beta}(X - Y)_{j\beta}]$$

$$- \omega \left[ \sum_{i\alpha}(X + Y)_{i\alpha}(X - Y)_{i\alpha} - 1 \right] + \sum_{i\alpha} Z_{i\alpha} F_{i\alpha} - \sum_{pq\sigma, p \leq q} W_{pq\sigma} (S_{pq\sigma} - \delta_{pq})$$

$$= G[\vec{X}, \vec{Y}, \omega] + \sum_{i\alpha} Z_{i\alpha} F_{i\alpha} - \sum_{pq\sigma, p \leq q} W_{pq\sigma} (S_{pq\sigma} - \delta_{pq})$$

(11.5)

The Lagrangian functional $L$ depends on the excitation energy and excitation vectors, the MO coefficients $\vec{C}$, and Lagrange multipliers $\vec{Z}$ and $\vec{W}$. In Eq. 11.5, the Fock matrix ($F_{pq\sigma}$) and overlap matrix ($S_{pq\sigma}$) are introduced. The Fock matrix is defined

$$F_{pq\sigma} = h_{pq\sigma} + \sum_{i\tau} [(pq\sigma|ii\tau) - c_x \delta_{\sigma\tau} (pi\sigma|iq\sigma)] + V_{pq\sigma}^{xc}$$

(11.6)

In Eq. 11.6, $h$ is the core Hamiltonian, the second term is a Coulomb integral, the third term is the exact exchange contribution, and the XC-potential is

$$V_{pq\sigma}^{xc} = \langle p\sigma|V_{\sigma}^{xc}|q\sigma \rangle = \int dr \phi_{p\sigma}(r) \frac{\delta E^{xc}}{\delta \rho_{\sigma}(r)} \phi_{q\sigma}(r)$$

(11.7)

where $\phi_{p\sigma}$ is a MO. The Lagrange multipliers enforce two constraints

1. $\vec{Z}$ enforces that the ground state Kohn-Sham equation has been solved, and therefore the ground state wavefunction is variationally optimized.
2. $\tilde{W}$ enforces that the MOs are orthonormal.

Based on the Lagrange multipliers, the Lagrangian functional is forced to obey the variational principle. In other words, the Lagrangian functional is stationary with respect to changes in the MO coefficients:

$$\frac{\partial L}{\partial C_{\mu\rho\sigma}} = 0 = \frac{\partial G}{\partial C_{\mu\rho\sigma}} + \sum_{i\alpha\tau} Z_{i\alpha\tau} \frac{\partial F_{i\alpha\tau}}{\partial C_{\mu\rho\sigma}} - \sum_{r\sigma, r' \leq s} W_{r\sigma} \frac{\partial S_{r\sigma}}{\partial C_{\mu\rho\sigma}}$$  \hspace{1cm} (11.8)

The most significant consequence of Eq. 11.8 is that derivatives of the Lagrangian functional with respect to geometric perturbations or external fields (for polarizabilities) can be evaluated by keeping the MO coefficients held constant at the ground state optimized values. This allows gradients of the excitation energy to be calculated at a comparable cost to a ground state energy gradient. Evaluation of Eq. 11.8 is required to determine the Lagrange multipliers, and makes frequent use of the transformation from atomic orbital indices ($\mu, \nu, \lambda, \kappa, \ldots$) to MO indices. This transformation is shown for an arbitrary quantity $V_{pq\sigma}$ below.

$$V_{pq\sigma} = \sum_{\mu \nu} C_{\mu p\sigma} V_{\mu \nu \sigma} C_{\nu q\sigma}$$  \hspace{1cm} (11.9)

After taking derivatives in Eq. 11.8 and some non-trivial algebraic manipulation, it is possible to evaluate $\tilde{Z}$

$$\sum_{j\beta\tau} (A + B)_{i\alpha\sigma} j\beta\tau Z_{j\beta\tau} = -R_{i\alpha\sigma}$$  \hspace{1cm} (11.10)

where the right hand side vector is

$$R_{i\alpha\sigma} = H^+_{i\alpha\sigma} [\tilde{T}] + \sum_b \left\{ (X + Y)_{ib\sigma} H^+_{ab\sigma} [(\tilde{X} + \tilde{Y})] + (X - Y)_{ib\sigma} H^-_{ab\sigma} [(\tilde{X} - \tilde{Y})] \right\} + 2 \sum_{kcrldv} g_{iakrc}^{\tilde{z}c} (X + Y)_{kcr} (X + Y)_{ldv} - \sum_j \left\{ (X + Y)_{ja\sigma} H^+_{ji\sigma} [(\tilde{X} + \tilde{Y})] + (X - Y)_{ja\sigma} H^-_{ji\sigma} [(\tilde{X} - \tilde{Y})] \right\}$$  \hspace{1cm} (11.11)
The vector $\vec{T}$ is the unrelaxed one-particle difference density matrix, defined as

$$T_{ab\tau} = \frac{1}{2} \sum_i \left\{ (X + Y)_{i\alpha\tau}(X + Y)_{i\beta\tau} + (X - Y)_{i\alpha\tau}(X - Y)_{i\beta\tau} \right\}$$  \hspace{1cm} (11.12)

$$T_{ij\tau} = -\frac{1}{2} \sum_a \left\{ (X + Y)_{i\alpha\tau}(X + Y)_{j\alpha\tau} + (X - Y)_{i\alpha\tau}(X - Y)_{j\alpha\tau} \right\}$$  \hspace{1cm} (11.13)

$$T_{ia\tau} = T_{ai\tau} = 0$$  \hspace{1cm} (11.14)

The linear transformation is

$$H^+_{pq\sigma}[\vec{V}] = \sum_{rs\tau} \left[ 2(r\sigma\tau|qp\sigma) + 2f^{xc}_{pq\sigma rs\tau} - c_x \delta_{\sigma\nu} [[[r\nu|ps\nu] + [r\nu|qs\nu]]] V_{rs\tau} \right]$$  \hspace{1cm} (11.15)

and the exchange-correlation third derivative is

$$g_{\sigma\tau\nu}^{xc} = -\frac{\delta^3 E^{xc}}{\delta \rho_\sigma(r) \delta \rho_\tau(r') \delta \rho_\nu(r'')}$$  \hspace{1cm} (11.16)

The Lagrange multiplier $\vec{W}$ can be evaluated after we obtain $\vec{Z}$

$$W_{ij\sigma} = \frac{1}{1 + \delta_{ij}} \left( Q_{ij\sigma} + H^+_{ij\sigma}[\vec{Z}] \right)$$  \hspace{1cm} (11.17)

$$W_{ab\sigma} = \frac{1}{1 + \delta_{ab}} Q_{ab\sigma}$$  \hspace{1cm} (11.18)

$$W_{ia\sigma} = Q_{ai\sigma} + \epsilon_{i\sigma} Z_{ia\sigma}$$  \hspace{1cm} (11.19)

The quantity $Q_{pq\sigma} = \sum_\mu \frac{\partial G[\vec{X},\vec{Y},\omega]}{\partial \mu_{p\sigma}} C_{\mu q\sigma}$. 
With $\vec{Z}$ and $\vec{W}$, the gradient of the Lagrangian can be evaluated to obtain the gradient of the excitation energy. The expression for the gradient of the excitation energy is

$$\omega^\xi = \sum_{\mu\nu\sigma} h^\xi_{\mu\nu} P_{\mu\nu\sigma} - \sum_{\mu\nu\sigma} S^\xi_{\mu\nu} W_{\mu\nu\sigma} + \sum_{\mu\nu} V^{xc}(\xi) P_{\mu\nu} + \sum_{\mu\nu\kappa\lambda\tau} (\mu\nu|\kappa\lambda)^\xi \Gamma_{\mu\nu\kappa\lambda\tau} \mu\nu\kappa\lambda\tau$$

+ \sum_{\mu\kappa\lambda\sigma\tau} f^{xc}(\xi)_{\mu\kappa|\lambda\sigma\tau} (X + Y)_{\mu\nu\sigma} (X + Y)_{\kappa\lambda\tau}\tag{11.20}$$

The superscript, $\xi$, indicates the derivative of a quantity with respect to a nuclear coordinate. When written as $(\xi)$, this indicates the derivative with respect to a nuclear coordinate with the MO coefficients held fixed at their ground state values. This is a consequence of the density functional theory contributions to the gradients implicitly depending on the MO coefficients. Here, two new quantities are defined, the relaxed one-particle difference density matrix ($\vec{P} = \vec{T} + \vec{Z}$) and the effective two-particle difference density matrix $\Gamma_{\mu\nu\kappa\lambda\tau}$. The value of $\Gamma_{\mu\nu\kappa\lambda\tau}$ is given in Eq. H.120 in Appendix H.

### 11.2.2 Calculating Dimensionless Displacements

Dimensionless displacements are related to the gradient of the excited state energy ($E^{0k}$, which is equivalent to $\omega$ from Section 11.2.1) along normal mode $Q_a$. This is diagrammed in Figure 11.1. In this section, the normal mode in mass-weighted units is written as $Q_a$ while it is written as $q_a$ for normal (dimensionless) coordinates. Based on approximations where the ground and excited state potential energy surfaces are harmonic and that there is no change in the normal mode frequencies when the ground and excited state are compared (i.e. no Duschinsky rotations$^{355}$), the dimensionless displacement is calculated as

$$V_{q_a} = \left( \frac{\partial E^{0k}}{\partial q_a} \right)_{q_a=0} = -\omega_{a0} \Delta_{a0}^{0k}\tag{11.21}$$

where $\omega_{a0}$ is the normal mode frequency and $\Delta_{a0}^{0k}$ is the dimensionless displacement of mode $q_a$ for the $n$th excited state. In general it is simpler to evaluate the gradient with respect to $Q_a$ more directly. This circumstance requires an additional step,$^{365}$

$$\frac{\partial E^{0k}}{\partial q_a} = \left( \frac{dQ_a}{dq_a} \right) \frac{\partial E^{0k}}{\partial Q_a} = \sqrt{\frac{h}{2\pi cv_{a0}}} \frac{\partial E^{0k}}{\partial Q_a} = \sqrt{\frac{h}{2\pi cv_{a0}}} V_{Q_a}\tag{11.22}$$
Figure 11.1. A depiction of the independent-mode displaced harmonic oscillator model, assuming a resonance Raman scattering process. Here, $\omega_L$ is the incident frequency of light, $\omega_s$ is the scattered frequency of light, and $\Delta_{k0}^a$ is the dimensionless displacement of normal mode $Q_a$.

The only variability in this expression is how the excited state gradient in terms of mass-weighted coordinates $V_{Q_a}$ is evaluated. Chapters 4, 6, 8, and 9 demonstrate that it is possible to evaluate the gradient numerically. Other research groups have demonstrated the use of analytical gradients of the excited state.\footnote{137,530} Numerical gradients of the excitation energy require finite differentiation, where excitation energies are calculated by stepping in the positive and negative direction along the normal modes.

11.2.2.1 Numerical Excited State Energy Gradients

The numerical evaluation of excited state energy gradients revolves around calculating the linear response of a molecule up to a particular excitation. For any molecule, there are $3N - 5$ or $3N - 6$ ($N$ is the number of atoms) normal modes. Performing a numerical evaluation of the excited state energy gradient requires either $6N - 10$ or $6N - 12$ calculations, because a step in the plus and minus direction along every normal mode is required. This can be reduced significantly by focusing on a portion of the normal modes in a wavenumber region.

For numerical evaluation of the excited state gradients, formulas analogous to those
discussed by Reiher et al.\textsuperscript{366} for the derivatives of the polarizability along normal mode $Q_a$ are used, substituting the excitation energy in place of the polarizability. These derivatives are expressed using a three-point central differences formula as:

$$
\left( \frac{\partial E_0}{\partial Q_a} \right)_{Q_a=0} = \frac{E_0^k(R_{eq} + s_R R_a) - E_0^k(R_{eq} - s_R R_a)}{2s_Qa|Q_a^{norm}|} \tag{11.23}
$$

In Eq. 11.23, $R_{eq}$ is a vector of the optimized coordinates of the molecule’s ground state, $R_a$ is the Cartesian normal mode vector, $s_R$ is the Cartesian step size (typically 0.01 is used), and $|Q_a^{norm}|$ is the norm of the normalized mass-weighted normal mode vector. The latter quantity is used to give the equation appropriate dimensions, but is clearly equal to one. In this expression, $s_{Q_a}$ is

$$
s_{Q_a} = \frac{s_R}{|R_a|} = s_R \left[ \sum_{i=1}^{3N} \left( \frac{Q_{a,i}^{norm}}{m_j} \right)^2 \right]^{-1/2} \quad j = \text{ceil}(i/3) \tag{11.24}
$$

Either the middle expression or the right side expression may be used to find $s_{Q_a}$. If the right side is used, the norm of the mass-weighted normal mode vector is found to obtain the normalized components of that vector ($Q_{a,i}^{norm}$), and then the mass of the jth atom is divided into that component. The notation “$\text{ceil}(i/3)$” indicates that non-integer values are rounded up.

11.2.2.2 Analytical Excited State Energy Gradients

If analytical geometry optimizations are available in a quantum chemistry program, a significant advantage can be used in calculating the dimensionless displacements. In the numerical method described above, the majority of the time spent involves the $6N - 10$ or $6N - 12$ calculations to obtain all of the simulation parameters. In general, for all but the smallest molecules, collection of that data can require weeks worth of CPU and wall time. Analytical gradients of the excited state energy, which come from performing an analytical excited state geometry optimization, are used to determine the dimensionless displacements and require one calculation. A side by side comparison of the numerical and analytical method shows that if you account for the redundant calculations (the ground state geometry optimization and normal mode analysis), with the analytical method a significant reduction in both CPU and wall time is observed. This does not mean that the numerical method is obsolete, because it is currently employed to evaluate property derivatives for Herzberg-Teller terms.

This section employs the review of spectroscopic simulation methods by Neese et
The analytical method involves two different techniques: analytical excited state geometry optimization (method I) and analytical excited state gradients at the ground state equilibrium position (method II). We will briefly examine both methods.

In method I, the dimensionless displacement is calculated by projecting the mass-weighted difference in Cartesian coordinates between the excited state and ground state equilibrium geometries onto the normal modes. This is expressed mathematically in terms of the mass-weighted displacement $\Delta Q_a$

$$\Delta Q_a = \sum_i L_{ia} D_i^{(m)}$$

(11.25)

where $L_{ia}$ are components of the normal mode vector for $q_a$ and $D_i^{(m)}$ is a vector containing the mass-weighted difference in Cartesian coordinates between the ground state and excited state optimized coordinates. Applying dimensional analysis, the units of $\Delta Q_a$ are $\sqrt{\text{mass} \cdot \text{length}}$, so the dimensionless displacement is obtained as

$$\Delta_a = \sqrt{\frac{\omega_a}{\hbar}} \Delta Q_a$$

(11.26)

where $\omega_a = 2\pi c \tilde{\nu}_{a0}$.

For method II, the dimensionless displacement is calculated by projecting the gradient of the excited state energy at the ground state equilibrium position onto the normal modes. This method is written as

$$V_{Q_a} = \sum_i \frac{1}{\sqrt{m_i}} V_{X,i} L_{ia}$$

(11.27)

where $m_i$ is the mass of the atom corresponding to component $i$ and $V_{X,i}$ is the Cartesian excited state energy gradient at the ground state equilibrium position. This is obtained from the first cycle of the excited state geometry optimization, assuming that the ground state equilibrium geometry is the starting point of that optimization. From the gradient $V_{Q_a}$, the dimensionless displacement is calculated from Eq. 11.21. Although both methods I and II can be used to determine the dimensionless displacement, we will focus on method II here.

### 11.3 Computational Details

For electronic separation $r_{12}$, the long-range corrected (LC-) approach takes the inter-electronic repulsion and separates it into separate short- and long-range terms, given
as

\[
\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta \text{erf}(\omega r_{12})]}{r_{12}} + \frac{\alpha + \beta \text{erf}(\omega r_{12})}{r_{12}} \tag{11.28}
\]

where \(\omega\) is the attenuation parameter, \(\alpha\) is a parameter allowing the incorporation of Hartree-Fock (HF) exchange, \(\beta\) is a parameter allowing for the incorporation of density functional theory (DFT) exchange, and the requirements: \(0 \leq \alpha \leq 1\), \(0 \leq \beta \leq 1\), \(0 \leq \alpha + \beta \leq 1\) should be satisfied. For all functionals, the definitions are included in Table 11.1.

Table 11.1. Definitions of the exchange-correlation functionals. The table is separated between the local and semilocal functionals, global hybrids, and long-range corrected hybrids. For the latter, we report the \(\alpha\), \(\beta\), and \(\omega\) parameters.

<table>
<thead>
<tr>
<th>Functional</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>Slater + VWN 5</td>
</tr>
<tr>
<td>BP86</td>
<td>Becke 88 + Perdew 86</td>
</tr>
<tr>
<td>PBE</td>
<td>PBEx + PBEc</td>
</tr>
<tr>
<td>B3LYP</td>
<td>Slater (80%) + Becke 88 (nonlocal, 72%) + Exact Exchange (20%) + LYP (81%) + VWN 1 RPA (19%) + PBEx (75%) + Exact Exchange (25%) + PBEc</td>
</tr>
<tr>
<td>PBE0</td>
<td>CAM-Becke 88 ((\alpha = 0.19), (\beta = 0.46), (\omega = 0.33)) + LYP</td>
</tr>
<tr>
<td>CAM-B3LYP</td>
<td>CAM-Becke 88 ((\alpha = 0.19), (\beta = 0.46), (\omega = 0.33)) + LYP</td>
</tr>
<tr>
<td>LC-PBE</td>
<td>CAM-PBE ((\alpha = 0.0), (\beta = 1.0), (\omega = 0.30)) + PBEc</td>
</tr>
<tr>
<td>LC-PBE0</td>
<td>CAM-PBE ((\alpha = 0.25), (\beta = 0.75), (\omega = 0.30)) + PBEc</td>
</tr>
<tr>
<td>BNL</td>
<td>Baer-Neuhauser-Livshits ((\alpha = 0.0), (\beta = 1.0), (\omega = 0.33)) + LYP</td>
</tr>
<tr>
<td>LC-(\omega)PBE</td>
<td>LC-(\omega)PBE ((\alpha = 0.0), (\beta = 1.0), (\omega = 0.30)) + PBEc</td>
</tr>
<tr>
<td>LC-(\omega)PBE0</td>
<td>LC-(\omega)PBE ((\alpha = 0.0), (\beta = 1.0), (\omega = 0.30)) + PBEc</td>
</tr>
</tbody>
</table>

The geometry optimization, normal mode analysis, and excited state energy gradient calculations were performed in a locally modified development version of the NWChem quantum chemistry program.\(^{437}\) One-photon absorption and resonance Raman scattering simulations used a locally developed program, TDSPEC.\(^{439}\) For every exchange-correlation functional tested, the optimized geometry and normal modes from the B3LYP functional was used. Each calculation used the 6-311G* basis set. Excited state energy gradient calculations used the following exchange-correlation functionals: LDA, BP86, PBE, B3LYP, PBE0, CAM-B3LYP, BNL, LC-PBE, LC-PBE0, LC-\(\omega\)PBE, LC-\(\omega\)PBE0, and Hartree-Fock (HF).

The results presented here were performed using Penn State’s high-performance computational cluster Lion-XF. All calculations were performed using 32 Intel Xeon 3.06 GHz processors. The program was compiled using the Intel 2011 SP1 Fortran compiler.
11.4 Results and Discussion

11.4.1 Timing Comparison of Numerical and Analytical Gradient Calculations for Rhodamine 6G

Figure 11.2. Timing data for the various functionals. Data assume the simulations include the normal modes between 400 and 1800 cm$^{-1}$ for rhodamine 6G (117 modes) and the calculation of data for one excitation. The figure on the left compares the logarithm of CPU times (in seconds) for analytical and numerical gradients. The figure on the right illustrates the increase in efficiency of the analytical gradients versus numerical gradients by how much faster the analytical gradient calculations are. Colors on the right graph are: violet = HF, LDA = blue, semilocal functionals = cyan, global hybrids = green, long-range corrected hybrids = red.

Figure 11.2 compares timing of the calculations required for analytical versus numerical gradients. For both types of calculations, the pertinent steps are:

1. Geometry optimization
2. Normal mode analysis
3. Gradients of the excitation energy

Because the first two steps are identical in both approaches (if the same functional is used to obtain the geometry and normal modes), we do not include them in the timing since they involve shifting the values by a constant. In the analytical approach, the evaluation of gradients requires one calculation. For the numerical approach, the gradients require $2 \times N_{modes}$ calculations. For R6G, if we include modes between 400 and 1800 cm$^{-1}$,
there are 117 normal modes total, so 234 TDDFT excitation energy calculations need to be done. Timings reported in Figure 11.2 are based on the amount of time required to complete the analytical gradient calculation or TDDFT excitation energy calculation, including the self-consistent field approach to optimize the ground state wavefunction.

As indicated in the left panel of Figure 11.2, the analytical gradient approach requires approximately two-orders of magnitude less time than the numerical method for all functionals studied. For example, using the B3LYP functional, an analytical gradient calculation requires 2492 seconds (~42 minutes) while each TDDFT excitation energy calculation for a numerical gradient calculation takes 1495 seconds (~25 minutes). When accounting for the 234 required TDDFT excitation energy calculations in the numerical procedure, 349830 seconds (over 4 days) are required for B3LYP. This is ~140× more efficient, from the standpoint of timing. The analytical gradients are also more practical for doing the calculations for large molecules, where repeated solution of the TDDFT equations can become a bottleneck.

11.4.2 Simulated One-Photon Absorption and Resonance Raman Scattering

For each exchange-correlation functional, the $S_1 \rightarrow S_0$ transition is examined. Because each functional determines a different excitation energy, the OPA spectra are shifted so that the absorption maximum is aligned with the experimental spectrum. Figure 11.3 shows the simulated OPA spectrum with each functional. The functionals are split into four panels and show very different behavior. For the local and semilocal functionals (LDA, BP86, and PBE), the spectra show a main peak with a vibronic shoulder at approximately 490 nm. Each functional in this case overestimates the intensity of the vibronic shoulder compared to the experimental spectrum.

The global hybrid (B3LYP and PBE0) functionals have very similar behavior. Both functionals significantly improve the description of the vibronic feature in the OPA spectrum. Interestingly, the long-range corrected hybrid (CAM-B3LYP, BNL, LC-PBE, LC-PBE0, LC-\(\omega\)PBE, LC-\(\omega\)PBEh) functionals are less consistent in their description of the OPA spectrum. BNL and LC-PBE0 yield poor spectra in comparison with experiment, where there vibronic structure is more intense than the main peak leading to a broad feature. This is contrasted by the other long-range corrected hybrids, which have spectra comparable to the global hybrid functionals. It was thought, because long-range corrected hybrids generally use 100% exact exchange at large interelectronic separation, that a pure HF calculation might elaborate on deficiencies of some of these functionals. The HF
Figure 11.3. Absorption spectra of rhodamine 6G using different exchange-correlation functionals. The experimental data is taken from Ref. 536. Spectra are shifted so that the absorption maximum coincides with the experimental absorption maximum.

calculation gives similar results to BNL and LC-PBE0, demonstrating the connection between these methods. Surprisingly, however, CAM-B3LYP, LC-PBE, LC-ωPBE, and LC-ωPBEh do not possess problems in the OPA spectrum so further investigation requires vibrational information provided by RRS.

Figure 11.4 shows the RRS spectra of rhodamine 6G using the same functionals. For comparison, the experimental surface-enhanced Raman scattering (SERS) spectrum is shown, which is measured at 514.5 nm. Although many peaks are present in the SERS spectrum, we focus on the modes at 616, 772, 1356, 1515, 1579, and 1656 cm\(^{-1}\). Aside from the mode at 1663 cm\(^{-1}\), the local and semilocal functionals underestimate the intensity of every feature in the SERS spectrum. The global hybrid, B3LYP, which we have
Figure 11.4. Resonance Raman spectra of rhodamine 6G using different exchange-correlation functionals. Simulations are performed assuming a wavelength of 514.5 nm.

Previously used in other studies to obtain good agreement with experiment, the modes at 1373 and 1518 cm\(^{-1}\) are underestimated, however.

Although the global hybrids PBE0 and B3LYP use similar amounts of exact exchange (25% and 20%, respectively), the simulated spectra from both functionals vary largely below 1000 cm\(^{-1}\). Many features that are not observed in the SERS spectrum appear in the PBE0 spectrum. Examining the semilocal functionals BP86 and PBE, we observe that the spectra are comparable. It may be surprising then that B3LYP and PBE0 give very different looking spectra, since B3LYP uses the same exchange functional as BP86.
and PBE0 uses the same exchange functional as PBE. Tentatively, we attribute these differences to sensitivity of the different exchange-correlation functionals to the structure and normal modes used in the calculations. For different functionals, the ground state optimized structure does not need to be identical, and this may impact the quality of the response properties we calculate. Further work in our lab is being done to quantify the effect of the geometry for large molecules.

![Resonance Raman spectra of rhodamine 6G calculated with B3LYP.](image)

**Figure 11.5.** Resonance Raman spectra of rhodamine 6G calculated with B3LYP. The figures are: (a) analytical gradient, (b) analytical gradient with displacement of the 1656 mode scaled by 70%, (c) numerical gradient, and (d) simulated RRS with parameters from Ref. 423. Simulations were performed at 532 nm.

RRS spectra using the long-range corrected hybrids and HF are split into two groups. The functionals CAM-B3LYP, LC-PBE, LC-\(\omega\)PBE, and LC-\(\omega\)PBEh give similar spectra. Recall that these functionals also yielded reasonable OPA spectra in comparison to the experimental data (Figure 11.3). Although the ratios of the peaks in the RRS spectra are sensitive to the functional used, it appears that the observed modes are identical for these functionals. The other functionals, BNL, LC-PBE0, and HF were characterized by poor agreement with the experimental OPA spectrum. From the RRS spectra, these functionals each have a large peak at 855 and 1730 cm\(^{-1}\). The broad vibronic features in
the OPA spectra for BNL, LC-PBE0, and HF are likely associated with the 1730 cm\(^{-1}\) mode, since that feature differs from the other functionals.

### 11.4.3 Analytical and Numerical Gradient Calculations with B3LYP

To better understand the analytical gradient results with B3LYP we compare to a RRS spectrum simulated with numerical gradients that was done previously. Figures 11.5(a) and 11.5(c) show the comparison of the analytical and numerical gradient simulations with a simulation using parameters from Ref. 423 (Figure 11.5(d)). We see that the same modes are predicted to couple to the \(S_1 \leftrightarrow S_0\) transition in the analytical and numerical methods, although the relative intensities differ. The analytical gradient method yields a spectrum comparable to the RRS spectrum reported in a previous study by our group.\(^{360}\)

In comparison to the experimental RRS spectrum, the data generated from numerical gradients is in better agreement (the peak at \(\sim 375\) cm\(^{-1}\) in the experimental spectrum was not included in the simulations). A possible explanation for this behavior is that the analytical gradient depends on two perturbations (the external electric field and change in geometry), meaning that it is a quadratic response property. Previous work has demonstrated that quadratic response properties are sensitive to the size of the basis set.\(^{438,448}\) The numerical gradient may be less sensitive to the size of the basis set because it depends only on linear response properties for simulating OPA and RRS, and therefore give a spectrum in better agreement with experiment.

#### Table 11.2. Dimensionless displacements for important modes in rhodamine 6G using numerical and analytical gradients determined using B3LYP. Percent differences are determined relative to the analytical gradient result.

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Numerical (\Delta)</th>
<th>Analytical (\Delta)</th>
<th>Absolute Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>616</td>
<td>-0.24</td>
<td>-0.24</td>
<td>0.00 (0.0)</td>
</tr>
<tr>
<td>772</td>
<td>-0.16</td>
<td>-0.12</td>
<td>0.04 (33.3)</td>
</tr>
<tr>
<td>1129</td>
<td>-0.12</td>
<td>-0.10</td>
<td>0.02 (20.0)</td>
</tr>
<tr>
<td>1182</td>
<td>0.09</td>
<td>0.07</td>
<td>0.02 (28.6)</td>
</tr>
<tr>
<td>1195</td>
<td>-0.10</td>
<td>-0.09</td>
<td>0.01 (10.0)</td>
</tr>
<tr>
<td>1298</td>
<td>-0.14</td>
<td>-0.12</td>
<td>0.02 (16.7)</td>
</tr>
<tr>
<td>1356</td>
<td>0.18</td>
<td>0.17</td>
<td>0.01 (6.0)</td>
</tr>
<tr>
<td>1515</td>
<td>-0.14</td>
<td>-0.13</td>
<td>0.01 (7.7)</td>
</tr>
<tr>
<td>1561</td>
<td>0.14</td>
<td>0.19</td>
<td>0.05 (26.3)</td>
</tr>
<tr>
<td>1579</td>
<td>0.12</td>
<td>0.11</td>
<td>0.01 (9.1)</td>
</tr>
<tr>
<td>1656</td>
<td>-0.20</td>
<td>-0.31</td>
<td>0.11 (35.5)</td>
</tr>
</tbody>
</table>
Table 11.2 shows a comparison of the dimensionless displacements from the numerical and analytical methods. In general, the parameters are similar. The modes at 1561 and 1656 cm\(^{-1}\) have the largest absolute deviations in the two methods. These differences are comparable to those calculated between the analytical and numerical gradient methods by Petrenko \textit{et al.} for trans-hexatriene with the same functional.\textsuperscript{359,530}

To obtain better agreement between the two methods, we tried scaling the intensity of the 1656 mode (Figure 11.5(b)). By reducing the intensity of that mode, the analytical gradient spectrum becomes comparable to the numerical one. Although the spectra still do not overlap perfectly, the agreement between both methods is improved by scaling the 1656 mode by 70%. Small differences in the other relative peak intensities are caused by the variations in the dimensionless displacements (Table 11.2).

### 11.5 Conclusion and Future Work

In this work we showed an implementation of analytical excitation energy gradients in the TDDFT framework. These calculations are demonstrated to work very efficiently because it is possible now to obtain vibronic coupling parameters in a short time period. For the molecule, rhodamine 6G, we observe that the best description of the potential energy surface is obtained using the global hybrid B3LYP functional. Interestingly, we see that the parameters from B3LYP differ substantially between the analytical and numerical energy gradient calculations, resulting in the emphasis of different parts of the resonance Raman spectrum.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{structures.png}
\caption{Structures of (a) betaine-30 (72 atoms) and (b) the push-pull julolidine donor, nitro group acceptor polyene (60 atoms).}
\end{figure}

Future studies with this work will likely require fully consistent calculations, where
the same functional is used in the optimization, normal mode analysis, and TDDFT energy gradients. This is currently possible in NWChem using an analytical Hessian of the ground state energy for the local, semilocal, and global hybrid functionals. For the long-range corrected functionals, analytical Hessians are not presently implemented so the normal modes would need to be obtained numerically. In molecules of the size of R6G numerical Hessian calculations are prohibitively expensive, so the best approach is implementing the analytical Hessian.

With analytical Hessians for all exchange-correlation functionals, we can revisit R6G to see if the spectra improve for any of the functionals. Because the long-range corrected functionals are specifically designed to handle charge-transfer states, it may also be interesting to examine large molecules like a push-pull julolidine donor, nitro group acceptor polyene or betaine-30. Both molecules have been studied experimentally (see Figure 11.6 for structures), so it should be possible to quantify the performance of the long-range corrected functionals with those systems.

A few other tests may help interpret the rhodamine 6G data more completely. As discussed in Section 11.4.3, we observe that the numerical gradients outperform the analytical gradients when comparing with simulations from experimental parameters. Two factors involved in obtaining the analytical gradients should be explored. Because it is clear that B3LYP gives the best description of RRS for rhodamine 6G, we could try changing the amount of Hartree-Fock exchange used in the calculations. A second consideration is the effect of the basis set. While it is too time-consuming to test a variety of basis sets for the numerical method, the efficiency of the analytical approach facilitates exploring how basis set size impacts the quality of the vibronic coupling constants.
Part VI

Outlook and Future Directions
Outlook

12.1 Dissertation Summary

This dissertation was presented in four parts. In the first part, “Describing electronic structure with density functional theory,” the accuracy of density functional theory calculations was tested for silver clusters and electron transfer complexes. It was demonstrated for the metal systems that the properties of silver are sensitive to the choice of the exchange-correlation energy functional, where the best performance was shown to come from the long-range corrected functional LC-PBE. Applying density functional theory to situations where explicit charge-transfer states exist, we illustrated that accurate representations of the potential energy surface, as probed by relative intensities in simulated resonance Raman scattering spectra, required the use of a long-range corrected functional.

The second part, “Vibronic coupling simulations of linear and nonlinear optical processes,” elaborated on extending the wavepacket dynamics approach for simulations of nonlinear optical properties using first principles calculations. A general framework was presented based on evaluation of vibrational overlap integrals in the harmonic oscillator approximation, where absorption and Raman scattering processes could be evaluated using the efficient time-dependent formalism. This model was then tested on small and medium sized molecules, illustrating that it can be used to accurately predict vibronic coupling in one-photon absorption, resonance Raman scattering, two-photon absorption, and resonance hyper-Raman scattering.

In the third part, “Hyper-Raman scattering of rhodamine 6G,” the vibronic calculations of resonance hyper-Raman scattering were tested on the fluorescent dye rhodamine 6G. Chapter 7 demonstrates the difficulty in interpreting spectra for nonlinear optical
processes. We initially thought that nonresonant hyper-Raman scattering was more important than resonant hyper-Raman scattering due to the poor agreement between the experimental surface-enhanced hyper-Raman scattering (SEHRS) spectra and simulated resonance hyper-Raman scattering spectra. After more effort involving the implementation of the vibronic theory of resonance hyper-Raman, we demonstrated that non-Condon effects were important for describing the SEHRS of rhodamine 6G. Finally, an interpretation of why non-Condon effects are important in rhodamine 6G is presented.

The final part, “Efficiently simulating optical processes: analytical excited state energy gradients,” demonstrates the efficiency of simulating spectra for linear optical properties. This technique makes use of the Lagrangian approach for time-dependent density functional theory, allowing gradients and optimizations of excitation energies to be performed in comparable times to the ground state energy. Exploiting the relationship between the gradient of the excitation energy and the vibronic coupling constants, it is possible to simulate one-photon absorption and resonance Raman scattering for large molecules after only 3 calculations (e.g. ground state geometry optimization, normal mode analysis, and excited state gradient/optimization). This contrasts the finite difference approach used in the earlier parts of the dissertation, where the excited state gradient, assuming a nonlinear polyatomic molecule, requires at least 6N-12 calculations, where N is the number of atoms in the molecule. By making the number of calculations independent of the size of the molecule, it is possible to study large systems without greatly increasing the time required to collect the data.

12.2 Future Directions for Vibronic Coupling Simulations

With the completion of the analytical excited state energy gradients, numerous applications are now possible. In particular, because the gradients are a quadratic response property (nonlinear response), several new implementations of properties can be done in the quantum chemistry program NWChem.

12.2.1 Analytical Transition Dipole Moment Gradients

Based on Eqs. 5.9 and 5.13, simulations including Herzberg-Teller terms for one-photon absorption and resonance Raman scattering require the derivative of the transition dipole moment along the normal modes. Currently, this is achieved by finite difference of the transition dipole moment. However, when the transition dipole moment is approximately zero (weakly allowed transition) or equal to zero (forbidden transition), it isn’t possible to
correctly determine the sign of the dipole moment at each step of the numerical derivative. This can be solved by doing the transition dipole moment gradient analytically. This has been demonstrated previously by a few research groups\textsuperscript{137,381} and can be used with the Lagrangian approach for determining gradients of the excitation energy to fully predict linear optical properties.

### 12.2.2 Analytical Polarizability Gradients

When vibronic effects are not significant, the model presented in Chapters 5 and 6 can overestimate relative intensities of peaks in resonance Raman spectra. A different approach for simulating nonresonant and resonant Raman scattering requires derivatives of the polarizability, rather than derivatives of the excitation energy. It has been illustrated by Rappoport and Furche\textsuperscript{537} that the Lagrangian approach for the excitation energy can be extended for calculating analytical gradients of the polarizability. The approach described would allow both gradients of the static and frequency-dependent polarizabilities for nonresonant Raman scattering to be determined in a single calculation, avoiding the time-consuming finite difference approach. In order to simulate resonance Raman scattering from polarizability derivatives, gradients of the polarizability at the molecule’s excitation energy must be calculated, and therefore the effects of a finite lifetime\textsuperscript{60,538} must be included to prevent the polarizability from diverging. The analytical gradients of polarizabilities including a finite lifetime have not been derived or implemented previously.

### 12.2.3 First Hyperpolarizabilities with Lifetime

The first hyperpolarizability ($\beta$) is related several interesting optical properties for molecules. Most relevant to this dissertation is that the derivative of $\beta$ along the normal modes is proportional to the intensity of hyper-Raman scattering. Analytical expressions for $\beta$ have been derived\textsuperscript{539} and implemented previously in several quantum chemistry programs. Like the analytical excitation energy gradients, the first hyperpolarizability is a quadratic response property. Implementation for Hartree-Fock wavefunctions should be straightforward, and for density functional theory the only additional quantity required is the third order functional derivative of the exchange-correlation functional, which is already implemented for several functionals in NWChem. It has also been demonstrated that $\beta$ can be evaluated when near a molecule’s excitation energy using quadratic response with lifetime effects.\textsuperscript{513} Implementing $\beta$ into NWChem would allow users to simulate nonresonant hyper-Raman scattering and other optical properties using
an efficient parallelized scheme such that calculations are possible for small and large molecules. Furthermore, first hyperpolarizabilities with lifetime effects would allow studies of resonance hyper-Raman scattering without using the vibronic approach. This is important for studying systems where resonance with a one- and two-photon transition is possible, such as zinc phthalocyanine.\textsuperscript{214}

### 12.2.4 Two-Photon Transition Moments

Two-photon transition moments, which are needed in the vibronic approach to simulate two-photon absorption and resonance hyper-Raman scattering, are available in the Dalton quantum chemistry program.\textsuperscript{84,181–183} One difficulty in using Dalton is that it is limited in its parallelization, which makes calculations of optical properties for large molecules prohibitive. It would be beneficial implementing calculations of two-photon transition moments into NWChem to take advantage of its efficient parallelization. The framework for these calculations involves the expressions for the quasienergy Lagrangian approach of Christiansen, Hättig, and Jørgensen.\textsuperscript{540,541} Implementation of the expressions for Hartree-Fock and density functional theory could follow Ref. 183. Like in Section 12.2.3, this project will benefit from the third order functional derivatives already being implemented for the analytical excitation energy gradients.

### 12.2.5 Vibronic Approach for Simulating Chiroptical Properties

Applications of circular dichroism and resonance vibrational Raman optical activity (RVROA) allow for characterization of chiral systems based on the response of molecules to circularly polarized light.\textsuperscript{542} In particular, RVROA benefits from resonance enhancement and can selectively identify chiral molecules. Theoretical studies have demonstrated the ability to simulate RVROA from polarizability derivatives\textsuperscript{543} and vibronic methods.\textsuperscript{544} Although RVROA is not as widely applied as resonance Raman scattering, Herzberg-Teller terms have never been calculated in a vibronic model for RVROA. Explicit use of non-Condon effects have been suggested for exploring the bis-(trifluoracetylcamphorato) copper(II) complex.\textsuperscript{545}

### 12.2.6 Vibronic Simulations Including Duschinsky Rotations

In this dissertation, it was assumed that there was no change in the normal modes going from the ground electronic state to an excited electronic state for the vibronic simulations. When mode mixing between the ground and excited electronic states occur, it is referred to
as a Duschinsky rotation. Simulations of one-photon absorption and resonance Raman scattering including Duschinsky rotations have illustrated that the relative intensities of features can depend significantly on the inclusion of this effect. It should be feasible to implement Duschinsky rotations for two-photon absorption and resonance hyper-Raman scattering, and study the impact of this effect for nonlinear optical properties. However, because the excited state normal modes are required, the second derivative (Hessian matrix) of the excited state energy is needed also. Calculating the Hessian is expensive for determining ground state normal modes, and would therefore be difficult for large molecules in an excited state. Evaluation of the excited state normal modes can either proceed by using a numerical Hessian, which requires finite difference of the analytical gradient, or an analytical Hessian of the excitation energy. Since analytical Hessians of excitation energies are not yet implemented in many quantum chemistry programs, the initial approach should involve testing Duschinsky rotations on small or medium sized molecules where the numerical Hessian is feasible.

12.2.7 Investigation of Solvation Effects on Resonance Hyper-Raman Scattering

Solvation effects can substantially impact the value of the polarizability and hyperpolarizabilities of a molecule, and therefore impact the intensities of optical processes. Using explicit and continuum solvent models, a detailed understanding of the impact of solvation on the optical properties can be obtained. In particular, it would be interesting to quantify the magnitude of changes in the vibronic coupling constants and derivatives of the transition moments in the presence of a solvent environment.
Appendices
A.1 Supplementary Information for Results Section

Optical absorbance spectra not presented in the main article for Ag$_n$ clusters ($n = 4$–$7$, $10$–$18$) are presented in Figures A.1 – A.9, where each figure contains the spectra for one of the silver clusters calculated with each XC functional. Results are compared to both experimental$^{314,315}$ and computational results.$^{320,321}$ The experimental work measured the absorbance spectra of isolated silver clusters in rare gas matrices for silver clusters Ag$_2$ to Ag$_{21}$. Calculations of optical properties by Bončič-Koutecky et al. were performed in an EOM-CC with single and double excitations (EOM-CCSD) framework for clusters between Ag$_2$ and Ag$_8$.

A.1.1 Absorbance Spectra

a. Ag$_4$. Absorbance spectra for the four atom silver cluster are shown in Figure A.1. Both BP and PBE yield nearly identical spectra with major transitions at 2.98, 4.20, and 5.20 eV. These results are nearly identical to those found by Harb et al. using the structures and calculated absorbance spectra with the BP functional.$^{314}$ Both GGAs have slightly redshifted peaks compared to the EOM-CCSD results, which shows three major transitions located at 3.20, 4.30, and 5.55 eV. The experimental results show three narrow transitions at 3.10, 4.15, and 4.50 eV. Overall, the agreement between the GGAs
Absorbance spectra for the Ag$_4$ cluster using the different functionals. Spectra are plotted for the $D_{2h}$ isomer with labels of the XC functional or method used to obtain them. Plots of the experimental (Ref. 320) and EOM-CCSD (Ref. 314) results were generated using digitizing software on the original spectra.

For the global hybrid functionals, the major transitions occur at 3.05, 4.15, and 5.35 eV. For both functionals the agreement is slightly better with both experiment and EOM-CCSD spectra compared with the results from the GGAs. There is also a noticeable decrease in the number of low-intensity states for spectra calculated with the global hybrid functionals when compared with the spectra from the PBE and BP functionals.

In the case of the LC-functionals, the spectra show slight differences from each other. For CAM-B3LYP, the main transitions occur at 3.05, 4.13, and 5.54 eV. LC-PBE gives major transitions at 3.11, 4.15, and 5.82 eV. LC-PBE0 has major transitions at 3.11, 4.29, and 5.87. Each of these functionals positions the excitation energies similar to the EOM-CCSD results, even though peak intensities do differ between the DFT and EOM-CCSD results. LC-PBE generally gave the most similar spectrum compared to the results derived experimentally. For the BNL functional, the main transitions are not well resolved in the spectral region above 3.50 eV. It seems that the BNL functional did not show the same improvement in comparing the prominent transition on its absorption spectrum at 3.00 eV to the experimental or EOM-CCSD results. The higher energy portion of the spectrum contains a lot of additional excitations making it difficult to compare that portion of the spectrum with either experiment or EOM-CCSD results.
b. Ag$_5$. For the five atom cluster, absorbance spectra are presented in Figure A.2. Like what was observed for the Ag$_4$ cluster, both the BP and PBE functionals have very similar spectra with two major transitions at 3.10 and 3.60 eV, and less intense features at higher energy. Experimental results show these transitions occur at 3.25 and 3.75 eV. The EOM-CCSD results show features at 3.55, 3.81, and 4.25 eV. Both peaks are redshifted for both GGAs by approximately 0.15 eV compared to experiment and 0.45 eV compared to EOM-CCSD.

The global hybrid functionals yield similar spectra, with major transitions at 3.30, 3.75, and 4.75 eV. PBE0 also gives a pronounced peak at 5.50 eV. There is improved agreement with the experimental spectrum when the global hybrid functionals are used. For both functionals, the relative intensities of the peaks at 3.30 and 3.75 eV are reversed from the observed experimental spectrum. The transition at 3.30 eV is still redshifted from the EOM-CCSD result, but not as much as it was for the GGAs. B3LYP also seems to improve the higher energy portion of the spectrum above 4.50 eV in comparison to the results from EOM-CCSD calculations.

The LC-functionals give comparable spectra for this cluster. For LC-PBE, LC-PBE0, and CAM-B3LYP, three major transitions are observed at approximately 3.40, 3.80, and 5.00 eV (LC-PBE has the last peak at 5.20 eV). These transitions are slightly blueshifted from the experimental results. The transition at 3.40 eV is redshifted slightly from the EOM-CCSD result, whereas the transition at 5.00 eV is blueshifted from the same result. BNL again gives a different looking absorption spectrum with major transitions at 3.25, 3.50, and a broad feature between 4.50 and 5.00 eV. This functional gives transitions that are redshifted from the experimental results. Also, it does not improve the spectrum much compared to the B3LYP and PBE0 functionals. The other LC-functionals improve agreement with the EOM-CCSD results compared with the GGAs and global hybrid functionals.

c. Ag$_6$. The absorbance spectra for the six atom cluster are shown in Figure A.3. The prominent features of the experimental spectrum are located at 3.63 and 4.15 eV, with a broad set of transitions between 4.90 and 5.10 eV. For all of the spectra from the present work, the strong feature at 4.15 eV is absent. This was observed in a previous study by Harb et al. as well, where they noted that the transition at 4.15 eV results from symmetry forbidden transitions in their calculations. These transitions may be allowed in the presence of the Ar matrix used in the experiment, but this is not accounted for in calculations for the present study.

For both GGAs, the prominent transition is found to occur at 3.30 eV with the
broader set of transitions occurring at 4.00 to 4.50 eV. The EOM-CCSD results give a prominent peak at 3.69 eV, with smaller features at 3.06, 4.83, and 5.84 eV. Results for both GGAs are found to be redshifted compared to both experimental and theoretical results. The higher energy portion of the spectra (above 4.50 eV) was not calculated for these functionals. B3LYP and PBE0 have three noticeable features on their absorbance spectra located at 2.60 and 3.45 eV, with broader features between 4.50 and 5.50 eV. The lower energy portion of the spectrum is still redshifted from the positions of the experimental and EOM-CCSD results, but not as significantly as what was observed for the GGAs.

The LC-functionals have similar spectra for this cluster. The major transition calculated for each functional is located between 3.45 and 3.60 eV. Both LC-PBE and LC-PBE0 position the prominent transition at comparable position with EOM-CCSD, but a small blueshift is observed with respect to the experimental spectrum. Also, it is noticeable that each of the LC-functionals shifts the small peak on the low energy side of the prominent transition to between 2.85 and 3.20 eV. This again compares very well to the EOM-CCSD results and experimental findings. These results appear to confirm that the $D_{3h}$ isomer is in fact responsible for several features in the experimental absorbance spectrum, which was difficult to see in the paper by Harb et al.$^{314}$

The higher energy
Figure A.3. Absorbance spectra for the Ag₆ cluster using the different functionals. Spectra are plotted for the D₃h isomer with labels of the XC functional or method used to obtain them. Plots of the experimental (Ref. 320) and EOM-CCSD (Ref. 314) results were generated using digitizing software on the original spectra.

portion of the spectrum for each LC-functional is blueshifted with respect to experiment and EOM-CCSD, but the magnitude of each shift varies depending on the functional.

d. Ag₇. Absorbance spectra for the seven atom cluster are shown in Figure A.4. The experimental spectrum shows a broad transition with two separate maxima at 3.60 and 3.75 eV, and also includes less intense transitions at 2.81 and 4.50 eV. The EOM-CCSD results position the strong transition at 3.89 eV, with the smaller features at 2.58 and 4.13 eV. For both GGAs, the strong features are located at 3.45 and 3.60 eV, which is redshifted from the locations on the experimental and EOM-CCSD spectra. The functionals place the lower energy transition at 2.80 eV, which agrees well with experiment but not with EOM-CCSD results.

For the global hybrid functionals, the main transition is located at 3.75 eV, and the absorbance spectrum has less intense transitions near 2.75 eV and 4.75 eV. This main transition is in better agreement with both experiment and EOM-CCSD than what was found for the GGAs. The LC-functionals place the main transition at 3.75 eV which is in good agreement with both experiment and EOM-CCSD results. The lowest energy excitation for each LC-functional is at around 2.60 eV which is close to what was found using EOM-CCSD calculations. This makes the agreement in that portion of the spectrum worse compared to the experimental results. However, the LC-functionals
Figure A.4. Absorbance spectra for the Ag$_7$ cluster using the different functionals. Spectra are plotted for the $D_{5h}$ isomer with labels of the XC functional or method used to obtain them. Plots of the experimental (Ref. 320) and EOM-CCSD (Ref. 314) results were generated using digitizing software on the original spectra.

CAM-B3LYP and LC-PBE0 place an excitation at nearly 4.50 eV, which agrees well with experimental results. The excitation ranges for LC-PBE and BNL were not calculated to high enough energy to resolve the high energy part of the spectrum.

e. Ag$_{10}$. Based on the results shown for the smaller silver clusters, it is apparent that the XC functionals that are similar in type give similar results. That is to say, the GGAs BP and PBE give very similar absorbance spectra. This is also true for the the global hybrid functionals and LC-functionals as well. Consequently, it was not necessary to calculate the optical properties of each cluster using every XC functional for the clusters larger than Ag$_8$. Based on the excellent agreement with experiment on calculating the ionization potentials and agreement with both EOM-CCSD and experiment for absorbance spectra, the LC-PBE functional was chosen to study the larger clusters. Because the GGA PBE and global hybrid functional PBE0 are based on the same XC functional as LC-PBE, they were also selected for modeling the larger silver clusters for comparison purposes.

For the ten atom silver cluster, absorbance spectra are presented in Figure A.5. The experimental absorbance spectrum is shown to have three peaks at 3.79, 3.98, and 4.15 eV. For the $D_{2d}$ isomer used in the present study, none of the functionals have very good agreement with the experimental spectrum. The PBE functional gives a large
Figure A.5. Absorbance spectra for the Ag₁₀ cluster using the different functionals. Spectra are plotted for the $D_{2d}$ isomer with labels of the XC functional or method used to obtain them. The plot of the experimental spectrum (Ref. 314) was generated using digitizing software.

Excitation at 3.17 eV and a broad feature between 3.50 and 4.50 eV. While the higher energy features of the spectrum seem to match the experimental results, the transition at 3.17 eV is absent from the experimental spectrum. PBE0 slightly blueshifts the results from the PBE functional, placing one peak at 3.30 eV and another at 4.25 eV. Again, the experimental spectrum does not have a peak around 3.30 eV. It seems that the higher energy part of the spectrum looks worse compared to experiment, because the broad feature becomes a single narrow peak for the PBE0 functional. The LC-PBE functional yields a similar spectrum to the PBE functional, but the prominent transition is blueshifted to 3.40 eV.

It is interesting that all of the XC functionals yielded absorbance spectra that compare poorly to the experimental spectrum. The Ag₁₀ absorbance spectrum presented in Figure A.5 is comparable to what was found for the Ag₉ cluster by Harb et al. They noted this in comparing the Ag₁₀ absorbance spectrum they collected to what was calculated using the BP functional. One possible reason for the difference in appearance, they describe, is that the spectrum for Ag₁₀ presented in the paper is actually that of Ag₉, because it is possible that Ag₁₀ fragments to form Ag₉. However, it also may be that the $D_{2d}$ cluster is not the most stable isomer of an Ag₁₀ so further investigation into the problem is worthwhile.
Figure A.6. Absorbance spectra for the Ag$_{12}$ cluster using the different functionals. Spectra are plotted for the $C_5$ isomer with labels of the XC functional or method used to obtain them. The plot of the experimental spectrum (Ref. 314) was generated using digitizing software.

f. Ag$_{12}$. Absorbance spectra for Ag$_{12}$ are shown in Figure A.6. The experimental spectrum shows a series of three peaks at 3.42, 3.91, and 4.38 eV. Of the three XC functionals, LC-PBE has the best agreement with the experimental results with small blueshifts for most of the spectrum. The peak locations for the absorbance spectrum from LC-PBE are 3.51, 3.84, and 4.47 eV. LC-PBE also captures the shoulder of the middle peak at approximately 4.05 eV. PBE0 also has good agreement with peaks located at 3.43, 3.98, and 4.53 eV. Both LC-PBE and PBE0 have small blueshifts of the lowest and highest energy peak of the spectrum. The PBE functional captures the three peaks on the spectrum, but they are all redshifted to 3.24, 3.65, and 4.00 eV.

g. Ag$_{14}$. The spectra for the Ag$_{14}$ cluster are given in Figure A.7. Three main transitions appear in the experimental spectrum at 3.48, 4.00, and 4.96 eV. The PBE functional yields intense transitions at 3.21, 3.37 and 3.41 with small broad features between 3.8 and 4.45 eV. The spectrum for this functional was only plotted up to 4.45 eV so the peak near 4.96 eV on the experimental spectrum was not accounted for. It is apparent that the peak positions from PBE are redshifted from their positions on the experimental spectrum. PBE0 captures two major excitations at 3.43 and 3.59 eV, and smaller peaks centered at 4.10 and 4.75 eV. LC-PBE results in a slight blueshift of the low energy part of the spectrum, with two large excitations and 3.58 and 3.68 eV,
Figure A.7. Absorbance spectra for the Ag\textsubscript{14} cluster using the different functionals. Spectra are plotted for the C\textsubscript{1} isomer with labels of the XC functional or method used to obtain them. The plot of the experimental spectrum (Ref. 314) was generated using digitizing software.

with smaller features at 4.20 eV and 4.80 eV. Both PBE0 and LC-PBE give very similar results and compare better with the experimental spectrum than the PBE functional.

h. Ag\textsubscript{16}. Absorbance spectra for the Ag\textsubscript{16} cluster are presented in Figure A.8. This cluster and the larger clusters yield absorbance spectra with one high intensity plasmon-like peak and a small broad shoulder at higher energy. For the experimental spectrum, the large intensity peak is centered at 3.51 eV with a shoulder between 3.88 and 4.18 eV. The PBE functional gives a large broad peak at 3.45 eV, with a shoulder at about 3.90 to 4.25 eV. This higher energy spectral features were not calculated beyond 4.20 eV for this functional. PBE0 places a large peak at 3.73 eV and a broad feature between 4.00 and 4.70 eV. LC-PBE gives a large peak at 3.75 eV and a broad feature between 4.20 and 5.10 eV. PBE in this case gives apparent good agreement with the experimental results, while both PBE0 and LC-PBE yield a blueshift for some or all of the spectrum. All three spectra include the red-edge shoulder that is also present in the experimental spectrum.

i. Ag\textsubscript{18}. Spectra taken from experimental data and DFT calculations for the Ag\textsubscript{18} cluster are presented in Figure A.9. The experimental spectrum has one large intensity transition at 3.62 eV with a shoulder at 4.04 eV. For PBE and PBE0, the spectrum was not plotted over a large enough spectral window to include the shoulder. For the
Figure A.8. Absorbance spectra for the Ag$_{16}$ cluster using the different functionals. Spectra are plotted for the $C_1$ isomer with labels of the XC functional or method used to obtain them. The plot of the experimental spectrum (Refs. 314 and 315) was generated using digitizing software.

main peak, PBE, PBE0, and LC-PBE give transition energies at 3.70, 4.09, and 4.14 eV, respectively. Each functional also captures a red-edge peak, seen on the experimental spectrum as a shoulder to the large peak. This is placed well for both PBE0 and LC-PBE. For this cluster, PBE redshifts the large excitation and PBE0 and LC-PBE result in a blueshift. Based on the overall appearance of the spectrum PBE0 captures the features of the spectrum most correctly.
Figure A.9. Absorbance spectra for the Ag_{18} cluster using the different functionals. Spectra are plotted for the C_1 isomer with labels of the XC functional or method used to obtain them. The plot of the experimental spectrum (Refs. 314 and 315) was generated using digitizing software.
Supplementary Information for “Understanding the Resonance Raman Scattering of Donor-Acceptor Complexes using Long-Range Corrected DFT”

B.1 Fitting Procedures

Fitting to the experimental absorbance spectrum was performed manually. First, with arbitrary values of the homogeneous linewidth (\(\Gamma_n\)) and inhomogeneous linewidth (\(\Theta\)), the absorbance spectrum was simulated using Eq. (1) in the main text. For HMB/TCNE, with only a single excited state contributing, the excited state was shifted in order to align the simulated absorbance maximum with the experimentally measured one. Different combinations of \(\Gamma_n\) and \(\Theta\) were tested until optimal values were determined. Scale factors were applied as the optimal fitting parameters were determined because the fit quality is difficult to judge when the peaks do not overlap. In this case, because the experimental absorbance spectrum looks predominantly Gaussian, the inhomogeneous linewidth was made large and is the main contribution to the peak shape.

For carbazole/TCNE, the process is more complicated because multiple excited states are contributing to the observed absorbance peak. In this situation, an initial guess for the peak positions for the CT1 and CT2 states was based on the experimental fit of Ref. 123. These peak positions were adjusted further for the B3LYP and LC-\(\omega\)PBE functionals. The peak positions relative to each other were not fixed because the TDDFT calculation places the maxima too far apart, and thus causes a valley between the maxima of each state. However, the order of states from the TDDFT calculations was maintained. For
this simulation, it was again found that the inhomogeneous linewidth is most important for the best fit, whereas the homogeneous lineshape gave reasonable fits when varied between 250 and 300 cm$^{-1}$.

**B.2 Hexamethylbenzene/TCNE**

The vibrational frequencies, dimensionless displacements, and normal mode assignments determined from experiment$^{107}$ for the HMB/TCNE complex, along with mode-specific reorganization energy values, are located in Table B.1. Data for the functionals B3LYP and LC-ωPBE are presented in Tables B.2 and B.3, respectively, where the normal mode frequencies are calculated using B3LYP/6-31G*. These modes were selected because they are the ones that match those assigned experimentally. It should be pointed out that other modes are found to contribute to the resonance Raman spectrum for these functionals that do not have a clear partner on the experimental spectrum, and that these are not reported into the data tables because they are numerous.

Mode assignments for the B3LYP functional were based on inspecting the normal modes with Jmol.$^{554}$ Although the modes are predominantly localized on either the HMB or TCNE structure, it is not possible to decouple the motions of the two molecules when they are complexed. This is indicated by the mode assignments for the B3LYP functional, where vibrational motions of one molecule in the complex result in small vibrations on the other molecule as well.

The data shown in Table B.4 show the overlap of modes of the HMB/TCNE complex with the modes of the free HMB and TCNE molecules. Structures for the free HMB and TCNE molecules are optimized separately (using B3LYP/6-31G*), so the overlaps can be used as an indication of how much the modes change as a result of complex formation. The procedure for determining the overlaps involves using quaternions to rotate the free molecule and overlap it with the same atoms corresponding to those in the complex. The overlap is then calculated by normalizing the dot product of the normal mode vectors from the free and complexed molecules.

As Table B.4 shows, the overlap between modes on the complex and modes of the free molecules is at least 60%, but never greater than 90%. This gives an indication that there are strong interactions between the HMB donor molecule and TCNE acceptor. Likely, these differences in the normal modes result from distortion of the structures of the molecules depending on whether they are complexed or uncomplexed. Also, the normal mode vibrational frequencies do not match exactly when comparing the complexed and
uncomplexed structures, which is another indication of the effects of the interactions between the two molecules.

**Table B.1.** Absorbance and resonance Raman modeling parameters based on experimental data.\textsuperscript{107} In the table, str = stretch and def = deformation.

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>(\Delta)</th>
<th>(\lambda_k) (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>165</td>
<td>-3.80</td>
<td>1191</td>
<td>D-A Intermolecular Str</td>
</tr>
<tr>
<td>450</td>
<td>1.34</td>
<td>404</td>
<td>HMB ((e_g) C-CH(_3) def)</td>
</tr>
<tr>
<td>542</td>
<td>0.59</td>
<td>94</td>
<td>(\nu_4) TCNE ((a_g) C-CN bend)</td>
</tr>
<tr>
<td>600</td>
<td>0.61</td>
<td>112</td>
<td>(\nu_3) TCNE ((a_g) C-C str)</td>
</tr>
<tr>
<td>968</td>
<td>0.44</td>
<td>94</td>
<td>HMB ((e_g) C-CH(_3) str and CH(_3) def)</td>
</tr>
<tr>
<td>1292</td>
<td>0.73</td>
<td>344</td>
<td>HMB ((a_1g) C-CH(_3) str and ring str)</td>
</tr>
<tr>
<td>1389</td>
<td>0.36</td>
<td>90</td>
<td>HMB ((a_1g) CH(_3) def)</td>
</tr>
<tr>
<td>1437</td>
<td>0.23</td>
<td>38</td>
<td>HMB (CH(_3) antisym defs)</td>
</tr>
<tr>
<td>1551</td>
<td>1.03</td>
<td>823</td>
<td>(\nu_2) TCNE ((a_g) C=C str)</td>
</tr>
<tr>
<td>1570</td>
<td>0.30</td>
<td>71</td>
<td>HMB ((e_g) ring str)</td>
</tr>
<tr>
<td>2222</td>
<td>0.48</td>
<td>256</td>
<td>(\nu_1) TCNE ((a_g) CN str)</td>
</tr>
</tbody>
</table>

**B.3 Carbazole/TCNE**

For both charge transfer states of the carbazole/TCNE complex, the vibrational frequencies, dimensionless displacements, and mode-specific reorganization energy values determined from experiment\textsuperscript{123} are located in Table B.5. Mode assignments are given in Table B.6. Normal mode assignments for experimental data are based on a study\textsuperscript{555} for uncomplexed carbazole. The fitting procedure used for this complex was based on that used for HMB/TCNE, where the large \(\Delta\) values associated with TCNE are assumed to be similar for both systems. This was rationalized based on the electron in this system moving from an orbital of the donor for both complexes to the TCNE LUMO.\textsuperscript{123} Data for the functionals B3LYP and LC-\(\omega\)PBE are presented in Tables B.7 and B.8, respectively, where the normal mode frequencies are calculated using B3LYP/6-31G*.

The data presented in Table B.9 shows the assignments of the normal modes based on the B3LYP/6-31G* calculations. As was seen for the HMB/TCNE system, the modes are mainly localized on one molecule (either carbazole or TCNE). However, it is apparent that motions due to vibrations on one molecule cause the other molecule in the complex to vibrate with smaller motions as well. Although it was not observed that any vibrations differ significantly when comparing the normal modes of the uncomplexed
Table B.2. Absorbance and resonance Raman modeling parameters based on the B3LYP functional. Vibrational frequencies are scaled by a factor of 0.98 for better agreement with experiment. In the table, str = stretch, def = deformation, opb = out of plane bending, ipb = in plane bending, and the vibrational motion in parentheses is weak but noticeable.

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>(\Delta)</th>
<th>(\lambda_k) (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>165.53</td>
<td>2.82</td>
<td>660</td>
<td>D-A Intermolecular Str</td>
</tr>
<tr>
<td>444.78</td>
<td>-0.02</td>
<td>0.07</td>
<td>HMB C-CH(_3) def, (TCNE C-CN opb)</td>
</tr>
<tr>
<td>525.69</td>
<td>-0.01</td>
<td>0.03</td>
<td>TCNE C-CN bend, (HMB C-H str)</td>
</tr>
<tr>
<td>603.13</td>
<td>0.19</td>
<td>11.2</td>
<td>TCNE C-C-C scissoring, (HMB C-CH(_3) def)</td>
</tr>
<tr>
<td>976.85</td>
<td>-0.08</td>
<td>3.0</td>
<td>HMB C-CH(_3) str and CH(_3) def (TCNE C-CN opb)</td>
</tr>
<tr>
<td>1290.86</td>
<td>-0.11</td>
<td>8.1</td>
<td>HMB C-CH(_3) str and ring str, (TCNE CN str)</td>
</tr>
<tr>
<td>1411.34</td>
<td>0.02</td>
<td>0.24</td>
<td>HMB CH(_3) def</td>
</tr>
<tr>
<td>1465.96</td>
<td>-0.05</td>
<td>1.6</td>
<td>HMB CH(_3) def, (TCNE C=C str)</td>
</tr>
<tr>
<td>1531.11</td>
<td>0.24</td>
<td>46</td>
<td>TCNE C=C str, (HMB CH(_3) def)</td>
</tr>
<tr>
<td>1581.40</td>
<td>0.01</td>
<td>0.16</td>
<td>HMB ring str and CH(_3) def, (TCNE C=C str)</td>
</tr>
<tr>
<td>2285.69</td>
<td>-0.11</td>
<td>14</td>
<td>TCNE CN str, (HMB ring str and CH(_3) def)</td>
</tr>
</tbody>
</table>

Table B.3. Absorbance and resonance Raman modeling parameters based on the LC-\(\omega\)PBE functional. Vibrational frequencies are scaled by a factor of 0.98 for better agreement with experiment. In the table, str = stretch, def = deformation, opb = out of plane bending, ipb = in plane bending, and the vibrational motion in parentheses is weak but noticeable.

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>(\Delta)</th>
<th>(\lambda_k) (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>165.53</td>
<td>2.12</td>
<td>371</td>
<td>D-A Intermolecular Str</td>
</tr>
<tr>
<td>444.78</td>
<td>-0.80</td>
<td>143</td>
<td>HMB C-CH(_3) def, (TCNE C-CN opb)</td>
</tr>
<tr>
<td>525.69</td>
<td>-0.24</td>
<td>15</td>
<td>TCNE C-CN bend, (HMB C-H str)</td>
</tr>
<tr>
<td>603.13</td>
<td>0.26</td>
<td>20</td>
<td>TCNE C-C-C scissoring, (HMB C-CH(_3) def)</td>
</tr>
<tr>
<td>976.85</td>
<td>-0.48</td>
<td>110</td>
<td>HMB C-CH(_3) str and CH(_3) def (TCNE C-CN opb)</td>
</tr>
<tr>
<td>1290.86</td>
<td>-0.37</td>
<td>90</td>
<td>HMB C-CH(_3) str and ring str, (TCNE CN str)</td>
</tr>
<tr>
<td>1411.34</td>
<td>-0.08</td>
<td>4.7</td>
<td>HMB CH(_3) def</td>
</tr>
<tr>
<td>1465.96</td>
<td>-0.33</td>
<td>79</td>
<td>HMB CH(_3) def, (TCNE C=C str)</td>
</tr>
<tr>
<td>1531.11</td>
<td>0.66</td>
<td>334</td>
<td>TCNE C=C str, (HMB CH(_3) def)</td>
</tr>
<tr>
<td>1581.40</td>
<td>0.27</td>
<td>56</td>
<td>HMB ring str and CH(_3) def, (TCNE C=C str)</td>
</tr>
<tr>
<td>2285.69</td>
<td>-0.20</td>
<td>47</td>
<td>TCNE CN str, (HMB ring str and CH(_3) def)</td>
</tr>
</tbody>
</table>
Table B.4. Comparison of normal modes from B3LYP of the uncomplexed HMB and TCNE molecules with the modes of the HMB/TCNE complex based on mode overlaps. Modes for both the complexed and uncomplexed molecules are scaled by 0.98. See previous tables for assignments of the modes for the complex.

<table>
<thead>
<tr>
<th>HMB/TCNE Frequency/cm(^{-1})</th>
<th>HMB Frequency/cm(^{-1})</th>
<th>TCNE Frequency/cm(^{-1})</th>
<th>Mode Overlap % of Overlap</th>
</tr>
</thead>
<tbody>
<tr>
<td>165.53</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>444.78</td>
<td>448.41</td>
<td>-</td>
<td>84</td>
</tr>
<tr>
<td>525.69</td>
<td>-</td>
<td>525.69</td>
<td>89</td>
</tr>
<tr>
<td>603.13</td>
<td>-</td>
<td>601.32</td>
<td>84</td>
</tr>
<tr>
<td>976.85</td>
<td>975.05</td>
<td>-</td>
<td>69</td>
</tr>
<tr>
<td>1290.86</td>
<td>1299.74</td>
<td>-</td>
<td>77</td>
</tr>
<tr>
<td>1411.34</td>
<td>1407.13</td>
<td>-</td>
<td>68</td>
</tr>
<tr>
<td>1465.96</td>
<td>1469.01</td>
<td>-</td>
<td>80</td>
</tr>
<tr>
<td>1531.11</td>
<td>-</td>
<td>1537.89</td>
<td>84</td>
</tr>
<tr>
<td>1581.40</td>
<td>1570.88</td>
<td>-</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>1589.87</td>
<td>-</td>
<td>65</td>
</tr>
<tr>
<td>2285.69</td>
<td>-</td>
<td>2289.18</td>
<td>75</td>
</tr>
</tbody>
</table>

molecules to those of the complex, it becomes complicated comparing modes based solely on vibrational frequencies as the system size gets larger.

Plots of the interference between the CT1 state and CT2 state are presented for excitation wavelengths of 488 nm, 601 nm, and 723 nm in Figures B.1, B.2 and B.3. These are normalized to the mode with maximum constructive interference. For both experiment and B3LYP in particular, there is clear evidence that detuning has an effect on the type of interference observed in the model used in this work.

Data shown in Table B.10 indicate that the overlap of the modes for the carbazole/TCNE complex with those of the free carbazole and TCNE molecules. The carbazole and TCNE normal modes are taken from structures of the individual molecules that were optimized using B3LYP/6-31G*. Interestingly, this particular complex has higher overlap between the uncomplexed and complexed structures, with mode overlaps of 85% or greater for each mode. Each of the modes with an overlap below 90% comes predominantly from motions on carbazole, and involves bending of the C–H bonds in that structure. The vibrational frequencies differ by less than 1 cm\(^{-1}\) for most modes, but variations are seen of up to 7 cm\(^{-1}\) for modes that primarily result from TCNE motions. This seems to indicate that TCNE is perturbed more strongly by forming the complex than carbazole.
Table B.5. Absorbance and resonance Raman modeling parameters based on experimental data.\textsuperscript{123}

<table>
<thead>
<tr>
<th>Frequency/cm\textsuperscript{-1}</th>
<th>CT1</th>
<th>CT2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Δ</td>
<td>(\lambda_k/cm\textsuperscript{-1})</td>
</tr>
<tr>
<td>242</td>
<td>0.450</td>
<td>25</td>
</tr>
<tr>
<td>428</td>
<td>0.650</td>
<td>90</td>
</tr>
<tr>
<td>529</td>
<td>0.200</td>
<td>11</td>
</tr>
<tr>
<td>551</td>
<td>0.430</td>
<td>51</td>
</tr>
<tr>
<td>595</td>
<td>0.300</td>
<td>27</td>
</tr>
<tr>
<td>615</td>
<td>0.200</td>
<td>25</td>
</tr>
<tr>
<td>654</td>
<td>0.350</td>
<td>40</td>
</tr>
<tr>
<td>1012</td>
<td>0.147</td>
<td>11</td>
</tr>
<tr>
<td>1108</td>
<td>0.205</td>
<td>23</td>
</tr>
<tr>
<td>1121</td>
<td>0.125</td>
<td>9</td>
</tr>
<tr>
<td>1204</td>
<td>0.150</td>
<td>14</td>
</tr>
<tr>
<td>1220</td>
<td>0.161</td>
<td>16</td>
</tr>
<tr>
<td>1238</td>
<td>0.153</td>
<td>15</td>
</tr>
<tr>
<td>1278</td>
<td>0.200</td>
<td>26</td>
</tr>
<tr>
<td>1286</td>
<td>0.130</td>
<td>11</td>
</tr>
<tr>
<td>1313</td>
<td>0.110</td>
<td>8</td>
</tr>
<tr>
<td>1323</td>
<td>0.201</td>
<td>27</td>
</tr>
<tr>
<td>1337</td>
<td>0.320</td>
<td>69</td>
</tr>
<tr>
<td>1392</td>
<td>0.390</td>
<td>106</td>
</tr>
<tr>
<td>1451</td>
<td>0.170</td>
<td>21</td>
</tr>
<tr>
<td>1462</td>
<td>0.250</td>
<td>46</td>
</tr>
<tr>
<td>1487</td>
<td>0.133</td>
<td>13</td>
</tr>
<tr>
<td>1495</td>
<td>0.355</td>
<td>94</td>
</tr>
<tr>
<td>1553</td>
<td>0.975</td>
<td>738</td>
</tr>
<tr>
<td>1577</td>
<td>0.316</td>
<td>79</td>
</tr>
<tr>
<td>1605</td>
<td>0.200</td>
<td>32</td>
</tr>
<tr>
<td>1629</td>
<td>0.460</td>
<td>172</td>
</tr>
<tr>
<td>2227</td>
<td>0.400</td>
<td>178</td>
</tr>
<tr>
<td>2236</td>
<td>0.100</td>
<td>11</td>
</tr>
</tbody>
</table>
Table B.6. Assignments of the normal modes in the carbazole/TCNE complex. In the table, str = stretch, def = deformation, opb = out of plane bending, and ipb = in plane bending.

<table>
<thead>
<tr>
<th>Frequency/cm(^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>242</td>
<td>TCNE</td>
</tr>
<tr>
<td>428 (\nu_8)</td>
<td>(a(_1) ring def)</td>
</tr>
<tr>
<td>529</td>
<td>TCNE</td>
</tr>
<tr>
<td>551 (\nu_{11})</td>
<td>(b(_2) C-H ipb and ring def)</td>
</tr>
<tr>
<td>595</td>
<td>TCNE</td>
</tr>
<tr>
<td>615 (\nu_{14})</td>
<td>(b(_2) C-H ipb and ring def)</td>
</tr>
<tr>
<td>654</td>
<td>(\nu_{15}) (a(_1) ring def)</td>
</tr>
<tr>
<td>1012 (\nu_{30})</td>
<td>(a(_1) C-H ipb and ring def)</td>
</tr>
<tr>
<td>1108 (\nu_{32})</td>
<td>(a(_1) C-H ipb and ring def)</td>
</tr>
<tr>
<td>1121 (\nu_{33})</td>
<td>(b(_2) C-H ipb and ring def)</td>
</tr>
<tr>
<td>1204 (\nu_{36})</td>
<td>(a(_1) C-H ipb and ring def)</td>
</tr>
<tr>
<td>1220 (\nu_{37})</td>
<td>(b(_2) N-H ipb)</td>
</tr>
<tr>
<td>1238 (\nu_{38})</td>
<td>(b(_2) C-H ipb and ring def)</td>
</tr>
<tr>
<td>1278</td>
<td>TCNE</td>
</tr>
<tr>
<td>1286 (\nu_{39})</td>
<td>(a(_1) C-H ipb and ring def)</td>
</tr>
<tr>
<td>1313 (\nu_{40})</td>
<td>(a(_1) C-H ipb and ring def)</td>
</tr>
<tr>
<td>1323 (\nu_{41})</td>
<td>(b(_2) C-H ipb and ring def, N-H ipb)</td>
</tr>
<tr>
<td>1337 (\nu_{42})</td>
<td>(a(_1) C-H ipb and ring def)</td>
</tr>
<tr>
<td>1392 (\nu_{43})</td>
<td>(b(_2) N-H ipb, C-H ipb and ring def)</td>
</tr>
<tr>
<td>1451 (\nu_{44})</td>
<td>(a(_1) C-H ipb and ring def)</td>
</tr>
<tr>
<td>1462 (\nu_{45})</td>
<td>(b(_2) C-H ipb and ring def, N-H ipb)</td>
</tr>
<tr>
<td>1487 (\nu_{46})</td>
<td>(a(_1) C-H ipb and ring def)</td>
</tr>
<tr>
<td>1495 (\nu_{47})</td>
<td>(b(_2) C-H + N-H ipb and ring def)</td>
</tr>
<tr>
<td>1553</td>
<td>TCNE</td>
</tr>
<tr>
<td>1577 (\nu_{48})</td>
<td>(a(_1) C-H ipb and ring def)</td>
</tr>
<tr>
<td>1605 (\nu_{49})</td>
<td>(b(_2) C-H + N-H ipb and ring def)</td>
</tr>
<tr>
<td>1629 (\nu_{51})</td>
<td>(a(_1) C-C str)</td>
</tr>
<tr>
<td>2227</td>
<td>TCNE</td>
</tr>
<tr>
<td>2236</td>
<td>TCNE</td>
</tr>
</tbody>
</table>
Table B.7. Absorbance and resonance Raman modeling parameters based on the B3LYP functional. Vibrational frequencies are scaled by a factor of 0.98 for better agreement with experiment.

<table>
<thead>
<tr>
<th>Frequency/cm$^{-1}$</th>
<th>CT1</th>
<th></th>
<th></th>
<th>CT2</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta$</td>
<td>$\lambda_k$/cm$^{-1}$</td>
<td>$\Delta$</td>
<td>$\lambda_k$/cm$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>252.11</td>
<td>0.220</td>
<td>6.1</td>
<td>0.080</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>424.07</td>
<td>0.409</td>
<td>36</td>
<td>0.484</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>526.08</td>
<td>-0.139</td>
<td>5.1</td>
<td>-0.090</td>
<td>2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>550.06</td>
<td>-0.538</td>
<td>80</td>
<td>0.062</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>585.49</td>
<td>-0.036</td>
<td>0.4</td>
<td>-0.137</td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>617.00</td>
<td>-0.264</td>
<td>21</td>
<td>0.041</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>654.33</td>
<td>-0.160</td>
<td>8.4</td>
<td>0.216</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1021.82</td>
<td>0.038</td>
<td>0.7</td>
<td>0.039</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1113.73</td>
<td>0.027</td>
<td>0.4</td>
<td>-0.239</td>
<td>32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1127.24</td>
<td>0.480</td>
<td>130</td>
<td>0.019</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1215.45</td>
<td>0.050</td>
<td>1.5</td>
<td>-0.071</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1226.96</td>
<td>0.593</td>
<td>216</td>
<td>0.065</td>
<td>2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1244.45</td>
<td>-0.387</td>
<td>93</td>
<td>-0.211</td>
<td>28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1278.24</td>
<td>0.044</td>
<td>1.2</td>
<td>0.021</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1298.77</td>
<td>0.080</td>
<td>4.2</td>
<td>0.133</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1322.94</td>
<td>0.095</td>
<td>6.0</td>
<td>0.194</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1344.85</td>
<td>0.180</td>
<td>22</td>
<td>-0.066</td>
<td>2.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1362.96</td>
<td>0.048</td>
<td>1.6</td>
<td>-0.145</td>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1411.45</td>
<td>0.723</td>
<td>369</td>
<td>-0.005</td>
<td>0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1463.04</td>
<td>-0.108</td>
<td>8.5</td>
<td>0.187</td>
<td>26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1477.85</td>
<td>0.484</td>
<td>173</td>
<td>-0.037</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1502.21</td>
<td>0.007</td>
<td>0.0</td>
<td>-0.134</td>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1512.28</td>
<td>-0.288</td>
<td>63</td>
<td>0.035</td>
<td>0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1537.44</td>
<td>-0.374</td>
<td>108</td>
<td>-0.265</td>
<td>54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1589.88</td>
<td>-0.278</td>
<td>62</td>
<td>-0.035</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1602.16</td>
<td>0.318</td>
<td>81</td>
<td>-0.034</td>
<td>0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1626.19</td>
<td>0.111</td>
<td>10</td>
<td>0.016</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2287.67</td>
<td>0.095</td>
<td>10</td>
<td>0.086</td>
<td>8.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2293.91</td>
<td>0.030</td>
<td>1.0</td>
<td>0.025</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table B.8. Absorbance and resonance Raman modeling parameters based on the LC-ωPBE functional. Vibrational frequencies are scaled by a factor of 0.98 for better agreement with experiment.

<table>
<thead>
<tr>
<th>Frequency/cm$^{-1}$</th>
<th>CT1</th>
<th>CT2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta$</td>
<td>$\Delta$</td>
</tr>
<tr>
<td>252.11</td>
<td>0.064</td>
<td>-0.001</td>
</tr>
<tr>
<td>424.07</td>
<td>0.442</td>
<td>0.491</td>
</tr>
<tr>
<td>526.08</td>
<td>-0.322</td>
<td>-0.303</td>
</tr>
<tr>
<td>550.06</td>
<td>0.157</td>
<td>-0.142</td>
</tr>
<tr>
<td>585.49</td>
<td>0.193</td>
<td>0.190</td>
</tr>
<tr>
<td>617.00</td>
<td>-0.120</td>
<td>0.017</td>
</tr>
<tr>
<td>654.33</td>
<td>-0.447</td>
<td>0.298</td>
</tr>
<tr>
<td>1021.82</td>
<td>0.050</td>
<td>-0.142</td>
</tr>
<tr>
<td>1113.73</td>
<td>0.167</td>
<td>0.017</td>
</tr>
<tr>
<td>1127.24</td>
<td>-0.197</td>
<td>0.181</td>
</tr>
<tr>
<td>1215.45</td>
<td>0.350</td>
<td>-0.094</td>
</tr>
<tr>
<td>1226.96</td>
<td>-0.107</td>
<td>0.187</td>
</tr>
<tr>
<td>1244.45</td>
<td>0.072</td>
<td>-0.055</td>
</tr>
<tr>
<td>1278.24</td>
<td>0.018</td>
<td>0.012</td>
</tr>
<tr>
<td>1298.77</td>
<td>0.223</td>
<td>0.251</td>
</tr>
<tr>
<td>1322.94</td>
<td>0.082</td>
<td>0.397</td>
</tr>
<tr>
<td>1344.85</td>
<td>0.086</td>
<td>0.103</td>
</tr>
<tr>
<td>1362.96</td>
<td>0.291</td>
<td>-0.309</td>
</tr>
<tr>
<td>1411.45</td>
<td>-0.015</td>
<td>0.067</td>
</tr>
<tr>
<td>1463.04</td>
<td>-0.129</td>
<td>0.468</td>
</tr>
<tr>
<td>1477.85</td>
<td>-0.121</td>
<td>0.058</td>
</tr>
<tr>
<td>1502.21</td>
<td>0.052</td>
<td>-0.373</td>
</tr>
<tr>
<td>1512.28</td>
<td>0.213</td>
<td>0.115</td>
</tr>
<tr>
<td>1537.44</td>
<td>-0.598</td>
<td>-0.600</td>
</tr>
<tr>
<td>1589.88</td>
<td>-0.090</td>
<td>-0.062</td>
</tr>
<tr>
<td>1602.16</td>
<td>-0.017</td>
<td>0.176</td>
</tr>
<tr>
<td>1626.19</td>
<td>-0.245</td>
<td>0.276</td>
</tr>
<tr>
<td>2287.67</td>
<td>0.176</td>
<td>0.174</td>
</tr>
<tr>
<td>2293.91</td>
<td>0.034</td>
<td>0.038</td>
</tr>
</tbody>
</table>
Table B.9. Vibrational frequencies (scaled by 0.98) and normal mode assignments for data calculated using B3LYP/6-31G*. In the table, str = stretch, def = deformation, opb = out of plane bending, ipb = in plane bending, ipr = in plane rocking, and the vibrational motion in parentheses is weak but noticeable.

<table>
<thead>
<tr>
<th>Frequency/cm$^{-1}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>252.11</td>
<td>TCNE ipr (Carb ring def and C-H str)</td>
</tr>
<tr>
<td>424.07</td>
<td>Carb op ring def (TCNE CN bending)</td>
</tr>
<tr>
<td>526.08</td>
<td>TCNE CN ipb (Carb C-H str)</td>
</tr>
<tr>
<td>550.06</td>
<td>Carb C-H ipb and ring def (TCNE opr)</td>
</tr>
<tr>
<td>585.49</td>
<td>TCNE CN opb (Carb C-H str)</td>
</tr>
<tr>
<td>617.00</td>
<td>Carb C-H ipb and ring def (TCNE C-CN bend)</td>
</tr>
<tr>
<td>654.33</td>
<td>Carb ring def (TCNE CN str)</td>
</tr>
<tr>
<td>1021.82</td>
<td>Carb C-H ipb and ring def (TCNE central C opb)</td>
</tr>
<tr>
<td>1113.73</td>
<td>Carb C-H ipb and ring def (TCNE CN str)</td>
</tr>
<tr>
<td>1127.24</td>
<td>Carb C-H ipb and ring def (TCNE central C opb)</td>
</tr>
<tr>
<td>1215.45</td>
<td>Carb C-H ipb and ring def (TCNE central C opb)</td>
</tr>
<tr>
<td>1226.96</td>
<td>Carb N-H and C-H ipb (TCNE central C ipb)</td>
</tr>
<tr>
<td>1244.45</td>
<td>Carb C-H ipb and ring def (TCNE cyanide C ipb)</td>
</tr>
<tr>
<td>1278.24</td>
<td>TCNE central C ipb and CN str (Carb ip str)</td>
</tr>
<tr>
<td>1298.77</td>
<td>Carb C-H ipb and ring def (TCNE central C ipb)</td>
</tr>
<tr>
<td>1322.94</td>
<td>Carb C-H ipb and ring def (TCNE central C ipb)</td>
</tr>
<tr>
<td>1344.85</td>
<td>Carb C-H ipb and ring def (TCNE central C ipb, N opb)</td>
</tr>
<tr>
<td>1362.96</td>
<td>Carb C-H ipb and ring def (TCNE central C ipb, N opb)</td>
</tr>
<tr>
<td>1411.45</td>
<td>Carb N-H and C-H ipb (TCNE central C ipb)</td>
</tr>
<tr>
<td>1463.04</td>
<td>Carb C-H ipb and ring def (TCNE central C opb)</td>
</tr>
<tr>
<td>1477.85</td>
<td>Carb C-H ipb and ring def and N-H bend (TCNE central C ipb)</td>
</tr>
<tr>
<td>1502.21</td>
<td>Carb C-H ipb and ring def</td>
</tr>
<tr>
<td>1512.28</td>
<td>Carb C-H and N-H ipb (TCNE central C str and CN ipb)</td>
</tr>
<tr>
<td>1537.44</td>
<td>TCNE central C-C str and CN str (small) (Carb C-H and N-H ipb)</td>
</tr>
<tr>
<td>1589.88</td>
<td>Carb C-H and N-H ipb and ring def (TCNE central C bend and CN ipb)</td>
</tr>
<tr>
<td>1602.16</td>
<td>Carb C-H and N-H ipb and ring def (TCNE central C-C str)</td>
</tr>
<tr>
<td>1626.19</td>
<td>Carb C-C str, C-H bend, and N-H bend (TCNE central C ipb)</td>
</tr>
<tr>
<td>2287.67</td>
<td>TCNE opposite CN stretch and central C bend (Carb C-H and C bending)</td>
</tr>
<tr>
<td>2293.91</td>
<td>TCNE all CN stretch</td>
</tr>
</tbody>
</table>
Table B.10. Comparison of normal modes from B3LYP of the uncomplexed carbazole and TCNE molecules with the modes of the carbazole/TCNE complex based on mode overlaps. Vibrational frequencies are scaled by 0.98 for both the complexed and uncomplexed molecules. See previous tables for assignments of the modes for the complex.

<table>
<thead>
<tr>
<th>Carbazole/TCNE Frequency/cm$^{-1}$</th>
<th>Carbazole Frequency/cm$^{-1}$</th>
<th>TCNE Frequency/cm$^{-1}$</th>
<th>Mode Overlap % of Overlap</th>
</tr>
</thead>
<tbody>
<tr>
<td>252.11</td>
<td>-</td>
<td>252.14</td>
<td>100</td>
</tr>
<tr>
<td>424.07</td>
<td>425.11</td>
<td>-</td>
<td>97</td>
</tr>
<tr>
<td>526.08</td>
<td>-</td>
<td>525.33</td>
<td>100</td>
</tr>
<tr>
<td>550.06</td>
<td>551.70</td>
<td>-</td>
<td>99</td>
</tr>
<tr>
<td>585.49</td>
<td>-</td>
<td>594.17</td>
<td>98</td>
</tr>
<tr>
<td>617.00</td>
<td>618.17</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>654.33</td>
<td>656.19</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>1021.82</td>
<td>1020.12</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>1113.73</td>
<td>1112.63</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>1127.24</td>
<td>1126.19</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>1215.45</td>
<td>1213.85</td>
<td>-</td>
<td>99</td>
</tr>
<tr>
<td>1226.96</td>
<td>1225.14</td>
<td>-</td>
<td>98</td>
</tr>
<tr>
<td>1244.45</td>
<td>1244.50</td>
<td>-</td>
<td>98</td>
</tr>
<tr>
<td>1278.24</td>
<td>-</td>
<td>1282.02</td>
<td>99</td>
</tr>
<tr>
<td>1298.77</td>
<td>1297.98</td>
<td>-</td>
<td>98</td>
</tr>
<tr>
<td>1322.94</td>
<td>1321.08</td>
<td>-</td>
<td>98</td>
</tr>
<tr>
<td>1344.85</td>
<td>1338.81</td>
<td>-</td>
<td>86</td>
</tr>
<tr>
<td>1362.96</td>
<td>1358.16</td>
<td>-</td>
<td>87</td>
</tr>
<tr>
<td>1411.45</td>
<td>1413.41</td>
<td>-</td>
<td>98</td>
</tr>
<tr>
<td>1463.04</td>
<td>1463.38</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>1477.85</td>
<td>1479.46</td>
<td>-</td>
<td>98</td>
</tr>
<tr>
<td>1502.21</td>
<td>1502.10</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>1512.28</td>
<td>1514.96</td>
<td>-</td>
<td>97</td>
</tr>
<tr>
<td>1537.44</td>
<td>-</td>
<td>1543.43</td>
<td>96</td>
</tr>
<tr>
<td>1589.88</td>
<td>1591.18</td>
<td>-</td>
<td>99</td>
</tr>
<tr>
<td>1602.16</td>
<td>1603.60</td>
<td>-</td>
<td>99</td>
</tr>
<tr>
<td>1626.19</td>
<td>1632.68</td>
<td>-</td>
<td>88</td>
</tr>
<tr>
<td>2287.67</td>
<td>-</td>
<td>2293.24</td>
<td>97</td>
</tr>
<tr>
<td>2293.91</td>
<td>-</td>
<td>2297.05</td>
<td>98</td>
</tr>
</tbody>
</table>
Figure B.1. Plots of the interference between the CT1 and CT2 states at different excitation wavelengths using experimental data from Ref. 123.

Figure B.2. Plots of the interference between the CT1 and CT2 states at different excitation wavelengths using B3LYP.
Figure B.3. Plots of the interference between the CT1 and CT2 states at different excitation wavelengths using LC-ωPBE.
Supplementary Information for “Vibronic Coupling Simulations for Linear and Nonlinear Optical Processes: Simulation Results”

C.1 Additional Results for Ammonia

The OPA spectrum is plotted for B3LYP (Fig. C.1(a)) showing highly structured vibronic features. The spacing of those features is $\sim 1000 \text{ cm}^{-1}$ which is on the order of the normal mode frequency of $\nu_2$ (999.79 cm$^{-1}$). This is similar to the observed structure for LC-PBE and CCSD, which is unsurprising because each method yields a very similar transition strength and although there are variations in the dimensionless displacements (Table C.1), they are difficult to resolve using the OPA spectra.

The simulated RRS spectrum from B3LYP is shown in Fig. C.1(b) using an excitation wavelength of 201 nm. Using a 200 cm$^{-1}$ lifetime gives good agreement with experiment, however, the intensity of combination bands is underestimated. The combination bands were also underestimated by LC-PBE and CCSD, indicating that the problem is the harmonic approximation and not the program or the methods used. This is confirmed in Table C.1, where the displacements and property derivatives are similar.

Simulated TPA spectra are shown in Figs. C.3 and C.4. At the present, no experimental TPA spectra are available for NH$_3$, so the comparisons for this molecule will involve only the data from theory. If only the FC term is considered, the TPA spectra look identical to the OPA spectra when compared. In TPA, the HT term contributes around 10-15% of the spectral intensity. This causes the progression in the total spectrum to become much more pronounced and also an increase in the overall spectral intensity. Unlike the OPA spectra where the maximum positive absorbance for the HT term is
Table C.1. Normal modes and frequencies (scaled by 0.98), dimensionless displacements and magnitudes of the transition dipole moment derivatives and two-photon transition moment derivatives for the $1^1A''$ excited state of NH$_3$ for B3LYP, LC-PBE and CCSD. Derivatives are reported with respect to mass-weighted normal coordinates, and in units of a.u. amu$^{-1/2}$ Bohr$^{-1}$.

<table>
<thead>
<tr>
<th>Method</th>
<th>Normal Mode, Frequency (cm$^{-1}$)</th>
<th>$\Delta$</th>
<th>$|\langle \mu^{(0)} \rangle a' |$</th>
<th>$|\langle \delta^{(0)} \rangle a' |$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCSD</td>
<td>$\nu_2$, 980</td>
<td>3.60</td>
<td>0.019</td>
<td>2.026</td>
</tr>
<tr>
<td></td>
<td>$\nu_4$, 1604</td>
<td>0.00</td>
<td>0.122</td>
<td>1.742</td>
</tr>
<tr>
<td></td>
<td>$\nu_4$, 1604</td>
<td>0.00</td>
<td>0.122</td>
<td>1.742</td>
</tr>
<tr>
<td></td>
<td>$\nu_1$, 3392</td>
<td>0.51</td>
<td>0.018</td>
<td>5.018</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$, 3520</td>
<td>0.00</td>
<td>0.320</td>
<td>2.048</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$, 3520</td>
<td>0.00</td>
<td>0.320</td>
<td>2.047</td>
</tr>
<tr>
<td>LC-PBE</td>
<td>$\nu_2$, 980</td>
<td>3.16</td>
<td>0.013</td>
<td>1.460</td>
</tr>
<tr>
<td></td>
<td>$\nu_4$, 1604</td>
<td>0.00</td>
<td>0.130</td>
<td>1.392</td>
</tr>
<tr>
<td></td>
<td>$\nu_4$, 1604</td>
<td>0.00</td>
<td>0.129</td>
<td>1.406</td>
</tr>
<tr>
<td></td>
<td>$\nu_1$, 3392</td>
<td>0.39</td>
<td>0.021</td>
<td>4.777</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$, 3520</td>
<td>0.00</td>
<td>0.273</td>
<td>1.323</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$, 3520</td>
<td>0.00</td>
<td>0.273</td>
<td>1.310</td>
</tr>
<tr>
<td>B3LYP</td>
<td>$\nu_2$, 980</td>
<td>3.34</td>
<td>0.013</td>
<td>1.684</td>
</tr>
<tr>
<td></td>
<td>$\nu_4$, 1604</td>
<td>0.00</td>
<td>0.124</td>
<td>1.805</td>
</tr>
<tr>
<td></td>
<td>$\nu_4$, 1604</td>
<td>0.00</td>
<td>0.124</td>
<td>1.784</td>
</tr>
<tr>
<td></td>
<td>$\nu_1$, 3392</td>
<td>0.38</td>
<td>0.013</td>
<td>5.474</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$, 3520</td>
<td>0.00</td>
<td>0.305</td>
<td>2.187</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$, 3520</td>
<td>0.00</td>
<td>0.305</td>
<td>2.257</td>
</tr>
</tbody>
</table>

About 100 times smaller than that of the FC term, the HT is on the same order of magnitude as the FC term in the TPA spectra. Consequently you can see the increase in $\sigma_{TPA}$ for the total TPA spectrum from each method.

Also, it is noticeable that the bandshape for the TPA HT term differs from that of the OPA HT term. Whereas $\sigma_{OPA}$ relates to the polarizability, $\sigma_{TPA}$ relates to the second-hyperpolarizability. Even though the expressions for the HT terms have a similar appearance for OPA and TPA, the equations defining the respective HT terms for each spectral type are not identical. Although it is tempting to solely use the magnitude of the two-photon transition strength or its derivatives to discuss the importance of the HT term in general, one must be mindful that the lineshape function is mode dependent for the HT term. The lineshape and the derivatives of the linear and quadratic response properties determine the importance of the HT term.

RHRS spectra for NH$_3$ are shown in Fig. C.4. A corresponding experimental RHRS spectrum was shown in Ref. 208 and compared to the RRS spectrum in that same article. In general, the same shortcomings observed in RRS exist for the simulated RHRS spectra.
Figure C.1. Simulated (a) OPA and (b) RRS spectra for NH$_3$ using B3LYP applying a 200 cm$^{-1}$ lifetime.

when in comparison to the experimental RHRS spectrum.
Figure C.2. Simulated B term RRS spectra using (a) CCSD and (b) LC-PBE applying a 200 cm$^{-1}$ lifetime.

Figure C.3. Simulated TPA spectra for NH$_3$ using CCSD and LC-PBE applying a 200 cm$^{-1}$ lifetime.
Figure C.4. Simulated (a) TPA and (b) RHRS spectra for NH$_3$ using B3LYP applying a 200 cm$^{-1}$ lifetime.
Table C.2. Normal modes and frequencies (scaled by 0.98), dimensionless displacements and magnitudes of the transition dipole moment derivatives and two-photon transition moment derivatives for the \( (1^1A_2) n\pi^* \) excited state of \( \text{CH}_2\text{O} \) for B3LYP, LC-PBE and CCSD. Derivatives are reported with respect to mass-weighted normal coordinates, and in units of a.u. \( \text{amu}^{-1/2} \text{Bohr}^{-1} \).

| Method | Normal Mode, Frequency (cm\(^{-1}\)) | \( \Delta \) | \( ||(\mu^{(0)})^\alpha'|| \) | \( ||(\delta^{(0)})^\alpha\beta'|| \) |
|--------|----------------------------------|-----------|----------------|----------------|
| CCSD   | \( \nu_2, 1170 \)               | 0.00      | 0.178          | 1.029          |
|        | \( \nu_1, 1221 \)               | 0.00      | 0.029          | 0.123          |
|        | \( \nu_3, 1483 \)               | 0.28      | 0.000          | 0.054          |
|        | \( \nu_4, 1767 \)               | 1.46      | 0.000          | 0.678          |
|        | \( \nu_5, 2833 \)               | -0.16     | 0.000          | 0.583          |
|        | \( \nu_5, 2900 \)               | 0.00      | 0.174          | 0.941          |
| LC-PBE | \( \nu_2, 1170 \)               | 0.00      | 0.156          | 0.782          |
|        | \( \nu_1, 1221 \)               | 0.00      | 0.031          | 0.116          |
|        | \( \nu_3, 1483 \)               | 0.33      | 0.001          | 0.054          |
|        | \( \nu_4, 1767 \)               | 1.23      | 0.001          | 0.674          |
|        | \( \nu_6, 2833 \)               | -0.17     | 0.000          | 0.521          |
|        | \( \nu_5, 2900 \)               | 0.00      | 0.180          | 0.844          |
| B3LYP  | \( \nu_2, 1170 \)               | 0.00      | 0.178          | 1.078          |
|        | \( \nu_1, 1221 \)               | 0.00      | 0.025          | 0.087          |
|        | \( \nu_3, 1483 \)               | 0.29      | 0.001          | 0.025          |
|        | \( \nu_4, 1767 \)               | 1.33      | 0.000          | 0.906          |
|        | \( \nu_6, 2833 \)               | -0.22     | 0.000          | 0.730          |
|        | \( \nu_5, 2900 \)               | 0.00      | 0.187          | 1.078          |

C.2 Additional Results for Formaldehyde

OPA spectra are shown in Figs. C.5 and C.6. These illustrate the situation where a FC inactive excitation is probed and only the HT term has intensity. Experimentally measured absorbance cross sections for isotopologues of \( \text{CH}_2\text{O} \) yield estimates of 0.001 \( \text{Å}^2 \text{molecule}^{-1} \). Although the present theory does not account for the dissociation of \( \text{CH}_2\text{O} \) when absorbing ultraviolet light and is therefore missing a lot of the features of the experimental absorbance spectrum, it is impressive that the simulations predict the correct magnitude for the peak absorbance cross section. However, the features in the simulated spectra are broader than the measured spectra. Using a smaller homogeneous broadening in the simulations would improve the agreement in the width of the features and cause the intensity to increase. It is likely that CCSD and DFT is overestimating the actual absorbance cross section. Clearly, the intensity of the absorbance is very small in comparison to the previous molecules which had dipole allowed excitations.
Figure C.5. Simulated CH₂O OPA spectra using CCSD and LC-PBE applying a 200 cm⁻¹ lifetime. High resolution experimental spectrum is adapted from Ref. 556 (see also Ref. 557).

Figure C.6. Simulated CH₂O OPA spectra using B3LYP applying a 200 cm⁻¹ lifetime. High resolution experimental spectrum is adapted from Ref. 556 (see also Ref. 557).

TPA spectra are shown in Fig. C.7 for B3LYP. The TPA spectrum from B3LYP is comparable to what was shown for LC-PBE. However the magnitude of the spectrum is overestimated compared to both LC-PBE and CCSD.

RHRS spectra simulated with the parameters from Table C.2 are shown in Fig. C.7. Analogous to the LC-PBE and CCSD RHRS spectra, the B3LYP spectrum is significantly underestimated compared to the NHRS spectrum (on the order of 100 or 1000×10⁻⁶⁴ cm⁴ s photon⁻¹ sr⁻¹). This indicates that neglecting the intermediate vibrational states are included in the sum-over states formalism is not a good approximation for this molecule.
Figure C.7. Simulated (a) TPA and (b) RHRS spectra for CH$_2$O using B3LYP applying a 200 cm$^{-1}$ lifetime.
Table C.3. Normal modes and frequencies (scaled by 0.98), dimensionless displacements and magnitudes of the transition dipole moment derivatives and two-photon transition moment derivatives for the $^1B_2(^1\Sigma^+_u)$ excited state of CS$_2$ for B3LYP, LC-PBE and CCSD. Derivatives are reported with respect mass-weighted normal coordinates, and in units of a.u. amu$^{-1/2}$ Bohr$^{-1}$.

| Method | Normal Mode, Frequency (cm$^{-1}$) | $\Delta$ | $||(|(\mu^{(0)})^{aa'}||$ | $||(|\delta^{(0)}{aa'})||$ |
|--------|----------------------------------|---------|----------------|----------------|
| CCSD   | $\nu_2$, 379                     | 0.00    | 0.000           | 8.717          |
|        | $\nu_2$, 379                     | 0.00    | 0.000           | 8.717          |
|        | $\nu_1$, 657                     | 1.75    | 0.031           | 0.000          |
|        | $\nu_3$, 1518                    | 0.00    | 0.000           | 8.568          |
| LC-PBE | $\nu_2$, 379                     | 0.00    | 0.000           | 6.300          |
|        | $\nu_2$, 379                     | 0.00    | 0.000           | 6.308          |
|        | $\nu_1$, 657                     | 1.58    | 0.012           | 0.000          |
|        | $\nu_3$, 1518                    | 0.00    | 0.000           | 4.321          |
| B3LYP  | $\nu_2$, 379                     | 0.00    | 0.000           | 18.456         |
|        | $\nu_2$, 379                     | 0.00    | 0.000           | 0.102          |
|        | $\nu_1$, 657                     | 1.39    | 0.004           | 0.176          |
|        | $\nu_3$, 1518                    | 0.00    | 0.000           | 4.812          |

C.3 Additional Results for Carbon Disulfide

OPA spectra are shown in Fig. C.8 including both excited states. A large $\sigma_{OPA}$ value is observed for CS$_2$ in the fourth excitation in the simulations which is caused by the large transition dipole moment. It is also interesting that each method predicts the fifth excitation, which is dipole forbidden, gains some intensity based on the nonzero transition dipole moment derivatives. For both excitations the spectrum appears with a large peak and lower intensity progression of peaks.

RRS spectra are shown in Figs. C.8 and C.9 at wavelengths on resonance with the fourth excitation. Each of the spectra is very intense, with cross sections on the order of $10^{-23}$ cm$^2$/sr. A study of the experimental RRS of CS$_2$ estimated the total Raman cross section as $77 \times 10^{-23}$ cm$^2$ for the mode at 653 cm$^{-1}$. For the $\nu_2$ fundamental in the simulations, the differential Raman scattering cross section is on the order of 1-2$ \times 10^{-23}$ cm$^2$/sr, which is clearly underestimated. This in part due to the homogeneous broadening, which is suggested to have the value 13 cm$^{-1}$ in Ref. 445. It was determined previously that the agreement between theory and experiment was partly due to inaccuracies of the XC-functional, and lack of solvent effects. Again, only $\nu_2$ shows activity in the RRS spectra which is intuitive based on the selection rules discussed above. It is also apparent that no combination bands may exist in the spectra because only one mode has a nonzero displacement. A and B term spectra indicate that CS$_2$ is largely an A term.
Table C.4. Normal modes and frequencies (scaled by 0.98), dimensionless displacements and magnitudes of the transition dipole moment derivatives and two-photon transition moment derivatives for the fifth excited state of CS$_2$ for B3LYP, LC-PBE and CCSD. Derivatives are reported with respect mass-weighted normal coordinates, and in units of a.u. amu$^{-1/2}$ Bohr$^{-1}$.

| Method   | Normal Mode, Frequency (cm$^{-1}$) | $\Delta$ | $||((\mu^{(0)})_{a'}^a||$ | $||((\delta^{(0)})_{aa'}^a||$ |
|----------|-----------------------------------|-----------|-----------------------------|-----------------------------|
| CCSD     | $\nu_2$, 379                      | 0.00      | 1.889                       | 0.002                       |
|          | $\nu_2$, 379                      | 0.00      | 1.889                       | 0.001                       |
|          | $\nu_1$, 657                      | 0.86      | 0.000                       | 246.264                     |
|          | $\nu_3$, 1518                     | 0.00      | 0.290                       | 34.479                      |
| LC-PBE   | $\nu_2$, 379                      | 0.00      | 1.647                       | 0.016                       |
|          | $\nu_2$, 379                      | 0.00      | 1.647                       | 0.073                       |
|          | $\nu_1$, 657                      | 1.13      | 0.000                       | 82.075                      |
|          | $\nu_3$, 1518                     | 0.00      | 0.346                       | 193.090                     |
| B3LYP    | $\nu_2$, 379                      | 0.00      | 3.876                       | 0.008                       |
|          | $\nu_2$, 379                      | 0.00      | 3.877                       | 0.010                       |
|          | $\nu_1$, 657                      | 1.16      | 0.027                       | 86.528                      |
|          | $\nu_3$, 1518                     | 0.00      | 0.190                       | 283.284                     |

scatterer, with a large resonance enhancement on the order of 10$^8$.

Similar to what was demonstrated for the OPA spectra (see main text and Fig. C.8), the agreement between the measured and simulated RRS spectra is poor. This is attributed to the harmonic model used in the present work. The broad peaks in the measured RRS spectrum are explained by the low resolution of the instrument used. Both OPA and RRS spectra can be used to obtain complementary information about the vibronic structure in molecules. Significant disagreement in the simulated OPA spectra for CS$_2$ suggests that the agreement in RRS spectra would be poor also. Furthermore, the measured RRS spectrum used an incident wavelength on the red edge of the absorbance peak. The red edge of the absorbance peak was poorly described or missing in simulations using parameters from CCSD and DFT, so precisely matching the measured spectrum is difficult.

TPA spectra shown in Figs. C.10, C.11 and C.12 show that the fourth state is optically dark and the fifth state is bright. This observation is clearly related to data tables presented in this section, where the two-photon transition moment and its derivative are large for the fifth excited state. The spectra establish that when both quantities in the FC and HT term prefactors are large, it is possible that the HT term is on the same order of magnitude or larger than the FC term. Still, based on the discussion of the anharmonicity of the excited states for small molecules, it is likely that the harmonic
model may not accurately describe the fifth excitation. Derivatives of properties for the fourth excitation are much smaller than those of the fifth excitation and therefore the fourth excitation is not observed in TPA. The data in this section are meant only to illustrate what would happen if the FC and HT terms were comparable.

RHRS spectra shown in Figs. C.10, C.11 and C.12 further elaborate on that idea. The spectra show the correct behavior, where modes that are active in RHRS are not active in RRS because CS$_2$ is a centrosymmetric molecule.$^{205,206}$ Observed combination bands involving in the B3LYP spectrum result from a very small displacement for $\nu_2$ (0.002). The RHRS cross sections, which are $\sim 10^{-57}$ cm$^4$ s photon$^{-1}$ sr$^{-1}$, are very large. Because the transition dipole moment or two-photon transition moment cannot be simultaneously nonzero for this system, the A term contributes no intensity. This system shows what can happen when one state is active in the B$_1$ term (fourth state) and another is active in the B$_2$ term (fifth state).

The overall RHRS intensity for CS$_2$ from experiment is estimated as $\sim 10^4$ weaker than the A term scatterer CH$_3$I.$^{208}$ Based on that observation, and the discussion above about the magnitude of the derivatives of the two-photon transition moment, it is likely that the simulated RHRS spectra have largely overestimated intensities. It is also important that the dissociation of CS$_2$ may compete with the scattering and an overall reduction of the RRS and RHRS intensity would result. Even with that in mind, it is clear that CS$_2$ is predicted as a B term scatterer in line with what was rationalized experimentally.
The measured RHRS spectrum of CS$_2$ is dominated by combination bands. Comparison of the simulated spectra to the measured one indicates that the simulated spectra capture none of the features in the measured spectrum. Contributions from $\nu_3$ are absent in the simulated spectra, and the combination bands determined by B3LYP do not match the observed combination bands. Again, this results from using the harmonic model to simulate the spectra and is unsurprising based on the results for the OPA and RRS spectra discussed above.
Figure C.10. Simulated (a) TPA and (b) RHRS spectra for CS$_2$ using CCSD applying a 100 cm$^{-1}$ lifetime. The experimental RHRS spectrum (at 406.16 nm) is adapted from Ref. 208.

Figure C.11. Simulated (a) TPA and (b) RHRS spectra for CS$_2$ using LC-PBE applying a 100 cm$^{-1}$ lifetime. The experimental RHRS spectrum (at 406.16 nm) is adapted from Ref. 208.
Figure C.12. Simulated (a) TPA and (b) RHRS spectra for CS$_2$ using B3LYP applying a 100 cm$^{-1}$ lifetime. The experimental RHRS spectrum (at 406.16 nm) is adapted from Ref. 208.
C.4 Additional Results for p-Nitroaniline

Fig. C.13 shows the frontier molecular orbitals of PNA involved in the second excitation. As shown, the transition shifts electron density from the HOMO, which is more localized on the -NH$_2$ group, to the LUMO that is positioned on the -NO$_2$ group. This state is classified as an intramolecular CT state, with properties summarized in the main text. The data show that LC-PBE positions the excitation 0.52 eV higher than B3LYP, and that B3LYP positions the excitation more closely to the experimental value. The LC-PBE value is reasonable in comparison to studies using configuration interaction and coupled cluster where explicit solvent resulted in a bathochromic shift around 0.3 eV. B3LYP yields a transition strength slightly smaller than LC-PBE, and both underestimate that quantity compared to the experimental estimate (4.36 a.u.). For the two-photon transition strengths B3LYP consistently yields larger values by $\sim$10%.

![Figure C.13. Frontier molecular orbitals of PNA from LC-PBE.](image-url)
Table C.5. Normal mode frequencies (scaled by 0.98), dimensionless displacements and magnitudes of the transition dipole moment derivatives and two-photon transition moment derivatives for the most intense excited state of PNA for B3LYP and LC-PBE. The table shows data for only a portion of the normal modes between 800 and 1700 cm\(^{-1}\). Derivatives are reported with respect to mass-weighted normal coordinates, and in units of a.u. amu\(^{-1/2}\) Bohr\(^{-1}\). Experimentally observed normal mode frequencies and dimensionless displacements are included.\(^{424}\)

| Method | Normal Mode Freq. (cm\(^{-1}\)) | \(\Delta\) | ||\((\mu^{ij}_{0})^{a'}||\) || ||\((\delta^{ij}_{0})^{aa'}||\) | Freq. (cm\(^{-1}\))/\(\Delta^{Exp}\) |
|---------|---------------------------------|----------------|----------------|--------------------|----------------|----------------|----------------|----------------|
| B3LYP   | 811                             | -0.38          | 0.010          | 1.664              | -               | 859/0.88       |
|         | 861                             | 1.07           | 0.059          | 2.081              | -               | 859/0.88       |
|         | 993                             | 0.07           | 0.037          | 0.752              | -               | 1112/0.288     |
|         | 1106                            | -0.39          | 0.304          | 11.824             | -               | 1112/0.288     |
|         | 1172                            | -0.12          | 0.004          | 2.281              | -               | 1112/0.288     |
|         | 1325                            | -0.19          | 0.103          | 9.700              | -               | 1112/0.288     |
|         | 1359                            | 0.53           | 0.488          | 5.950              | 1338/1.433      |
|         | 1505                            | 0.01           | 0.209          | 2.592              | 1498/0.382      |
|         | 1593                            | 0.03           | 0.148          | 4.553              | -               | 1498/0.382     |
|         | 1632                            | -0.07          | 0.364          | 16.619             | 1599/0.496      |
| LC-PBE  | 811                             | -0.26          | 0.023          | 3.217              | -               | 859/0.88       |
|         | 861                             | 1.03           | 0.060          | 2.805              | -               | 859/0.88       |
|         | 993                             | 0.06           | 0.064          | 0.187              | -               | 1112/0.288     |
|         | 1106                            | 0.34           | 0.299          | 5.494              | 1112/0.288      |
|         | 1172                            | -0.07          | 0.015          | 1.636              | -               | 1112/0.288     |
|         | 1325                            | -0.51          | 0.089          | 1.757              | -               | 1112/0.288     |
|         | 1359                            | 1.02           | 0.430          | 8.700              | 1338/1.433      |
|         | 1505                            | 0.25           | 0.160          | 0.690              | 1498/0.382      |
|         | 1593                            | -0.18          | 0.128          | 1.400              | -               | 1498/0.382     |
|         | 1632                            | 0.48           | 0.353          | 5.518              | 1599/0.496      |
Supplementary Information for “Probing One-Photon Inaccessible Electronic States with High Sensitivity: Wavelength Scanned Surface Enhanced Hyper-Raman Scattering”

D.1 Fitting of the Experimental SEHRS Spectra

Peak areas were calculated by fitting each spectrum with multiple Lorentzians and a constant baseline. The fit equations’ accuracy was determined by monitoring the residual; the lower residual produced the more accurate fit. Once the residuals were optimized, the equations were individually integrated to provide the peak areas. Though not used, width is also reported in the output. Figure D.1 shows an example spectrum from 880 nm, with fit data residuals, and sample peak data output.

D.2 Concentration study

To check for the influence of R6G dimers, we recorded SEHRS spectra with concentrations of R6G between $10^{-5}$ and $10^{-10}$ M. No changes in the spectral features were observed, except for a decrease in signal at lower concentrations. The spectra reported in Figure D.1 were taken at a concentration of $10^{-7}$ M; however, we have recorded spectra with concentrations as low as $10^{-10}$ M R6G. Figure D.2 shows a spectrum taken with a Rhodamine 6G concentration of $10^{-10}$ M at 880 nm.
Figure D.1. Comparison of the experimental and fitted spectrum obtained for $\lambda_{ex}=880$ nm.

D.3 Theoretical Methods

Expressions for the one-photon absorption (OPA), two-photon absorption (TPA), and resonance hyper-Raman scattering cross sections are shown in Chapter 5. The parameters $\Gamma_n$ and $\Theta$ are the homogeneous broadening and inhomogeneous broadening, respectively.

The ground state equilibrium geometry and normal modes for the R6G complexes was determined using the B3LYP functional and 6-311G* basis set. Optical properties needed for simulating OPA, including the excited state energies used for determining the dimensionless displacements, were calculated using the TDDFT linear response method in NWChem. $^{334}$ The two-photon transition matrix elements were calculated using quadratic response theory as implemented in the Dalton program. $^{436}$

Simulation parameters for the OPA and TPA spectrum were determined by shifting the peak position and changing the peak width to match the experimental absorbance spectrum using a mixture of homogeneous and inhomogeneous broadening. Peak height was normalized to match the experimental absorbance spectrum by applying a scale factor to the DFT results. This accounts for lack of solvent effects in the calculations and shortcomings in the XC-potential used.

The following parameters were used to simulate the OPA spectrum: $\Gamma_{S_1} = 500$ cm$^{-1}$,
Figure D.2. SEHRS of R6G on Ag [R6G]=10^{-10} M at 880 nm. Raw data (left) and baseline corrected data (right).

Γ_{S_2} = 1400 \text{ cm}^{-1}, \Gamma_{S_1} = 625 \text{ cm}^{-1}, \Theta = 0 \text{ cm}^{-1}, \text{ and a scale factor of 1.59. For the TPA spectrum we used: } \Gamma_{S_1} = 600 \text{ cm}^{-1}, \Gamma_{S_2} = 400 \text{ cm}^{-1}, \Gamma_{S_3} = 625 \text{ cm}^{-1}, \Theta = 0 \text{ cm}^{-1}, \text{ and a scale factor of 37.9. We also found that it was necessary to scale the S_2 state two-photon transition moment by an additional factor of 1.5.}

The differential hyper-Raman scattering cross section is given by Equation D.1.\(^{24}\)

\[
\frac{d\sigma}{d\Omega} = \frac{16\pi^2h^3\alpha^3\nu_s^4P_i}{Nc^2e^6} \langle \beta_{\alpha\beta\gamma} \rangle
\]  
\text{(D.1)}

where \(\alpha\) is the fine structure constant, \(\nu_s\) is the frequency of the scattered radiation, \(P_i\) is the population of the initial vibrational state, \(N\) is the number of scatters per unit volume, \(h\) is Planck’s constant, \(c\) is the speed of light, and \(\beta_{\alpha\beta\gamma}\) is the hyperpolarizability. The \(\langle \rangle\) indicates that the hyperpolarizability tensors were obtained assuming averaging over all orientations of the molecule with respect to the incident light.\(^{408}\)

Away from strong resonances the hyperpolarizability can be written using geometric derivatives of the electronic hyperpolarizability as in Equation D.2.\(^{408}\)

\[
\beta_{\alpha\beta\gamma} = b_{\nu_a}^\prime \beta_{\alpha\beta\gamma}^e = \sqrt{\frac{h}{8\pi^2c\nu_a}} \frac{\partial \beta_{\alpha\beta\gamma}^e}{\partial Q_a}
\]  
\text{(D.2)}

where \(Q_a\) is the normal mode with vibrational frequency \(\nu_a\). The hyperpolarizability
derivatives needed to simulate the off resonance hyper-Raman spectrum were calculated from using three-point finite-differentiation of the static hyperpolarizability. These calculations were done using the response module of the ADF program.\textsuperscript{558} We used the BP86 XC-functional and a TZP basis set. We also include the off resonance hyper-Raman spectrum calculated with Dalton2011,\textsuperscript{559} using the B3LYP XC-functional and a 6-311G* basis set.

D.4 Comparison of Theory and Experiment

To understand in more detail the SEHRS spectra of R6G we calculated the off-resonance hyper-Raman spectra using TDDFT. The comparison between the simulated off-resonance spectra with the experimental SEHRS spectrum obtained at 1050 nm is presented in Figure D.3. Overall we see that there is a good agreement between the simulated and measured spectra, both with respect to band positions and intensities. However, there are some noticeable differences between the simulated spectra and that measured experimentally. For example, in the simulations, the 1315 band is the strongest whereas experimentally it is the band at 1535. This is most likely due to the neglect of surface and resonance effects in the simulations. Despite these differences, the good agreement enabled a detailed assignment of the experimental spectrum. As we discuss in the manuscript the good agreement results because the hyper-Raman spectrum of R6G is dominated by the off-resonance spectrum.
Figure D.3. Simulated off-resonance hyper-Raman spectrum using BP86 (top) and B3LYP (middle), and experimental SEHRS spectrum obtained at 1050 nm (bottom).
Supplementary Information for “Probing Two-Photon Properties of Molecules: Large Non-Condon Effects Dominate the Resonance Hyper-Raman Scattering of Rhodamine 6G”

E.1 Experimental Methods

E.1.1 Experimental Set-up

The Raman and hyper Raman experiments were carried out with a Ti:sapphire laser (Tsunami, Spectra-Physics) that is pumped with a 532 nm Nd:YAG laser (Millenium XV, Spectra-Physics). The wavelength range of the Ti:sapphire is 690 - 1050 nm, and it generates a 5 ps pulse (as measured with an autocorrelator) at a rate of 81 MHz. For most wavelengths, the output can be modulated between 0.3 and 3 Watts using a half-wave plate and Glan polarizer (Thorlabs). Vertical polarization is then doubled in a frequency doubler (Spectra-Physics), and the horizontal polarization is converted to vertical polarization with a periscope before it is used to excite the sample. The beam is then sent into an inverted microscope (Ti-U, Nikon) where a dichroic mirror reflects the excitation beam through any of two objectives (20× or 60×) which is focused on the sample. The objective collects the back-scattered light, transmitting it through the dichroic, and then either through the eyepiece, a NIR camera (UM-300, Uniq Vision), or to a spectrometer (Acton, Princeton Instruments) with a back-lit CCD LN-cooled detector (PIXIS 100, Princeton Instruments). The Raman spectrum of liquid cyclohexane was used to calibrate the spectrometer at 440 nm, and this calibration was used to set the calibration of rhodamine 6G at a 880 nm excitation.
E.1.2 Nanoparticle cluster synthesis

Silver nanoparticles are synthesized using the citrate reduction method specified by Lee and Meisel. Specifically, nanoparticles were experimentally determined to be SEHRS active when both the silver nitrate and sodium citrate are at the same concentration \((1 \times 10^{-3} \text{ M})\) when creating the nanoparticles. The nanoparticle extinction spectrum has a maximum at 498 nm.

E.1.3 RHR measurements

For the solution hyper Raman measurements, an aqueous solution of rhodamine 6G is prepared at \(10^{-4} \text{ M}\). This solution was placed in a quartz cuvette, into which 0.5 W of 825 nm light was focused through a 60× objective (Nikon, NA = 0.8). Total acquisition time is 60 minutes.

E.1.4 SEHRS measurements

Rhodamine 6G is added to the nanoparticle sample at a concentration of about \(10^{-7}\) M, unless specified otherwise. After approximately one hour, a small amount of sodium chloride solution (0.1 M) is added to the colloids to force them to aggregate. Immediately after adding the sodium chloride, the colloids change to a darker color and 24 hours after the addition all of the aggregates precipitate out of solution. With agitation, the nanoparticles continue to aggregate into “clusters” which are large enough to see with the naked eye. For the SEHRS measurements, \(\sim 3 \text{ mW}\) of 825 nm radiation is focused through a 20× objective (Nikon, NA = 0.5) on a single nanoparticle cluster. The total acquisition time is 120 seconds.

E.2 Theoretical Methods

The theoretical spectra were simulated using the time-dependent formalism for spectroscopy. Equations for simulations in Chapter 8 are shown in Chapter 5.

The ground state equilibrium geometry and normal modes for the R6G complexes was determined using the B3LYP functional and 6-311G* basis set in NWChem. Optical properties needed for simulating TPA and the resonance hyper-Raman scattering were calculated using linear and quadratic response theory as implemented in the Dalton
Simulation parameters for the OPA and TPA spectrum were determined by shifting the peak position and changing the peak width to match the experimental absorbance spectrum using a mixture of homogeneous and inhomogeneous broadening. Peak height was normalized for the $S_3$ state to match the experimental absorbance spectrum by applying a scale factor to the DFT results. This accounts for lack of solvent effects in the calculations and shortcomings in the XC-potential used.

The following parameters were used to simulate the TPA and resonance hyper-Raman spectra: $\Gamma_{S_1} = 600$ cm$^{-1}$, $\Gamma_{S_2} = 400$ cm$^{-1}$, $\Gamma_{S_3} = 550$ cm$^{-1}$, $\Theta = 0$ cm$^{-1}$ (no inhomogeneous broadening), and a scale factor of 1.432 (to normalize the most intense feature of the TPA spectrum to the experimental spectrum). Intensity scaling was not performed on the RHRS spectra. The $S_1$, $S_2$, and $S_3$ states of R6G calculated with B3LYP/6-311G* were repositioned from their calculated values. A collective shift of all three states was not possible, so each state was shifted so that a direct wavelength comparison between experimental and simulated spectra could be performed.

The OPA and TPA transition dipole moment calculated using B3LYP/aug-cc-pVDZ for para-nitroaniline were found to be 3.49 a.u. and 2029.15 a.u., respectively. This leads to a RHRS cross section of $4.1 \times 10^{-58}$ cm$^4$ s photon$^{-1}$ sr$^{-1}$ on resonance with this state.

### E.3 Interference effects

Generally, interference in the present model results from three contributions: the sign of the transition moments $\mu^{0k}$ and $S^{0k}$ and their derivatives, the sign/phase of the vibronic contribution to the integrals (nuclear overlap integrals), and detuning from resonance. The former effect is illustrated in the main text, along with Ref. S8. Depending on the incident photon frequency relative to the excitation energy, the exponential term in the integral (corresponding to the denominator in the sum-over-states formula) can be positive or negative, causing interference from detuning. Noting that the hyperpolarizability can be written as: $\beta = A + B_1 + B_2$, and that the RHRS intensity can be written $I^{RHRS} \propto |\beta|^2$, it is evident that numerous cross terms exist regardless of whether one or several excited states are used in the simulation. Because the vibronic contribution to the A and B terms in RHRS are different, it is possible that negative signs result from the different cross terms. Note that this effect is not separable from the detuning, and therefore is always present in the simulation when the A and B terms are included.
In Figure E.2, spectra are shown illustrating the different contributions from the sum of the A and B terms for the three excited states of R6G plus an interference term. The interference contribution is calculated as prescribed in Ref. S8. In this case, the interference solely accounts for the increase or decrease in the differential hyper-Raman cross section resulting from cross terms between different excited states. We focus on the B terms in particular because they are most important to the total magnitude of the interference.

Figures E.2(a) and (b) show the total RHRS spectrum at 825 nm and 1046 nm, respectively. Using the results from first principles calculations for the signs of transition moments and their derivatives, the sign of the interference is positive at 825 nm (constructive interference) and negative at 1046 nm (destructive interference). Comparing Figures E.2(a) and (c), it is clear that when only the B_2 term from the S_1 state and B_1 term from the S_2 state are included at 825 nm, the majority of the total intensity of the spectrum and interference are recovered. Quantitatively, $1.96 \times 10^{-58} \text{cm}^4 \text{s photon}^{-1} \text{sr}^{-1}$ (76%) of the interference is accounted for by those terms at 825 nm. When the orientation of the transition dipole moment derivative for the mode at 1535 cm$^{-1}$ is changed to parallel with S_20 (Figure E.2(e)), the sign of the interference for that mode is reversed. This effect is reproducible as shown in Figures S1(b), (d), and (f) simulated at 1046 nm. Peaks that are present in Figure E.2(b) and absent in (d) result from the A term for the S_1 state. In comparing the two figures it is observed that the dominant interference results from the B_2 term from the S_1 state and B_1 term from the S_2 state at 1046 nm.

Figure E.2 shows the contribution of each excited state to the total RHRS intensity, along with the interference, at four wavelengths. The incident wavelengths are: 1046 nm (9560 cm$^{-1}$), 894 nm (11186 cm$^{-1}$), 825 nm (12121 cm$^{-1}$), and 791 nm (12642 cm$^{-1}$). For these simulations, the orientation of the transition moments and their derivatives are held constant at their first principles calculated values. As can be seen in the figure, transitioning from the red-edge of an absorbance peak to the blue edge (i.e. going from 1046 to 894 nm or 825 to 791 nm) causes the sign of the interference to change. This confirms that the detuning effect is also important for examining the interference effects in R6G.
Figure E.1. Relative contributions of the $S_1$ (red line), $S_2$ (green line), and $S_3$ (blue line) states to the total RHRS intensity (black line). Also shown is the magnitude and sign of the interference (purple line). (a) and (b) show simulation results at 825 nm and 1046 nm with the sign of the transition moments and their derivatives based on first principles calculations. (c) shows the total intensity derived from the $B_2$ term of the $S_1$ state and $B_1$ term of the $S_2$ state at 825 nm, along with individual contributions from those terms and interference between them. (d) uses the same terms as (c), except with a wavelength of 1046 nm. (e) and (f) are identical to (c) and (d), respectively, but have the derivative of the transition dipole moment along the 1535 cm$^{-1}$ mode oriented parallel to $S_{20}$. 
Figure E.2. Relative contributions of the A+B terms of each excited state and the interference to the total RHRS differential cross sections at four wavelengths. Colors are identical to the plots shown in Figure E.1.
Supplementary Information for “Investigation of Linear and Nonlinear Raman Scattering for Isotopologues of Ru(bpy)$_3^{2+}$”

This document contains the following tables:

1. F.1 - excitation energies, one-photon and two-photon transition strengths for the lowest 10 singlet excited states.
2. F.2 - Full-width at half maximum, vibrational reorganization energies, and solvent reorganization energies for the lowest 10 singlet excited states.
3. F.3 - Dimensionless displacements for the the most important normal modes in the resonance Raman spectrum of Rubpy.
4. F.4 - Dimensionless displacements for the the most important normal modes in the resonance Raman spectrum of Rubpy-d24.
5. F.5 - Assignments of the $S_5/S_6 \leftarrow S_0$ and $S_7/S_8 \leftarrow S_0$ transitions with B3LYP.
6. F.6 - Assignments of the $S_5/S_6 \leftarrow S_0$ and $S_7/S_8 \leftarrow S_0$ transitions with LC-PBE.
7. F.1 - Frontier orbitals involved in the $S_5/S_6 \leftarrow S_0$ and $S_7/S_8 \leftarrow S_0$ transitions with B3LYP.
8. F.2 - Frontier orbitals involved in the $S_5/S_6 \leftarrow S_0$ and $S_7/S_8 \leftarrow S_0$ transitions with LC-PBE.
Table F.1. Unshifted vertical electronic excitation energies, one-photon \((M^{k0})^2\) and two-photon \(\delta_{TPA}^{k0}\) transition strengths.

<table>
<thead>
<tr>
<th>State</th>
<th>B3LYP</th>
<th></th>
<th></th>
<th></th>
<th>LC-PBE</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(E^{k0}) (eV)</td>
<td>((M^{k0})^2)</td>
<td>(\delta_{TPA}^{k0})</td>
<td></td>
<td>(E^{k0}) (eV)</td>
<td>((M^{k0})^2)</td>
<td>(\delta_{TPA}^{k0})</td>
<td></td>
</tr>
<tr>
<td>(S_1)</td>
<td>2.62</td>
<td>0.018</td>
<td>1.22</td>
<td></td>
<td>3.28</td>
<td>0.002</td>
<td>94.80</td>
<td></td>
</tr>
<tr>
<td>(S_2)</td>
<td>2.63</td>
<td>0.001</td>
<td>72.10</td>
<td></td>
<td>3.28</td>
<td>0.001</td>
<td>94.80</td>
<td></td>
</tr>
<tr>
<td>(S_3)</td>
<td>2.63</td>
<td>0.001</td>
<td>73.20</td>
<td></td>
<td>3.32</td>
<td>0.020</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>(S_4)</td>
<td>2.81</td>
<td>0.002</td>
<td>0.01</td>
<td></td>
<td>3.50</td>
<td>0.001</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>(S_5)</td>
<td>2.83</td>
<td>0.122</td>
<td>65.60</td>
<td></td>
<td>3.52</td>
<td>1.069</td>
<td>449.00</td>
<td></td>
</tr>
<tr>
<td>(S_6)</td>
<td>2.83</td>
<td>0.124</td>
<td>66.80</td>
<td></td>
<td>3.52</td>
<td>1.043</td>
<td>440.00</td>
<td></td>
</tr>
<tr>
<td>(S_7)</td>
<td>2.97</td>
<td>1.396</td>
<td>683.00</td>
<td></td>
<td>3.55</td>
<td>0.590</td>
<td>196.00</td>
<td></td>
</tr>
<tr>
<td>(S_8)</td>
<td>2.97</td>
<td>1.398</td>
<td>686.00</td>
<td></td>
<td>3.55</td>
<td>0.543</td>
<td>178.00</td>
<td></td>
</tr>
<tr>
<td>(S_9)</td>
<td>3.17</td>
<td>0.000</td>
<td>2160.00</td>
<td></td>
<td>3.77</td>
<td>0.081</td>
<td>59.40</td>
<td></td>
</tr>
<tr>
<td>(S_{10})</td>
<td>3.45</td>
<td>0.070</td>
<td>0.00</td>
<td></td>
<td>3.77</td>
<td>0.080</td>
<td>57.80</td>
<td></td>
</tr>
</tbody>
</table>
Table F.2. Simulation parameters for the lineshape function in cm$^{-1}$. The electronic homogeneous FWHM parameters for each state is given, where the dimensionless lineshape parameter was set at a constant 0.10 for all states. Vibrational ($\lambda_{vib}$) and solvent ($\lambda_{solv}$) reorganization energies are also reported.

<table>
<thead>
<tr>
<th>State</th>
<th>$\Gamma_{k}^{FWHM}$</th>
<th>$\lambda_{vib}$ Rubpy</th>
<th>$\lambda_{vib}$ Rubpy-d24</th>
<th>$\lambda_{solv}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_1$</td>
<td>800</td>
<td>565</td>
<td>559</td>
<td>287</td>
</tr>
<tr>
<td>$S_2$</td>
<td>800</td>
<td>551</td>
<td>580</td>
<td>287</td>
</tr>
<tr>
<td>$S_3$</td>
<td>800</td>
<td>504</td>
<td>496</td>
<td>287</td>
</tr>
<tr>
<td>$S_4$</td>
<td>800</td>
<td>417</td>
<td>417</td>
<td>287</td>
</tr>
<tr>
<td>$S_5$</td>
<td>800</td>
<td>426</td>
<td>419</td>
<td>287</td>
</tr>
<tr>
<td>$S_6$</td>
<td>800</td>
<td>435</td>
<td>449</td>
<td>287</td>
</tr>
<tr>
<td>$S_7$</td>
<td>1600</td>
<td>376</td>
<td>371</td>
<td>1146</td>
</tr>
<tr>
<td>$S_8$</td>
<td>1600</td>
<td>380</td>
<td>390</td>
<td>1146</td>
</tr>
<tr>
<td>$S_9$</td>
<td>800</td>
<td>306</td>
<td>306</td>
<td>287</td>
</tr>
<tr>
<td>$S_{10}$</td>
<td>800</td>
<td>402</td>
<td>398</td>
<td>287</td>
</tr>
<tr>
<td>LC-PBE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_1$</td>
<td>800</td>
<td>685</td>
<td>755</td>
<td>287</td>
</tr>
<tr>
<td>$S_2$</td>
<td>800</td>
<td>686</td>
<td>753</td>
<td>287</td>
</tr>
<tr>
<td>$S_3$</td>
<td>800</td>
<td>822</td>
<td>905</td>
<td>287</td>
</tr>
<tr>
<td>$S_4$</td>
<td>800</td>
<td>620</td>
<td>673</td>
<td>287</td>
</tr>
<tr>
<td>$S_5$</td>
<td>1450</td>
<td>640</td>
<td>697</td>
<td>942</td>
</tr>
<tr>
<td>$S_6$</td>
<td>1450</td>
<td>640</td>
<td>705</td>
<td>942</td>
</tr>
<tr>
<td>$S_7$</td>
<td>2500</td>
<td>445</td>
<td>496</td>
<td>2799</td>
</tr>
<tr>
<td>$S_8$</td>
<td>2500</td>
<td>451</td>
<td>509</td>
<td>2799</td>
</tr>
<tr>
<td>$S_9$</td>
<td>800</td>
<td>841</td>
<td>1264</td>
<td>287</td>
</tr>
<tr>
<td>$S_{10}$</td>
<td>800</td>
<td>848</td>
<td>1260</td>
<td>287</td>
</tr>
</tbody>
</table>
Table F.3. Experimental and theoretical normal mode frequencies (scaled by 0.98 from B3LYP values), and dimensionless displacements for the 8 most important normal modes of Rubpy.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Exp. Freq. (cm$^{-1}$)</th>
<th>B3LYP Freq. (cm$^{-1}$)</th>
<th>$\Delta_{B3LYP}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(S_5, S_6), (S_7, S_8)$</td>
</tr>
<tr>
<td>1</td>
<td>673</td>
<td>664</td>
<td>(-0.37, -0.37), (-0.43, -0.43)</td>
</tr>
<tr>
<td>2</td>
<td>1027</td>
<td>1030</td>
<td>(-0.12, -0.12), (-0.07, -0.06)</td>
</tr>
<tr>
<td>3</td>
<td>1174</td>
<td>1183</td>
<td>( 0.24, 0.24), ( 0.19, 0.19)</td>
</tr>
<tr>
<td>4</td>
<td>1272</td>
<td>1284</td>
<td>( 0.12, 0.15), ( 0.04, 0.04)</td>
</tr>
<tr>
<td>5</td>
<td>1320</td>
<td>1310</td>
<td>(-0.37, -0.31), (-0.33, -0.30)</td>
</tr>
<tr>
<td>6</td>
<td>1492</td>
<td>1491</td>
<td>(-0.40, -0.44), (-0.36, -0.38)</td>
</tr>
<tr>
<td>7</td>
<td>1565</td>
<td>1571</td>
<td>(-0.28, -0.30), (-0.27, -0.28)</td>
</tr>
<tr>
<td>8</td>
<td>1609</td>
<td>1608</td>
<td>( 0.14, 0.15), ( 0.19, 0.20)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mode</th>
<th>Exp. Freq. (cm$^{-1}$)</th>
<th>B3LYP Freq. (cm$^{-1}$)</th>
<th>$\Delta_{LC-PBE}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(S_5, S_6), (S_7, S_8)$</td>
</tr>
<tr>
<td>1</td>
<td>673</td>
<td>664</td>
<td>(-0.28, -0.28), (-0.46, -0.46)</td>
</tr>
<tr>
<td>2</td>
<td>1027</td>
<td>1030</td>
<td>(-0.23, -0.23), (-0.04, -0.04)</td>
</tr>
<tr>
<td>3</td>
<td>1174</td>
<td>1183</td>
<td>( 0.32, 0.32), ( 0.26, 0.26)</td>
</tr>
<tr>
<td>4</td>
<td>1272</td>
<td>1284</td>
<td>( 0.33, 0.33), ( 0.22, 0.23)</td>
</tr>
<tr>
<td>5</td>
<td>1320</td>
<td>1310</td>
<td>(-0.45, -0.44), (-0.37, -0.35)</td>
</tr>
<tr>
<td>6</td>
<td>1492</td>
<td>1491</td>
<td>(-0.54, -0.54), (-0.42, -0.43)</td>
</tr>
<tr>
<td>7</td>
<td>1565</td>
<td>1571</td>
<td>(-0.28, -0.28), (-0.24, -0.25)</td>
</tr>
<tr>
<td>8</td>
<td>1609</td>
<td>1608</td>
<td>( 0.11, 0.11), ( 0.11, 0.11)</td>
</tr>
</tbody>
</table>
Table F.4. Experimental and theoretical normal mode frequencies (scaled by 0.98 from B3LYP values), and dimensionless displacements for the 9 most important normal modes of Rubpy-d24.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Exp. Freq. (cm$^{-1}$)</th>
<th>B3LYP Freq. (cm$^{-1}$)</th>
<th>$\Delta_{B3LYP}$ $(S_5, S_6), (S_7, S_8)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>643</td>
<td>637</td>
<td>(0.35, 0.35), (0.41, 0.41)</td>
</tr>
<tr>
<td>2</td>
<td>849</td>
<td>851</td>
<td>(0.24, 0.24), (0.22, 0.22)</td>
</tr>
<tr>
<td>3</td>
<td>1005</td>
<td>1009</td>
<td>(0.08, 0.08), (0.02, 0.02)</td>
</tr>
<tr>
<td>4</td>
<td>1201</td>
<td>1200</td>
<td>(0.24, 0.22), (0.20, 0.19)</td>
</tr>
<tr>
<td>5</td>
<td>1259</td>
<td>1260</td>
<td>(-0.06, -0.05), (-0.10, -0.10)</td>
</tr>
<tr>
<td>6</td>
<td>1303</td>
<td>1308</td>
<td>(-0.06, -0.06), (0.03, 0.03)</td>
</tr>
<tr>
<td>7</td>
<td>1426</td>
<td>1418</td>
<td>(-0.44, -0.49), (-0.39, -0.41)</td>
</tr>
<tr>
<td>8</td>
<td>1527</td>
<td>1531</td>
<td>(0.37, 0.38), (0.34, 0.34)</td>
</tr>
<tr>
<td>9</td>
<td>1573</td>
<td>1568</td>
<td>(-0.20, -0.21), (-0.25, -0.26)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mode</th>
<th>Exp. Freq. (cm$^{-1}$)</th>
<th>B3LYP Freq. (cm$^{-1}$)</th>
<th>$\Delta_{LC-PBE}$ $(S_5, S_6), (S_7, S_8)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>643</td>
<td>637</td>
<td>(0.32, 0.32), (0.47, 0.47)</td>
</tr>
<tr>
<td>2</td>
<td>849</td>
<td>851</td>
<td>(0.32, 0.32), (0.29, 0.29)</td>
</tr>
<tr>
<td>3</td>
<td>1005</td>
<td>1009</td>
<td>(0.17, 0.17), (0.02, 0.02)</td>
</tr>
<tr>
<td>4</td>
<td>1201</td>
<td>1200</td>
<td>(0.33, 0.33), (0.27, 0.26)</td>
</tr>
<tr>
<td>5</td>
<td>1259</td>
<td>1260</td>
<td>(0.03, 0.03), (0.02, 0.02)</td>
</tr>
<tr>
<td>6</td>
<td>1303</td>
<td>1308</td>
<td>(-0.20, -0.20), (-0.09, -0.09)</td>
</tr>
<tr>
<td>7</td>
<td>1426</td>
<td>1418</td>
<td>(-0.65, -0.65), (-0.50, -0.51)</td>
</tr>
<tr>
<td>8</td>
<td>1527</td>
<td>1531</td>
<td>(0.40, 0.41), (0.34, 0.34)</td>
</tr>
<tr>
<td>9</td>
<td>1573</td>
<td>1568</td>
<td>(-0.15, -0.15), (-0.15, -0.15)</td>
</tr>
</tbody>
</table>
Table F.5. Assignments of the S₅/S₆ ← S₀ and S₇/S₈ ← S₀ transitions of Rubpy using B3LYP. Only transitions with a 10% or larger contribution are listed (H = HOMO, L = LUMO).

<table>
<thead>
<tr>
<th>State</th>
<th>Orbitals Involved</th>
<th>% Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>H-2→L</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>H-1→L</td>
<td>29</td>
</tr>
<tr>
<td>6</td>
<td>H-2→L</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>H-1→L</td>
<td>49</td>
</tr>
<tr>
<td>7</td>
<td>H-2→L</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>H-2→L+2</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>H-1→L</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>H-1→L+1</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>H-1→L+2</td>
<td>27</td>
</tr>
<tr>
<td>8</td>
<td>H-2→L</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>H-2→L+1</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>H-2→L+2</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>H-1→L+1</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>H-1→L+2</td>
<td>11</td>
</tr>
</tbody>
</table>

Table F.6. Assignments of the S₅/S₆ ← S₀ and S₇/S₈ ← S₀ transitions of Rubpy using LC-PBE. Only transitions with a 10% or larger contribution are listed (H = HOMO, L = LUMO)

<table>
<thead>
<tr>
<th>State</th>
<th>Orbitals Involved</th>
<th>% Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>H-1→L</td>
<td>92</td>
</tr>
<tr>
<td>6</td>
<td>H-2→L</td>
<td>92</td>
</tr>
<tr>
<td>7</td>
<td>H-2→L+1</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>H-2→L+2</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>H-1→L+1</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>H-1→L+2</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>H→L+12</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>H-2→L+1</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>H-2→L+2</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>H-1→L+1</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>H-1→L+2</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>H→L+11</td>
<td>10</td>
</tr>
</tbody>
</table>
Figure F.1. Frontier orbitals involved in the $S_5/S_6 \leftarrow S_0$ and $S_7/S_8 \leftarrow S_0$ transitions using B3LYP.
Figure F.2. Frontier orbitals involved in the $S_5/S_6 \leftarrow S_0$ and $S_7/S_8 \leftarrow S_0$ transitions using LC-PBE.
Derivation of Linear Response Equations in Time-Dependent Density Functional Theory

G.1 Classical Linear Response Theory

Before pursuing the quantum mechanical version of linear response theory, it is beneficial to derive expressions for the classical response of system to with respect to a mechanical force (i.e. an electric field). This derivation follows from chapter 11 of Ref. 560. The reason for this is twofold. First, the expressions used in classical linear response theory are relatively simple, so we can obtain a lot of information without too much time spent on the derivation. Second, the relationships between different quantities in classical linear response theory allow us to concretely define different variables by a physical meaning. This latter point is important because the quantum expressions are necessarily complicated and it is easy to become overwhelmed in notation. Before the derivation, some definitions of important quantities in this section must be given.

Using statistical mechanics (the basis of classical linear response theory), it is possible to describe systems at thermodynamic equilibrium. It is our goal to investigate a system that deviates slightly from equilibrium, and quantify the response of the system to an applied perturbation. This perturbation can be either static or time-dependent. However, the perturbation is assumed to be “weak,” which is a term we will detail in the next section when making a mathematical connection to the description of linear response. Being more succinct, linear response theory is a perturbative expansion about equilibrium where only the linear terms of the perturbation are used.

In order to quantify linear response, we start by assuming that our system is described by a Hamiltonian $\hat{H}_0$. In the presence of an external perturbation (force), the Hamiltonian
changes to $\hat{H} = \hat{H}_0 + \hat{H}_1$, where the perturbation $\hat{H}_1$ is of the form $\hat{H}_1(t) = -\hat{A}F(t)$. Here, $F(t)$ is the external force (possibly time-dependent) and $\hat{A}$ is an operator that represents a dynamical variable $A(r^N, p^N)$ that couples to the force, which is a function of all positions ($r^N$) and momenta ($p^N$) of the particles of the system ($N$ is the number of particles). If, for instance, we have an external electric field $\varepsilon(t)$ perturbing a one-dimensional classical system involving one particle with charge $q$, $\hat{H}_1(t) = -qx\varepsilon(t)$, or $\hat{A} = \hat{x} = x$ and $F(t) = q\varepsilon(t)$. We can also have a sum of these external perturbations, but we will restrict our attention to a single perturbation for simplicity. For a dynamical variable $B(r^N, p^N)$ (quantum mechanically represented by operator $\hat{B}$), we want to characterize the expectation value of the change in $B$, $\langle \Delta B \rangle$, caused by the perturbation.

Physically, linear response theory seeks to quantify the linear relationship between the small force $F(t)$ and the response $\langle \Delta B \rangle$.

G.1.1 Static Response

Now we’ll focus on the response of a system to a static perturbation, where we may write $F(t) = F$. For this case, we are trying to determine $\langle \Delta B \rangle = \langle B \rangle - \langle B \rangle_0$, which is given by ($\beta = 1/k_BT$, with $\langle B \rangle$ as the expectation value of $B$ for the full Hamiltonian and $\langle B \rangle_0$ as the expectation value of $B$ for $\hat{H}_0$)

$$\langle B \rangle_0 = \frac{\int r^N \int p^N B e^{-\beta H_0}}{\int r^N \int p^N e^{-\beta H_0}} \quad \text{(G.1)}$$

$$\langle B \rangle = \frac{\int r^N \int p^N B e^{-\beta(H_0+H_1)}}{\int r^N \int p^N e^{-\beta(H_0+H_1)}} \quad \text{(G.2)}$$

For a brief introduction to the concepts of the expectation value in statistical mechanics, see chapter 1 of Ref. 561 or chapters 2 and 3 of Ref. 562. Here, we use the fact that the perturbation is weak ($\beta H_1 \ll 1 \leq \beta H_0$) and expand the exponential to first order in the perturbation

$$e^{-\beta(H_0+H_1)} = e^{-\beta H_0}(1 - \beta H_1) \quad \text{(G.3)}$$

We follow Nitzan’s book and define the shorthand notation in the following, where $\int r^N \int p^N = \int \int$. Hence,
\[ \langle B \rangle = \frac{\int \int Be^{-\beta H_0}(1 - \beta H_1)}{\int \int e^{-\beta H_0}(1 - \beta H_1)} \]
\[ = \frac{\int \int Be^{-\beta H_0}(1 - \beta H_1)}{\int \int e^{-\beta H_0}} \left[ \frac{\int \int e^{-\beta H_0}}{\int \int e^{-\beta H_0}} \right] \]
\[ = \frac{\langle B \rangle_0 - \beta \langle BH_1 \rangle_0}{1 - \beta \langle H_1 \rangle_0} \left[ 1 + \beta \langle H_1 \rangle_0 \right] \]
\[ = \frac{\langle B \rangle_0 - \beta \langle BH_1 \rangle_0(1 + \beta \langle H_1 \rangle_0)}{1 - \beta^2 \langle H_1 \rangle_0^2} \] (G.4)
\[ = (\langle B \rangle_0 - \beta \langle BH_1 \rangle_0)(1 + \beta \langle H_1 \rangle_0) \]
\[ = \langle B \rangle_0 + \beta \langle B \rangle_0 \langle H_1 \rangle_0 - \beta \langle BH_1 \rangle_0 - \beta^2 \langle BH_1 \rangle_0 \langle H_1 \rangle_0 \]
\[ = \langle B \rangle_0 + \beta \langle B \rangle_0 \langle H_1 \rangle_0 - \beta \langle BH_1 \rangle_0 - \beta^2 \langle BH_1 \rangle_0 \langle H_1 \rangle_0 \]

We used the fact that the perturbation is weak to eliminate the dependence of the expectation value on \(\beta^2 \langle H_1 \rangle_0^2\). The final term in Eq. G.4 can be neglected because it is proportional to \(H_1^2\) (i.e. it is nonlinear). We can now determine the linear response as (keep in mind that \(H_1 = -AF\))

\[ \langle \Delta B \rangle = \langle B \rangle - \langle B \rangle_0 \]
\[ = \langle B \rangle_0 + \beta \langle B \rangle_0 \langle H_1 \rangle_0 - \beta \langle BH_1 \rangle_0 - \langle B \rangle_0 \]
\[ = -\beta (\langle BH_1 \rangle_0 - \langle B \rangle_0 \langle H_1 \rangle_0) = -\beta (\langle AFB \rangle_0 - \langle B \rangle_0 \langle AF \rangle_0) \]
\[ = -\beta F (\langle AB \rangle_0 - \langle A \rangle_0 \langle B \rangle_0) = -\beta F \langle \delta A \delta B \rangle_0 = \chi_{AB} F \] (G.5)

In Eq. G.5, we have defined the linear response function \(\chi_{AB} = -\beta \langle \delta A \delta B \rangle_0\), which is a correlation function of the fluctuations in \(A\) and \(B\). Intuitively, if the perturbing force, which contains observable \(A\), is strongly coupled to the second observable \(B\), we expect that the linear response of the system is large. The linear response function is also referred to as the linear susceptibility in the literature. According to Eq. G.5 the linear response function allows the relationship between the response of \(B\) and the external perturbation \(H_1\) to be quantified. It is clear in this equation how the response is related to the external force.

Eq. G.5 is the key result of our derivation of classical linear response theory. Although the expressions in quantum mechanics will be much more complicated, we expect there to be some correspondence between our result for the classical linear response theory and quantum linear response theory. In other words, we should see during the derivation for a quantum system that the equations can be written comparable to the classical
expression where we have a response function multiplied by the external perturbation. It must, however, be established that the quantum mechanical linear response theory derived in the following sections is in the zero-temperature limit, so $\beta$ will not appear in any expressions following this section.

G.2 Quantum Mechanical Linear Response Theory

G.2.1 Time-Dependent Perturbations for a Non-Interacting System

For a system of independent particles (meaning no interactions between particles) we can write the system as a set of orbitals, $\phi_i$, with time-dependent one-electron Schrödinger equations

$$\left[ \hat{h}^{\text{eff}}(r) - i \frac{\partial}{\partial t} \right] \phi_i(r, t) = 0 \quad (G.6)$$

We define $\hat{h}^{\text{eff}}(r)$ as the effective Hamiltonian of the system (containing the kinetic energy of electron) and the time-dependent orbitals are defined

$$\phi_i(r, t) = e^{-i \hat{h}^{\text{eff}}(r)t} \phi_i(r) = e^{-i \epsilon_i t} \phi_i(r) \quad (G.7)$$

This expression is only true if the effective Hamiltonian is time-independent. In the case where the effective Hamiltonian is time-dependent, the exponential contains a time-integral of the Hamiltonian, dependent on the actual form of the Hamiltonian. Note that the time-independent orbitals are solutions to the time-independent one-electron Schrödinger equations

$$\left[ \hat{h}^{\text{eff}}(r) - \epsilon_i \right] \phi_i(r) = 0 \quad (G.8)$$

Now consider a time-dependent perturbation of Eq. G.1, with the perturbation operator defined

$$\hat{H}'(t) = \delta \hat{v}_{\text{ext}}(r, t) = \delta \hat{v}_{\text{ext}}(r) F(t) \quad (G.9)$$

The operator for the external perturbation is given by $\delta \hat{v}_{\text{ext}}(r)$ and the time-dependent part of the perturbation, including the field strength, is denoted by $F(t)$. A typical operator is $\delta \hat{v}_{\text{ext}}(r) = \hat{\mu} = -e \mathbf{r} = -e(x, y, z)$ and the field strength is typically written as $F(t) = \varepsilon_0 \cos(\omega t)$. 
We shift focus now to the wavefunction. The perturbed orbitals take the form
\[ \phi'_i = \phi_i + \delta\phi_i, \]
where
\[ \delta\phi_i(r, t) = \sum_j \phi_j(r, t)C_{ji}(t) = \sum_j e^{-i\hat{\epsilon}jt} \phi_j(r, t)C_{ji}(t) = \sum_j e^{-i\epsilon_jt} \phi_j(r, t)C_{ji}(t) \quad (G.10) \]

Following from chapter 4 of Ref. 563, we can derive the expression for the expansion coefficients \( C_{ji}(t) \) by inserting \( \delta\phi_i(r, t) \) into the time-dependent Schrödinger equation, multiplying by \( \phi_k^* (r) \) on the left side of the equation, and integrating the expression over \( r \). This is shown below

\[
\int \phi_k^* (r) \left[ \hat{h}^{\text{eff}}(r) + \delta\hat{\nu}_{\text{ext}}(r, t) \right] \delta\phi_i(r, t) dr = i \int \phi_k^* (r) \frac{\partial}{\partial t} \delta\phi_i(r, t) dr \quad (G.11)
\]

\[
\sum_j \int \phi_k^* (r) \left[ \hat{h}^{\text{eff}}(r) + \delta\hat{\nu}_{\text{ext}}(r, t) \right] e^{-i\epsilon_jt} \phi_j(r)C_{ji}(t) dr
= i \sum_j \int \phi_k^* (r) \frac{\partial}{\partial t} e^{-i\epsilon_jt} \phi_j(r)C_{ji}(t) dr \quad (G.12)
\]

This expression can be manipulated algebraically, in order to solve for the expansion coefficients

\[
\sum_j e^{-i\epsilon_jt} C_{ji}(t) \left[ \varepsilon_j \int \phi_k^* (r) \phi_j(r) dr + \int \phi_k^* (r) \delta\hat{\nu}_{\text{ext}}(r, t) \phi_j(r) dr \right]
= i \sum_j \left[ \int \phi_k^* (r) (-i\varepsilon_j) e^{-i\epsilon_jt} \phi_j(r) C_{ji}(t) dr + \int \phi_k^* (r) e^{-i\epsilon_jt} \phi_j(r) \hat{C}_{ji}(t) dr \right] \quad (G.13)
\]

\[
= i \sum_j \left[ \left( \hat{C}_{ji}(t) - i\varepsilon_j C_{ji}(t) \right) e^{-i\epsilon_jt} \int \phi_k^* (r) \phi_j(r) dr \right]
\]

Eq. G.13 can be simplified using that \( \int \phi_k^* (r) \phi_j(r) dr = \delta_{kj} \), where \( \delta_{kj} \) is the Kronecker delta, and defining the integral \( \int \phi_k^* (r) \delta\hat{\nu}_{\text{ext}}(r, t) \phi_j(r) dr = \delta\nu_{kj}^{\text{ext}}(t) \) such that

\[
\sum_j e^{-i\epsilon_jt} C_{ji}(t) \left[ \varepsilon_j \delta_{kj} + \delta\nu_{kj}^{\text{ext}}(t) \right] = i \sum_j \left[ \left( \hat{C}_{ji}(t) - i\varepsilon_j C_{ji}(t) \right) e^{-i\epsilon_jt} \delta_{kj} \right] \quad (G.14)
\]
Collecting identical terms allows this to be simplified

\[ \sum_j e^{-i\epsilon_j t} C_{ji}(t) \delta v_{k_j}^{ext}(t) = i \sum_j \dot{C}_{ji}(t) e^{-i\epsilon_j t} \delta_{kj} = i \dot{C}_{ki}(t) e^{-i\epsilon_k t} \]

\[ \dot{C}_{ki}(t) = -i \sum_j e^{i(\epsilon_k - \epsilon_j)t} C_{ji}(t) \delta v_{k_j}^{ext}(t) \]

(G.15)

Based on the assumption that the perturbation is small, we can safely assume that $C_{ji}(t)$ remains near its unperturbed value. Note that $\dot{C}_{ji}(t)$ is the time-derivative of $C_{ji}(t)$. If the perturbation is switched on at $t = -\infty$ (the time chosen is arbitrary, but $t = -\infty$ is used as a matter of mathematical convenience), we have by definition that $C_{ji}(t = -\infty) = \delta_{ji}$. It will soon become apparent that this choice of the initial time for the perturbation is related to Fourier transforms. Therefore

\[ \dot{C}_{ki}(t) = -i \sum_j e^{i(\epsilon_k - \epsilon_j)t} C_{ji}(t) \delta v_{k_j}^{ext}(t) \]

\[ = -i \sum_j e^{i(\epsilon_k - \epsilon_j)t} \delta_{ji} \delta v_{k_j}^{ext}(t) \]

\[ = -i e^{i(\epsilon_k - \epsilon_i)t} \delta v_{ki}^{ext}(t) \]

(G.16)

This may now be integrated to find the expansion coefficients

\[ \int_{-\infty}^{t} \dot{C}_{ki}(t') dt' = -i \int_{-\infty}^{t} e^{i(\epsilon_k - \epsilon_i)t'} \delta v_{ki}^{ext}(t') dt' \]

\[ C_{ki}(t) = C_{ki}(-\infty) - i \int_{-\infty}^{t} e^{i(\epsilon_k - \epsilon_i)t'} \delta v_{ki}^{ext}(t') dt' \]

\[ = \delta_{ki} - i \int_{-\infty}^{t} e^{i(\epsilon_k - \epsilon_i)t'} \delta v_{ki}^{ext}(t') dt' \]

(G.17)

The important solution to the equation occurs when $i \neq k$, where

\[ C_{ki}(t) = -i \int_{-\infty}^{t} e^{i(\epsilon_k - \epsilon_i)t'} \delta v_{ki}^{ext}(t') dt' \]

\[ = -i \int_{-\infty}^{t} e^{i(\epsilon_k - \epsilon_i)t'} \int \phi_k^{*}(r') \delta v_{ki}^{ext}(r', t') \phi_i(r') dr' dt' \]

(G.18)
This expression is a key result of first-order time-dependent perturbation theory. We now have an expression for the time-dependent expansion coefficients. These will be used to simplify some of the equations later in this section.

Recall that the ground state electron density may be written

$$\rho(r) = \sum_{i}^{\text{occ}} |\phi_i(r)|^2$$

(G.19)

For the perturbed orbitals $\phi'_i$, we find the time-dependent electron density as

$$\rho'(r,t) = \sum_{i}^{\text{occ}} |\phi'_i(r,t)|^2 = \sum_{i}^{\text{occ}} (\phi'_i(r,t))^* (\phi'_i(r,t))$$

$$= \sum_{i} (\phi_i(r,t) + \delta\phi_i(r,t))^* (\phi_i(r,t) + \delta\phi_i(r,t))$$

$$= \sum_{i} |\phi_i(r,t)|^2 + \sum_{i} (\phi_i^*(r,t)\delta\phi_i(r,t) + \phi_i(r,t)\delta\phi_i^*(r,t)) + \sum_{i} |\delta\phi_i(r,t)|^2$$

$$= \rho(r,t) + \delta\rho(r,t) + \text{nonlinear term}$$

(G.20)

The first term is the time-dependent electron density of the unperturbed orbitals and the second term is the first order change in the electron density (also known as the linear response of the electron density). The final term is a nonlinear term in the perturbed electron density, and will be ignored since we’re only dealing with linear response at the moment. Focusing on the first order change in the electron density, we can use the definition of the perturbed orbitals and the time-dependent orbitals to expand Eq. G.20
Collecting everything besides the external potential, we obtain

\[ \delta \rho(r, t) = \sum_{i}^{occ} (\phi^*_i(r, t) \delta \phi_i(r, t) + \phi_i(r, t) \delta \phi^*_i(r, t)) \]

\[ = \sum_{i}^{occ} \left( e^{i \xi_i t} \phi^*_i(r) \sum_{a \neq i} \phi_a(r, t) C_{ai}(t) + e^{-i \xi_i t} \phi_i(r) \sum_{a \neq i} \phi'^*_a(r, t) C'_{ai}(t) \right) \]

\[ = \sum_{i}^{occ} \sum_{a \neq i} \left( e^{i(\epsilon_i - \epsilon_a) t} \phi^*_i(r) \phi_a(r, t) C_{ai}(t) + e^{i(\epsilon_a - \epsilon_i) t} \phi_i(r) \phi'^*_a(r, t) C'_{ai}(t) \right) \]

\[ = \sum_{i}^{occ} \sum_{a \neq i} \left[ -i \int_{-\infty}^{t} e^{i(\epsilon_i - \epsilon_a) t'} \int \phi'^*_a(r') e^{-i(\epsilon_i - \epsilon_a) t + i(\epsilon_a - \epsilon_i) t'} \right] \delta \mu_{ext}(t', t') \phi_i(r) \phi'^*_a(r') \]

\[ + e^{i(\epsilon_a - \epsilon_i) t} \phi_i(r) \phi'^*_a(r') \left[ i \int_{-\infty}^{t} e^{-i(\epsilon_a - \epsilon_i) t'} \int \phi'(a, r') e^{i(\epsilon_a - \epsilon_i) t + i(\epsilon_i - \epsilon_a) t'} \right] \delta \mu_{ext}(t', t') \phi_i(r') \phi'^*_{a}(r') \]

\[ = \sum_{i}^{occ} \sum_{a \neq i} \left[ -i \int_{-\infty}^{t} \delta \mu_{ext}(r', t') \left( \phi^*_i(r) \phi_a(r, t) \phi'^*_a(r') e^{-i(\epsilon_i - \epsilon_a) t} \right) \phi_i(r') \phi'^*_{a}(r') \right] \]

\[ = \sum_{i}^{occ} \sum_{a \neq i} \Theta(t - t') \left( \phi^*_i(r) \phi_a(r, t) \phi'^*_a(r') e^{-i(\epsilon_i - \epsilon_a) (t - t')} \right) \]

\[ - \Theta(t - t') \phi_i(r) \phi'^*_a(r) \phi_a(r', t) \phi'^*_{a}(r') e^{-i(\epsilon_a - \epsilon_i) (t - t')} \]

\[ = \int_{-\infty}^{\infty} \delta \mu_{ext}(r', t') \chi(r, r', t - t') dr' dt' \]

(G.21)

Collecting everything besides the external potential, we obtain

\[ \delta \rho(r, t) = -i \int_{-\infty}^{t} \delta \mu_{ext}(r', t') \sum_{i}^{occ} \sum_{a \neq i} \left( \phi^*_i(r) \phi_a(r, t) \phi'^*_a(r') e^{-i(\epsilon_i - \epsilon_a) (t - t')} \right) \]

\[ - \phi_i(r) \phi'^*_a(r) \phi_a(r', t) \phi'^*_{a}(r') e^{-i(\epsilon_a - \epsilon_i) (t - t')} \]

\[ = -i \int_{-\infty}^{\infty} \delta \mu_{ext}(r', t') \sum_{i}^{occ} \sum_{a \neq i} \left( \Theta(t - t') \phi^*_i(r) \phi_a(r, t) \phi'^*_a(r') e^{-i(\epsilon_i - \epsilon_a) (t - t')} \right) \]

\[ - \Theta(t - t') \phi_i(r) \phi'^*_a(r) \phi_a(r', t) \phi'^*_{a}(r') e^{-i(\epsilon_a - \epsilon_i) (t - t')} \]

\[ = \int_{-\infty}^{\infty} \delta \mu_{ext}(r', t') \chi(r, r', t - t') dr' dt' \]

(G.22)

In Eq. G.22 we defined the linear response function, \( \chi(r, r', t - t') \), for the system of noninteracting particles as the contents of the curly brackets. Like what was shown in
the classical linear response theory, the linear response function is used to relate the observable (first order change in the electron density) and external perturbation. To derive the final form of Eq. G.22, the Heaviside step function is used where

\[
\Theta(t - t') = \begin{cases} 
0 & t' > t \\
1 & t' < t
\end{cases}
\]  

(G.23)

Throughout the remainder of this work we will use the definition of the Fourier transform

\[
f(\omega) = \int_{-\infty}^{\infty} F(t) e^{i\omega t} dt
\]  

(G.24)

and the Fourier convolution theorem

\[
h(t) = \int_{-\infty}^{\infty} g(t - t') f(t') dt' \quad \iff \quad h(\omega) = g(\omega) f(\omega)
\]  

(G.25)

Hence Eq. G.22 may be written equivalently in the frequency-domain

\[
\delta \rho(r, \omega) = \int \delta \hat{\upsilon}_{\text{ext}}(r', \omega) \chi(r, r', \omega) dr'
\]  

(G.26)

Eq. G.26 is the key equation in quantum linear response theory, illustrating the relationship between the observable (the first order change in the electron density) and the external potential via the linear response function, \( \chi(r, r', \omega) \). Of course, one must be mindful that this expression is only useful when all of the particles are non-interacting.

It is now important to write the explicit expression for the linear response function in the frequency-domain. Here we use the change of variables \( \tau = t - t' \). Based on Eq. G.22 we need the Fourier transforms of exponentials multiplied by Heaviside functions. These are given below

\[
\int_{-\infty}^{\infty} \Theta(\tau) e^{-i(\varepsilon_a - \varepsilon_i)\tau} e^{i\omega \tau} d\tau = \int_{0}^{\infty} e^{-i(\varepsilon_a - \varepsilon_i - \omega)\tau} d\tau \\
= \lim_{\eta \to 0} \frac{e^{-i(\varepsilon_a - \varepsilon_i - (\omega + i\eta))\tau}}{-i(\varepsilon_a - \varepsilon_i - (\omega + i\eta))} \bigg|_{\tau=0}^{\infty} \\
= \lim_{\eta \to 0} \frac{-1}{-i(\varepsilon_a - \varepsilon_i - (\omega + i\eta))}
\]  

(G.27)
\[ \int_{-\infty}^{\infty} \Theta(\tau)e^{-i(\varepsilon_i - \varepsilon_a)\tau}e^{i\omega\tau}d\tau = \int_{0}^{\infty} e^{-i(\varepsilon_i - \varepsilon_a - \omega)\tau}d\tau \]
\[ = \lim_{\eta \to 0} \frac{e^{-i(\varepsilon_i - \varepsilon_a - (\omega + i\eta))\tau}}{-i(\varepsilon_i - \varepsilon_a - (\omega + i\eta))} \bigg|_{\tau = 0} \]
\[ = \lim_{\eta \to 0} \frac{-1}{-i(\varepsilon_i - \varepsilon_a - (\omega + i\eta))} \]

The infinitesimal \( \eta \) is introduced into the integral to make it convergent at the boundary conditions (alternatively it can be thought of as enforcing the adiabatic approximation\(^{58}\)). The frequency-dependent linear response function is therefore

\[
\chi(r, r', \omega) = -i \lim_{\eta \to 0} \sum_{i}^{\text{occ}} \sum_{i \neq a} \left\{ \phi_i^* (r) \phi_a^* (r') \phi_a (r') \phi_i (r') \right\} - \phi_i (r) \phi_a^* (r) \phi_a (r') \phi_i^* (r') \]
\[ = \lim_{\eta \to 0} \sum_{i}^{\text{occ}} \sum_{i \neq a} \left\{ \frac{\phi_i^* (r) \phi_a^* (r') \phi_i (r')}{\omega + i\eta - (\varepsilon_a - \varepsilon_i)} - \frac{\phi_i (r) \phi_a^* (r) \phi_i^* (r')}{\omega + i\eta + (\varepsilon_a - \varepsilon_i)} \right\} \]

\[(G.29)\]

Using occupation numbers, where \( n_i \neq 0 \) for occupied orbitals and \( n_i = 0 \) for virtual orbitals, it is possible to relax the restricted summation to go over all orbitals, since cancellation would happen if \( i = a \). Noting that \( i \) and \( a \) are dummy indices, we can write for the second term that orbitals indexed by \( a \) are occupied and \( i \) are virtual. This allows us to rewrite the numerator and denominator of the second term to look the those of the first term. Performing these operations gives

\[
\chi(r, r', \omega) = \lim_{\eta \to 0} \sum_{i} \sum_{a} \sum_{s} n_s \left\{ \frac{\phi_i^* (r) \phi_a^* (r') \phi_i^* (r')}{\omega + i\eta - (\varepsilon_a - \varepsilon_i)} \delta_{is} - \frac{\phi_i^* (r) \phi_a^* (r') \phi_i^* (r')}{\omega + i\eta + (\varepsilon_a - \varepsilon_i)} \delta_{as} \right\} \]
\[ = \lim_{\eta \to 0} \sum_{i} \sum_{a} (n_i - n_a) \frac{\phi_i^* (r) \phi_a^* (r') \phi_i (r')}{\omega + i\eta - (\varepsilon_a - \varepsilon_i)} \]

\[(G.30)\]

Assuming real orbitals, letting \( \eta \to 0 \), and noticing that the response function goes to zero if \( n_i = n_a \), we obtain
\[
\chi(r, r', \omega) = \sum_i \sum_a (n_i - n_a) \frac{\phi_i(r)\phi_a(r)\phi_a(r')\phi_i(r')}{\omega - (\varepsilon_a - \varepsilon_i)}
\]

\[
= \sum_i \sum_a \left\{ n_i \frac{\phi_i(r)\phi_a(r)\phi_a(r')\phi_i(r')}{\omega - (\varepsilon_a - \varepsilon_i)} - n_a \frac{\phi_i(r)\phi_a(r)\phi_a(r')\phi_i(r')}{\omega - (\varepsilon_a - \varepsilon_i)} \right\}
\]

\[
= \sum_i \sum_a \left\{ n_i \frac{\phi_i(r)\phi_a(r)\phi_a(r')\phi_i(r')}{\varepsilon_i - \varepsilon_a + \omega} + n_a \frac{\phi_i(r)\phi_a(r)\phi_a(r')\phi_i(r')}{\varepsilon_a - \varepsilon_i - \omega} \right\}
\]

We can interchange the indices in the second term because the sums are over all orbitals. In doing so, we must restrict the sums such that \( a \) refers to virtual orbitals and \( i \) refers to occupied orbitals. This results in

\[
\chi(r, r', \omega) = \sum_{i, \text{occ}} \sum_{a, \text{virt}} n_i \phi_i(r)\phi_a(r)\phi_a(r')\phi_i(r') \left\{ \frac{1}{\varepsilon_i - \varepsilon_a + \omega} + \frac{1}{\varepsilon_a - \varepsilon_i - \omega} \right\}
\]

\[
= \sum_{i, \text{occ}} \sum_{a, \text{virt}} n_i \phi_i(r)\phi_a(r)\phi_a(r')\phi_i(r') \left\{ \frac{2(\varepsilon_i - \varepsilon_a)}{\varepsilon_i - \varepsilon_a} \right\} \quad \text{(G.32)}
\]

An interesting result can be obtained if we use real orbitals and examine the frequency-dependent density response,

\[
\delta \rho(r, \omega) = \sum_i (\phi_i^*(r, \omega)\delta \phi_i(r, \omega) + \phi_i(r, \omega)\delta \phi_i^*(r, \omega)) = 2 \sum_i \phi_i(r, \omega)\delta \phi_i(r, \omega)
\]

\[
= \int \delta \hat{t}^{\text{ext}}(r', \omega) \chi(r, r', \omega)dr'
\]

\[
= 2 \sum_i \phi_i(r) \sum_a \phi_a(r) \left( \frac{1}{\varepsilon_i - \varepsilon_a + \omega} + \frac{1}{\varepsilon_a - \varepsilon_i - \omega} \right) \int \phi_a(r')\delta \hat{t}^{\text{ext}}(r', \omega)\phi_i(r')dr'
\]

\[
= 2 \sum_i \phi_i(r) \sum_a \phi_a(r) \left( \frac{\varepsilon_i - \varepsilon_a}{(\varepsilon_i - \varepsilon_a)^2 - \omega^2} \right) \int \phi_a(r')\delta \hat{t}^{\text{ext}}(r', \omega)\phi_i(r')dr'
\]

\[
= 2 \sum_i \phi_i(r) \sum_a \phi_a(r)\delta\chi_{ai}(\omega)
\]

\[
\text{(G.33)}
\]

The frequency-dependent expansion coefficients, \( \delta\chi_{ai}(\omega) \), are defined
\[ C_{ai}(\omega) = \left[ \frac{\varepsilon_i - \varepsilon_a}{(\varepsilon_i - \varepsilon_a)^2 - \omega^2} \right] \int \phi_a(r') \delta \hat{\upsilon}_{\text{ext}}(r', \omega) \phi_i(r') dr' \] (G.34)

In Eq. G.34, a factor of \( \frac{1}{2} \) is introduced to prevent double counting. It is clear this is necessary when comparing Eqs. G.32 and G.34. Briefly examining the expansion coefficients, if we let \( \omega = 0 \), we recover the time-independent perturbation theory result (see, for instance, Eq. 9.26 of Ref. 564)

\[ C_{ai}(\omega = 0) = \frac{\int \phi_a(r') \delta \hat{\upsilon}_{\text{ext}}(r', \omega = 0) \phi_i(r') dr'}{\varepsilon_i - \varepsilon_a} \] (G.35)

Note that G.35 is defined only when \( i \neq a \).

To summarize this section, it is pertinent to understand the key findings. The most important step was deriving the relationship between the first-order density response, \( \delta \rho(r, \omega) \), the linear susceptibility, \( \chi(r, r', \omega) \), and the external potential, \( \delta \hat{\upsilon}_{\text{ext}}(r', \omega) \). While Eq. G.26 appears more complicated than the classical analogue, Eq. G.5, the main point is that both expressions show how a change in an observable is related to the external force through the linear susceptibility (or linear response function). Aside from the quantum expression being more notation heavy, both the classical and quantum results are similar. As we will see, bookkeeping the complexity of this notation is the only significant challenge in deriving the quantum linear response theory, in the framework of density functional theory.

### G.2.2 Changes in Potential for Time-Dependent Density Functional Theory

Unfortunately, we almost never deal with systems of particles that do not interact. In density functional theory (DFT), we need to account for the interactions between electrons since it is a quasi-independent particle formalism. The first order potential function, \( \delta v_{\text{eff}}(r, \omega) \), is written based on Kohn-Sham DFT (KS-DFT) as

\[ \delta v_{\text{eff}}(r, \omega) = \delta v_{\text{Coul}}(r, \omega) + \delta v_{\text{xc}}(r, \omega) + \delta v_{\text{ext}}(r, \omega) \] (G.36)

The individual contributions to the potential function are the Coulomb (or Hartree)
potential $\delta u_{\text{Coul}}(r, \omega)$, the exchange-correlation potential $\delta u_{xc}(r, \omega)$, and the external potential $\delta u_{\text{ext}}(r, \omega)$. The former contributions are defined as follows

$$\delta u_{\text{Coul}}(r, \omega) = \int dr_2 \frac{\delta \rho(r_2, \omega)}{|r - r_2|}$$  \hspace{1cm} (G.37)

$$\delta u_{xc}(r, \omega) = \int dr_2 f_{xc}(r, r_2, \omega) \delta \rho(r_2, \omega)$$  \hspace{1cm} (G.38)

$$f_{xc}(r, r_2, t - t_2) = \frac{\delta V_{xc}(r, t)}{\delta \rho(r_2, t_2)} = \frac{\delta^2 A_{xc}[\rho]}{\delta \rho(r_2, t_2) \delta \rho(r, t)}$$  \hspace{1cm} (G.39)

The quantity $f_{xc}(r, r_2, \omega)$ is commonly referred to in the literature as the exchange-correlation kernel, the second order functional derivative of the exchange-correlation action functional ($A_{xc}[\rho]$) with respect to the electron density. It must be stressed that the action functional does not obey causality (that is, that the external perturbation happens before the response of the molecule). This issue has been resolved, but in general the expression for the action is complicated to handle. It is still worthwhile, in the author’s opinion, to establish the existence of the action functional because it is a fundamentally different quantity than the exchange-correlation energy functional. This is also useful for understanding the discussion that follows this paragraph. In time-independent DFT, the exchange-correlation kernel $f_{xc}(r, r_2)$ is the second order functional derivative of the exchange-correlation energy functional ($E_{xc}[\rho]$). Both interaction potentials depend on the first order change in the electron density, which is related to the presence of the additional external potential.

The exchange-correlation kernel is a nonlocal function of both space (it depends on both $r$ and $r_2$) and time (it depends on both $t$ and $t_2$). A consequence of this nonlocality is that it is difficult and computationally expensive to calculate the exchange-correlation kernel in time-dependent DFT (TDDFT). A commonly used approximation in TDDFT is known as the adiabatic approximation, where the exchange-correlation kernel is defined

$$f_{xc}(r, r_2, t - t_2) \cong \delta(t - t_2) \frac{\delta^2 E_{xc}[\rho]}{\delta \rho(r_2) \delta \rho(r)}$$ \hspace{1cm} (G.40)
The adiabatic approximation effectively takes the exchange-correlation kernel and causes it to depend on a single time. In other words, the adiabatic approximation is a local approximation in time. If we take the simplest form for the exchange-correlation energy functional, the Local Density Approximation (or Homogeneous Electron Gas), where the exchange-correlation energy functional is local in space, the adiabatic local density approximation (ALDA) is employed

\[ f_{xc}(r, r_2, t - t_2) \cong f^{ALDA}_{xc}(r, r_2, t - t_2) = \delta(r - r_2) \delta(t - t_2) \frac{\delta^2 E^{LDA}_{xc}[\rho]}{\delta \rho(r)^2} \] (G.41)

The remaining focus of this section is relating the linear response of a DFT reference wavefunction to the true linear response of the same system. The KS-DFT equations describe the real system of interacting electrons based on a fictitious system of non-interacting electrons that result in the same electron density as the real system. The major result of the previous section was deriving the linear response function of a system of non-interacting particles, which can be used to relate the first order KS potential (\(\delta v_{KS}(r, \omega)\), defined in Eq. G.36) and the first order change in the electron density. Based on this discussion, the first order density change in the electron density which defines the TDDFT equations is given by

\[ \delta \rho(r, \omega) = \int \left[ \delta v_{\text{ext}}(r_1, \omega) + \delta v_{\text{Coul}}(r_1, \omega) + \delta v_{xc}(r_1, \omega) \right] \cdot \chi_{KS}(r, r_1, \omega) dr_1 = \int \delta v_{KS}(r_1, \omega) \cdot \chi_{KS}(r, r_1, \omega) dr_1 \] (G.42)

Here, we write the linear response function for the system of non-interacting particles as \(\chi_{KS}(r, r_1, \omega)\). For the true linear response of the system, the expression for the first order density change is

\[ \delta \rho(r, \omega) = \int \delta v_{\text{ext}}(r_1, \omega) \chi(r, r_1, \omega) dr_1 \] (G.43)

Based on the definitions of the Coulomb and exchange-correlation potentials, we may also write
\[ \delta u_{\text{Coul}}(r_1, \omega) = \int dr_2 \frac{dr' \delta u_{\text{ext}}(r', \omega) \chi(r_2, r', \omega)}{|r_1 - r_2|} \]  
\( \text{(G.44)} \)

\[ \delta u_{xc}(r_1, \omega) = \int dr_2 f_{xc}(r_1, r_2, \omega) \int dr' \delta u_{\text{ext}}(r', \omega) \chi(r_2, r', \omega) \]  
\( \text{(G.45)} \)

Equating Eqs. G.42 and G.43 gives

\[ \int \delta u_{\text{ext}}(r_1, \omega) \chi(r, r_1, \omega) \, dr_1 = \int [\delta u_{\text{ext}}(r_1, \omega) + \delta u_{\text{Coul}}(r_1, \omega) + \delta u_{xc}(r_1, \omega)] \cdot \chi_{KS}(r, r_1, \omega) \, dr_1 \]  
\( \text{(G.46)} \)

The integrals on the right side of the expression can be written explicitly as

\[ \int dr_1 \delta u_{\text{ext}}(r_1, \omega) \chi(r, r_1, \omega) \]
\[ = \int dr_1 [\delta u_{\text{ext}}(r_1, \omega) + \delta u_{\text{Coul}}(r_1, \omega) + \delta u_{xc}(r_1, \omega)] \cdot \chi_{KS}(r, r_1, \omega) \]
\[ = \int dr_1 \delta u_{\text{ext}}(r_1, \omega) \chi_{KS}(r, r_1, \omega) \]
\[ + \int dr_1 \int dr_2 \chi_{KS}(r, r_1, \omega) \left\{ \frac{1}{|r_1 - r_2|} \right\} \int dr' \delta u_{\text{ext}}(r', \omega) \chi(r_2, r', \omega) \]
\[ + \int dr_1 \int dr_2 \chi_{KS}(r, r_1, \omega) f_{xc}(r_1, r_2, \omega) \int dr' \delta u_{\text{ext}}(r', \omega) \chi(r_2, r', \omega) \]  
\( \text{(G.47)} \)

The distances in the formula \((r, r_1, r_2, \text{ and } r')\) are essentially dummy variables. As a consequence, we may rename the distance variables as we want for convenience in notation. On the left hand side, it is convenient to relabel \(r_1\) with \(r'\). On the right hand side, for the first integral only, we will do the same relabeling. This gives
\[
\int dr' \chi(r, r', \omega) \delta v_{\text{ext}}(r', \omega) \\
= \int dr' \left\{ \chi_{\text{KS}}(r, r', \omega) \\
+ \int dr_1 \int dr_2 \chi_{\text{KS}}(r, r_1, \omega) \left[ \frac{1}{|r_1 - r_2|} + f_{xc}(r_1, r_2, \omega) \right] \chi(r_2, r', \omega) \right\} \delta v_{\text{ext}}(r', \omega)
\]

(G.48)

By comparing the left side and right side of the integral expression, we can extract the definition of the true linear response function

\[
\chi(r, r', \omega) = \chi_{\text{KS}}(r, r', \omega) \\
+ \int dr_1 \int dr_2 \chi_{\text{KS}}(r, r_1, \omega) \left[ \frac{1}{|r_1 - r_2|} + f_{xc}(r_1, r_2, \omega) \right] \chi(r_2, r', \omega)
\]

(G.49)

Unfortunately, the true linear response function appears on both sides of Eq. G.49. This is caused by the first order potential change, which depends on the first order change in the electron density. Based on Eq. G.49, a self-consistent method must be used to determine the linear response function. This is analogous to the ground state KS-DFT equations where the variational problem is solved self-consistently because the KS potential depends on the electron density, which is determined from the orbitals that determined from that potential. One more interesting observation is that the linear response function can be viewed as a functional derivative

\[
\delta \rho(r, t - t_2) = \int \chi(r, r_2, t - t_2) \delta v_{\text{ext}}(r_2, t - t_2) dr_2 \\
= \int \frac{\delta \rho(r, t)}{\delta v_{\text{ext}}(r_2, t_2)} \delta v_{\text{ext}}(r_2, t - t_2) dr_2
\]

(G.50)

While we won’t make use of this observation, it provides a useful connection between the first order change in the electron density and the linear response function. Eq. G.50 also hints that there are other avenues we could have chosen to derive linear response theory based on a DFT reference (see Ref. 59 also).
G.2.3 Solution to the TDDFT Perturbation Problem

In order to solve the linear response problem, it is necessary to determine the first order change in the electron density. The previous sections define this observable in terms of the external potential and linear response function. Because we use finite basis sets, it is beneficial to cast the equations in terms of the first order change in the density matrix so that we can work with unperturbed KS orbitals. In the basis of unperturbed KS orbitals, the first order change in the electron density can be written

$$
\delta \rho_\sigma(r, \omega) = \sum_{i,j} \phi_{i\sigma}(r) \phi^*_{j\sigma}(r) + \sum_{j,i} \phi_{j\sigma}(r) \phi^*_{i\sigma}(r)
$$

(G.51)

The sum in the latter form of Eq. G.51 runs over all pairs $i,j$. The index $\sigma$ accounts for the spin of the electrons. We still need to relate the first order change in the density matrix to the linear response function in order to write the TDDFT linear response equations in more compact form.

We can define the external potential operator in second quantization

$$
\delta \hat{v}_{ext}(r, \omega) = \sum_{i,j,\sigma} \delta v_{ij\sigma}(r, \omega) \hat{\rho}_{ij\sigma} = \sum_{i,j,\sigma} \delta v_{ij\sigma}(r, \omega) \hat{a}_i^\dagger \hat{a}_j
$$

(G.52)

Here we introduce the density operator, $\hat{\rho}_{ij\sigma}$, which is defined in terms of the raising and lowering operators, $\hat{a}_i^\dagger$ and $\hat{a}_j$, respectively. Instead of working with individual orbitals, we follow Ref. 58 where the wavefunction (defining a state, such as the ground state of the system) is used to derive the first order change in the density matrix (also called the linear response of the density matrix). The time-dependent wavefunction and first order change in the wavefunction are defined ($\Psi_0$ is the ground state wavefunction)

$$
\Psi(t) = \Psi_0(t) + \delta \Psi_0(t)
$$

(G.53)

$$
\delta \Psi_0(t) = -i \sum_{I \neq 0} \Psi_I(t) \int_{-\infty}^t \langle \Psi_I(t') | \delta \hat{w}(t') | \Psi_0(t') \rangle dt'
$$

(G.54)
where

\[ \Psi_I(t) = e^{-iE_I t} \Psi_I \]  
(G.55)

\[ \delta \hat{w}(t) = e^{-\eta(t'-t)} \delta \hat{\nu}_{ext}(t) \]  
(G.56)

In Eq. G.55, \( E_I \) is the energy of state \( \Psi_I \), and the subscripts 0 and \( I \) refer to the ground state and a particular excited state, respectively. For the external potential, \( \eta \) is the same positive infinitesimal defined in Eqs. G.27 and G.28 used to enforce the adiabatic approximation at all times \( t \).

The density matrix, in the presence of the external perturbation, may be written

\[ P'(t) = \langle \Psi(t)|\hat{\rho}|\Psi(t)\rangle 
= (\langle \Psi_0(t)| + \langle \delta \Psi_0(t)|) \hat{\rho} (|\Psi_0(t)\rangle + |\delta \Psi_0(t)\rangle) \]  
(G.57)

\[ = \langle \Psi_0(t)|\hat{\rho}|\Psi_0(t)\rangle + \langle \Psi_0(t)|\hat{\rho}|\delta \Psi_0(t)\rangle + \langle \delta \Psi_0(t)|\hat{\rho}|\Psi_0(t)\rangle + \ldots \]

Ignoring the nonlinear terms involving the products of the first order change in the density matrix, the \( ij \) component of the density matrix can be written

\[ P'_{ij\sigma}(t) = P_{ij\sigma}(t) + \delta P_{ij\sigma}(t) \]  
(G.58)

with

\[ P_{ij\sigma}(t) = \langle \Psi_0(t)|\hat{\rho}_{ij\sigma}|\Psi_0(t)\rangle \]  
(G.59)

\[ = \langle \Psi_0(t)|\hat{a}_{i\sigma}^{\dagger}\hat{a}_{j\sigma}|\Psi_0(t)\rangle \]

\[ \delta P_{ij\sigma}(t) = \langle \Psi_0(t)|\hat{\rho}_{ij\sigma}|\delta \Psi_0(t)\rangle + \langle \delta \Psi_0(t)|\hat{\rho}_{ij\sigma}|\Psi_0(t)\rangle 
= \langle \Psi_0(t)|\hat{a}_{i\sigma}^{\dagger}\hat{a}_{j\sigma}|\delta \Psi_0(t)\rangle + \langle \delta \Psi_0(t)|\hat{a}_{i\sigma}^{\dagger}\hat{a}_{j\sigma}|\Psi_0(t)\rangle \]  
(G.60)

Using the definition of the first order change in the wavefunction, Eq. G.54, the first
order change in the density matrix can be written more explicitly

\[ \delta P_{ij\sigma}(t_1) = \langle \Psi_0(t_1)|\hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma}|\Psi_0(t_1) \rangle + \langle \delta \Psi_0(t_1)|\hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma}|\Psi_0(t_1) \rangle \]

\[ = \langle \Psi_0(t_1)|\hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma}\left(-i \sum_{I \neq 0} |\Psi_I(t_1)\rangle \int_{-\infty}^{t_1} \langle \Psi_I(t)|\delta \hat{w}(t)|\Psi_0(t)\rangle dt \right) \]

\[ + \left(i \sum_{I \neq 0} \langle \Psi_I(t_1)| \int_{-\infty}^{t_1} \langle \Psi_0(t)|\delta \hat{w}(t)|\Psi_I(t)\rangle dt \right) \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma}|\Psi_0(t_1) \rangle \]  

\[ = \int_{-\infty}^{t_1} \sum_{I \neq 0} \left[ -i \langle \Psi_0(t_1)|\hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma}|\Psi_I(t_1)\rangle \langle \Psi_I(t)|\delta \hat{w}(t)|\Psi_0(t)\rangle \right. \]

\[ + \left. i \langle \Psi_0(t)|\delta \hat{w}(t)|\Psi_I(t)\rangle \langle \Psi_I(t_1)|\hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma}|\Psi_0(t_1) \rangle \right] dt \]

Employing the definition of the external perturbation gives

\[ \delta P_{i\sigma}(t_1) = \sum_{kl\tau} \int_{-\infty}^{t_1} \sum_{I \neq 0} \left[ -i \langle \Psi_0(t_1)|\hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma}|\Psi_I(t_1)\rangle \right. \]

\[ \times \langle \Psi_I(t)|\hat{a}_{k\tau}^\dagger \hat{a}_{l\tau}\delta \hat{V}_{kl\tau}^{ext}(t)e^{-\eta(t_1-t)}|\Psi_0(t)\rangle \]

\[ + i \langle \Psi_0(t)|\hat{a}_{k\tau}^\dagger \hat{a}_{l\tau}\delta \hat{V}_{kl\tau}^{ext}(t)e^{-\eta(t_1-t)}|\Psi_I(t)\rangle \]

\[ \times \langle \Psi_I(t_1)|\hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma}|\Psi_0(t_1) \rangle \left] dt \right. \]

It is now important to extract the time-propagators from the time-dependent wavefunctions. This yields
\[ \delta P_{ij\sigma}(t_1) = \sum_{kl\tau} \int_{-\infty}^{t_1} \sum_{I \neq 0} \left[ -i \langle \Psi_0 | \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} | \Psi_I \rangle e^{-i(E_I - E_0)t_1} \right. \\
\times \langle \Psi_I | \hat{a}_{k\tau}^\dagger \hat{a}_{l\tau} \delta v_{kl\tau}^{\text{ext}}(t) | \Psi_0 \rangle e^{-i(E_0 - E_I)t - \eta(t_1 - t)} \\
\left. + i \langle \Psi_0 | \hat{a}_{k\tau}^\dagger \hat{a}_{l\tau} \delta v_{kl\tau}^{\text{ext}}(t) | \Psi_I \rangle e^{-i(E_I - E_0)t - \eta(t_1 - t)} \right] \\
\times \langle \Psi_I | \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} | \Psi_0 \rangle e^{-i(E_0 - E_I)t_1} \right] dt \\
\sum_{kl\tau} \int_{-\infty}^{t_1} (-i) \sum_{I \neq 0} \left[ \langle \Psi_0 | \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} | \Psi_I \rangle \langle \Psi_I | \hat{a}_{k\tau}^\dagger \hat{a}_{l\tau} | \Psi_0 \rangle e^{-i(E_I - E_0)(t_1 - t) + i^2 \eta(t_1 - t)} \right] \\
\delta v_{kl\tau}^{\text{ext}}(t) dt \\
= \sum_{kl\tau} \int_{-\infty}^{t_1} \left\{ - \Theta(t_1 - t) \sum_{I \neq 0} \left[ \langle \Psi_0 | \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} | \Psi_I \rangle \langle \Psi_I | \hat{a}_{k\tau}^\dagger \hat{a}_{l\tau} | \Psi_0 \rangle e^{-i(E_I - E_0 - i\eta)(t_1 - t)} \right. \\
\left. - \langle \Psi_0 | \hat{a}_{k\tau}^\dagger \hat{a}_{l\tau} | \Psi_I \rangle \langle \Psi_I | \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} | \Psi_0 \rangle e^{-i(E_0 - E_I - i\eta)(t_1 - t)} \right] \right\} \delta v_{kl\tau}^{\text{ext}}(t) dt \right) \] (G.63)

where \( \Theta(t_1 - t) \) is the Heaviside function. Comparing Eqs. G.22 and G.63, we see that the term in curly brackets in Eq. G.63 is the time-domain expression for the linear response function, \( \chi_{ij\sigma,kl\tau}(t_1 - t) \). We can therefore write

\[ \delta P_{ij\sigma}(t_1) = \sum_{kl\tau} \int_{-\infty}^{t_1} \chi_{ij\sigma,kl\tau}(t_1 - t) \delta v_{kl\tau}^{\text{ext}}(t) dt \] (G.64)

or alternatively, employing the Fourier convolution theorem

\[ \delta P_{ij\sigma}(\omega) = \sum_{kl\tau} \chi_{ij\sigma,kl\tau}(\omega) \delta v_{kl\tau}^{\text{ext}}(\omega) \] (G.65)

The frequency dependent linear response function is determined by evaluating the integrals in Eq. G.63.
\[
\int_{-\infty}^{\infty} \Theta(t_1 - t)e^{-i(E_I - E_0 - i\eta)(t_1 - t)}e^{i\omega(t_1 - t)}dt \\
= 0 + \int_{t_1}^{\infty} e^{-i(E_I - E_0 - i\eta - \omega)(t_1 - t)}dt \\
= \left. \frac{e^{-i(E_I - E_0 - i\eta - \omega)(t_1 - t)}}{-i(E_I - E_0 - i\eta - \omega)} \right|_{t=t_1} = \frac{1}{i(E_I - E_0 - i\eta - \omega)}
\]  

\[G.66\]

\[
\int_{-\infty}^{\infty} \Theta(t_1 - t)e^{-i(E_0 - E_I - i\eta)(t_1 - t)}e^{i\omega(t_1 - t)}dt = \frac{1}{i(E_0 - E_I - i\eta - \omega)}
\]  

\[G.67\]

Hence, the frequency-dependent linear response function is

\[
\chi_{ij\sigma,kl\tau}(\omega) = -i \sum_{I \neq 0} \frac{\langle \Psi_0 | \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} | \Psi_I \rangle \langle \Psi_I | \hat{a}_{k\tau}^\dagger \hat{a}_{l\tau} | \Psi_0 \rangle}{i(E_I - E_0 - i\eta - \omega)} - \frac{\langle \Psi_0 | \hat{a}_{k\tau}^\dagger \hat{a}_{l\tau} | \Psi_I \rangle \langle \Psi_I | \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} | \Psi_0 \rangle}{i(E_0 - E_I - i\eta - \omega)}
\]

\[G.68\]

\[
= \sum_{I \neq 0} \frac{\langle \Psi_0 | \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} | \Psi_I \rangle \langle \Psi_I | \hat{a}_{k\tau}^\dagger \hat{a}_{l\tau} | \Psi_0 \rangle}{\omega - (E_I - E_0) + i\eta} - \frac{\langle \Psi_0 | \hat{a}_{k\tau}^\dagger \hat{a}_{l\tau} | \Psi_I \rangle \langle \Psi_I | \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} | \Psi_0 \rangle}{\omega + (E_I - E_0) + i\eta}
\]

\[G.68\]

This is Eq. 3.12 from Ref. 58.

A relevant circumstance is the case of a single-particle system (i.e. a system that can be written as a set of one-particle equations, like KS-DFT). In this case, the Schrödinger equation is

\[
\hat{h}\phi_{i\sigma} = \epsilon_{i\sigma}\phi_{i\sigma}
\]  

\[G.69\]

Assuming that the particle is initially in orbital \(\phi_{m\mu}\) and the unperturbed orbitals are an orthonormal basis set, the linear response function is given as (for a transition to orbital \(\phi_{n\mu}\), letting \(\eta \to 0\) and doing the substitution \(i\) for \(j\) and vice versa to be consistent with Casida)
\[ \chi_{ij\sigma,kl\tau}(\omega) = \frac{\langle \phi_{m\mu}|\hat{a}^\dagger_{j\sigma}|\phi_{n\mu}\rangle\langle \phi_{n\mu}|\hat{a}^\dagger_{k\tau}|\phi_{m\mu}\rangle}{\omega - (\epsilon_{n\mu} - \epsilon_{m\mu})} - \frac{\langle \phi_{m\mu}|\hat{a}^\dagger_{k\tau}|\phi_{n\mu}\rangle\langle \phi_{n\mu}|\hat{a}^\dagger_{j\sigma}|\phi_{m\mu}\rangle}{\omega + (\epsilon_{n\mu} - \epsilon_{m\mu})} \]

\[ = \delta_{\sigma\tau} \left[ \frac{\langle \phi_{m\mu}|\delta_{in}\delta_{\sigma\mu}\phi_{j\sigma}\rangle\langle \phi_{n\mu}|\delta_{im}\delta_{\sigma\mu}\phi_{k\sigma}\rangle}{\omega - (\epsilon_{n\mu} - \epsilon_{m\mu})} - \frac{\langle \phi_{m\mu}|\delta_{in}\delta_{\sigma\mu}\phi_{k\sigma}\rangle\langle \phi_{n\mu}|\delta_{im}\delta_{\sigma\mu}\phi_{j\sigma}\rangle}{\omega + (\epsilon_{n\mu} - \epsilon_{m\mu})} \right] \]

\[ = \delta_{\sigma\tau} \left[ \frac{\delta_{in}\delta_{\sigma\mu}\delta_{jm}\delta_{\sigma\mu}\delta_{nk}\delta_{\mu\sigma}}{\omega - (\epsilon_{n\mu} - \epsilon_{m\mu})} - \frac{\delta_{in}\delta_{\sigma\mu}\delta_{nk}\delta_{\sigma\mu}\delta_{jm}\delta_{\mu\sigma}}{\omega + (\epsilon_{n\mu} - \epsilon_{m\mu})} \right] \]

\[ = \delta_{\sigma\tau} \left[ \frac{\delta_{ik}\delta_{lj}}{\omega - (\epsilon_{n\mu} - \epsilon_{m\mu})} - \frac{\delta_{lj}\delta_{ik}}{\omega + (\epsilon_{n\mu} - \epsilon_{m\mu})} \right] \]

\[ = \delta_{\sigma\tau}\delta_{\sigma\mu}\delta_{ik}\delta_{jl} \left[ \frac{1}{\omega - (\epsilon_{n\sigma} - \epsilon_{m\sigma})} - \frac{1}{\omega + (\epsilon_{n\sigma} - \epsilon_{m\sigma})} \right] \]

\[ \text{(G.70)} \]

In simplifying this expression, we made copious use of a few identities based on Kronecker deltas. The first is that \( \delta_{ij} = \delta_{ji} \). The other identity is that \( \delta_{ab}\delta_{bc} = \delta_{ac} \). Since we have two independent terms in the linear response function, the dummy indices \( n \) and \( m \) in the those terms can be chosen to simplify Eq. G.70 slightly more. Choosing \( n = i \) in the first term and \( n = j \) in the second term, we obtain

\[ \chi_{ij\sigma,kl\tau}(\omega) = \delta_{\sigma\tau}\delta_{\sigma\mu}\delta_{ik}\delta_{jl} \left[ \frac{1}{\omega - (\epsilon_{i\sigma} - \epsilon_{m\sigma})} - \frac{1}{\omega - (\epsilon_{m\sigma} - \epsilon_{j\sigma})} \right] \]

\[ = \delta_{\sigma\tau}\delta_{\sigma\mu}\delta_{ik}\delta_{jl} \left[ \frac{\delta_{jm}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})} - \frac{\delta_{im}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})} \right] \]

\[ = \delta_{\sigma\tau}\delta_{\sigma\mu}\delta_{ik}\delta_{jl} \left[ \frac{\delta_{jm} - \delta_{im}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})} \right] \]

\[ \text{(G.71)} \]

For a system of \( N \) independent particles, we sum over the orbitals (index \( m \)) and spin (index \( \mu \)), while including the occupation numbers \( n_{m\mu} \). The linear response function is then
\[
\chi_{ij\sigma,kl\tau}(\omega) = \sum_{m,\mu} n_{m\mu} \delta_{\sigma\tau} \delta_{\mu\mu} \delta_{ik} \delta_{jl} \left[ \frac{\delta_{jm} - \delta_{im}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})} \right]
\]
\[
= \sum_{m,\mu} \delta_{\sigma\tau} \delta_{ik} \delta_{jl} \left[ \frac{n_{m\mu} \delta_{jm} \delta_{\mu\mu} - n_{m\mu} \delta_{im} \delta_{\tau\mu}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})} \right]
\]
\[
= \delta_{\sigma\tau} \delta_{ik} \delta_{jl} \left[ \frac{n_{j\sigma} - n_{i\sigma}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})} \right]
\]

(G.72)

The summation in Eq. G.72 disappears due to the Kronecker deltas. This confirms Eq. 3.14 in Ref. 58, Eq. 33 in Ref. 59, and the ratio in Eq. 7 of Ref. 36.

We can now write the linear response of the electron density

\[
\delta \rho_\sigma(r, \omega) = \sum_{i,j} \delta P_{ij\sigma}(\omega) \phi_{i\sigma}(r) \phi_{j\sigma}^*(r)
\]
\[
= \sum_{i,j} \sum_{k,l,\tau} \chi_{ij\sigma,kl\tau}(\omega) \delta \nu_{kl\tau}^{ext}(\omega) \phi_{i\sigma}(r) \phi_{j\sigma}^*(r)
\]

(G.73)

Substitution of \(i = a\) and \(j = i\) (for consistency with the literature on TDDFT)

\[
\delta \rho_\sigma(r, \omega) = \sum_{a,i} \sum_{k,l,\tau} \chi_{a\sigma,kl\tau}(\omega) \delta \nu_{kl\tau}^{ext}(\omega) \phi_{a\sigma}(r) \phi_{i\sigma}^*(r)
\]
\[
= \sum_{a,i} \sum_{k,l,\tau} \delta_{\sigma\tau} \delta_{ak} \delta_{il} \left[ \frac{n_{i\sigma} - n_{a\sigma}}{\omega - (\epsilon_{a\sigma} - \epsilon_{i\sigma})} \right] \delta \nu_{kl\tau}^{ext}(\omega) \phi_{a\sigma}(r) \phi_{i\sigma}^*(r)
\]
\[
= \sum_{a,i} \sum_{k,l,\tau} \delta_{\sigma\tau} \delta_{ak} \delta_{il} \left[ \frac{n_{i\sigma} - n_{a\sigma}}{\omega - (\epsilon_{a\sigma} - \epsilon_{i\sigma})} \right] \int dr' \phi_{a\sigma}^*(r') \delta \nu_{kl\tau}^{ext}(r', \omega) \phi_{i\sigma}(r') \phi_{a\sigma}(r) \phi_{i\sigma}^*(r)
\]
\[
= \sum_{a,i} \left[ \frac{n_{i\sigma} - n_{a\sigma}}{\omega - (\epsilon_{a\sigma} - \epsilon_{i\sigma})} \right] \int dr' \phi_{a\sigma}^*(r') \phi_{i\sigma}(r') \delta \nu_{kl\tau}^{ext}(r', \omega) \phi_{a\sigma}(r) \phi_{i\sigma}^*(r)
\]
\[
= \int dr' \delta \nu_{kl\tau}^{ext}(r', \omega) \left\{ \sum_{a,i} (n_{i\sigma} - n_{a\sigma}) \phi_{a\sigma}^*(r') \phi_{i\sigma}(r') \phi_{a\sigma}(r) \phi_{i\sigma}^*(r) \right\}
\]

(G.74)

The term in curly brackets is the linear response function of the non-interacting system, \(\chi_{KS}(r, r', \omega)\), as defined in Eq. G.30 of Section 2.1. Basically, we just showed that there's more than one way to get to Eq. G.74, although the route we took in the present section
is more practical because it is based on how most modern quantum chemistry programs work (using finite basis sets, and hence density matrices). Comparing Eqs. G.33 and G.51, we see that $\delta P_{ia\sigma}(\omega) = C_{ia\sigma}(\omega)$ and $\delta P_{ai\sigma}(\omega) = C_{ia\sigma}^*(\omega)$.

For TDDFT, we are interested in calculating the perturbed orbitals of a system of interacting particles. The potential in this case is written using Eq. G.36 (we'll denote it as $\delta \upsilon_{eff}(\omega)$). To determine the linear response of the density matrix in TDDFT, we use Eq. G.65 with the effective potential $\delta \upsilon_{eff}(\omega)$ in place of the external potential, since the TDDFT equations use a quasi-independent particle system as a reference. This is written

$$
\delta P_{ai\sigma}(\omega) = \sum_{kl\tau} \chi_{ai\sigma,kl\tau}(\omega) \delta \upsilon_{eff}^{kl\tau}(\omega)
\]

$$
= \sum_{kl\tau} \delta_{\sigma\tau} \delta_{ak} \delta_{il} \delta \upsilon_{eff}^{kl\tau}(\omega) \left[ \frac{n_{i\sigma} - n_{a\sigma}}{\omega - (\epsilon_{a\sigma} - \epsilon_{i\sigma})} \right]
$$

$$
= \delta \upsilon_{ai\sigma}^{eff}(\omega) \left[ \frac{n_{i\sigma} - n_{a\sigma}}{\omega - (\epsilon_{a\sigma} - \epsilon_{i\sigma})} \right]
$$

$$
= \left[ \frac{n_{i\sigma} - n_{a\sigma}}{\omega - (\epsilon_{a\sigma} - \epsilon_{i\sigma})} \right] \int dr' \phi^*_{a\sigma}(r') \delta \upsilon_{eff}(\omega) \phi_{i\sigma}(r')
$$

$$
= \left[ \frac{n_{i\sigma} - n_{a\sigma}}{\omega - (\epsilon_{a\sigma} - \epsilon_{i\sigma})} \right] \int dr' \phi^*_{a\sigma}(r') \left\{ \delta \upsilon_{Coul}(\omega) + \delta \upsilon_{xc}(\omega) + \delta \upsilon_{ext}(\omega) \right\} \phi_{i\sigma}(r')
$$

$$
= \left[ \frac{n_{i\sigma} - n_{a\sigma}}{\omega - (\epsilon_{a\sigma} - \epsilon_{i\sigma})} \right] \left\{ \delta \upsilon_{Coul}^{ai\sigma}(\omega) + \delta \upsilon_{xc}^{ai\sigma}(\omega) + \delta \upsilon_{ext}^{ai\sigma}(\omega) \right\}
$$

(G.75)

The matrix elements of the external, Coulomb, and exchange-correlation potentials are defined

$$
\delta \upsilon_{ext}^{ai\sigma}(\omega) = \int dr' \phi^*_{a\sigma}(r') \delta \upsilon_{ext}(\omega) \phi_{i\sigma}(r')
$$

(G.76)

$$
\delta \upsilon_{Coul}^{ai\sigma}(\omega) = \int dr' \phi^*_{a\sigma}(r') \delta \upsilon_{Coul}(\omega) \phi_{i\sigma}(r')
$$

$$
= \int dr' \int dr'' \phi^*_{a\sigma}(r') \delta \rho_{\tau}(r'',\omega) \left| r' - r'' \right| \phi_{i\sigma}(r')
$$

(G.77)
\[ \delta u_{\text{xc}}^{\text{Coul}}(\omega) = \int dr' \int dr'' \phi_{\alpha \sigma}^* (r') f_{\text{xc}}^{\sigma\tau} (r', r'', \omega) \delta P_{b j \tau} (\omega) \phi_{\tau \sigma}^* (r'') \delta P_{b j \tau} (\omega) \]

because the Coulomb and exchange-correlation potentials depend on the first order change in the electron density, we can use Eq. G.51 to recast Eqs. G.77 and G.78 in terms of the first order change in the density matrix.

\[ \delta u_{\text{xc}}^{\text{Coul}}(\omega) = \sum_{b, j, \tau} \left\{ \int dr' \int dr'' \phi_{\alpha \sigma}^* (r') \phi_{\tau \sigma} (r'') \frac{1}{|r' - r''|} \phi_{b \tau} (r'') \phi_{b \tau}^* (r') \delta P_{b j \tau} (\omega) \right\} \delta P_{b j \tau} (\omega) \quad (G.79) \]

The quantities in the curly brackets define the coupling matrix contributions from the Coulomb potential \( K_{\text{Coul}}^{\text{Coul}}(r', r'') \) and the exchange-correlation potential \( K_{\text{xc}}(r', r'', \omega) \). The sum of these contributions defines the coupling matrix

\[ K_{a i \sigma, b j \tau} (r', r'', \omega) = K_{a i \sigma, b j \tau}^{\text{Coul}} (r', r'') + K_{a i \sigma, b j \tau}^{\text{xc}} (r', r'', \omega) \quad (G.81) \]

We can also write the sum of the Coulomb and exchange-correlation potentials as
\[ \delta v_{\text{Coul}}^{\text{ext}}(\omega) + \delta v_{\text{Coul}}^{\text{ext}}(\omega) = \sum_{b,j,\tau} \left[ K_{\text{Coul},bj\tau}(r',r'') + K_{\text{Coul},bj\tau}(r',r'',\omega) \right] \delta P_{bj\tau}(\omega) \]
\[ = \sum_{b,j,\tau} K_{\text{Coul},bj\tau}(r',r'',\omega) \delta P_{bj\tau}(\omega) \quad \text{(G.82)} \]

Now we can solve Eq. G.75 for the external potential

\[ \delta P_{a\sigma}(\omega) = \frac{n_{a\sigma} - n_{a\sigma}}{\omega - (\epsilon_{a\sigma} - \epsilon_{i\sigma})} \left\{ \sum_{b,j,\tau} K_{a\sigma,bj\tau}(r',r'',\omega) \delta P_{bj\tau}(\omega) + \delta v_{\text{Coul}}^{\text{ext}}(\omega) \right\} \quad \text{(G.83)} \]

\[ \delta v_{\text{Coul}}^{\text{ext}}(\omega) = \frac{\omega - (\epsilon_{a\sigma} - \epsilon_{i\sigma}) \delta P_{a\sigma}(\omega)}{n_{i\sigma} - n_{a\sigma}} - \sum_{b,j,\tau} K_{a\sigma,bj\tau}(r',r'',\omega) \delta P_{bj\tau}(\omega) \quad \text{(G.84)} \]

In order to condense Eq. G.84, notice that \( \delta P_{a\sigma}(\omega) = \sum_{b,j,\tau} \delta_{\sigma\tau} \delta_{ab} \delta_{ij} \cdot \delta P_{bj\tau}(\omega) \), which allows us to write

\[ \delta v_{a\sigma}^{\text{ext}}(\omega) = \sum_{b,j,\tau} \left[ \delta_{\sigma\tau} \delta_{ab} \delta_{ij} \frac{\omega - (\epsilon_{b\sigma} - \epsilon_{j\sigma})}{n_{j\sigma} - n_{b\sigma}} - K_{a\sigma,bj\tau}(r',r'',\omega) \right] \delta P_{bj\tau}(\omega) \quad \text{(G.85)} \]

Here we stress that \( b \neq j \) because the equality of those indices will create a discontinuity.

At this point it is insightful to compare the coupling matrix of TDDFT to that of time-dependent Hartree Fock (TDHF, sometimes also called the random phase approximation, RPA). In TDHF, the coupling matrix is given as

\[ K_{a\sigma,bj\tau}(r',r'') = K^{\text{Coul}}_{a\sigma,bj\tau}(r',r'') + K^{\text{EXX}}_{a\sigma,bj\tau}(r',r'') \quad \text{(G.86)} \]

The exact exchange (EXX) from Hartree Fock has a coupling matrix given by

\[ K^{\text{EXX}}_{a\sigma,bj\tau}(r',r'') = -\delta_{\sigma\tau} \int dr' \int dr'' \phi_{a\sigma}^*(r') \phi_{b\sigma}(r') \frac{1}{|r' - r''|} \phi_{i\sigma}(r'') \phi_{j\sigma}(r'') \quad \text{(G.87)} \]

Based solely on comparison of the electronic exchange contributions to the coupling
matrix (Eqs. G.80 and G.87), we see that the TDDFT coupling matrix depends on the frequency whereas the TDHF coupling matrix is frequency independent. Employing the adiabatic approximation makes the TDDFT coupling matrix frequency independent as well, and in that case the TDDFT coupling matrix and TDHF coupling matrix are most similar (but not identical, unless of course you’re doing a DFT calculation with 100% exact exchange and no correlation energy functional contribution).

Taking a step backwards for a moment, we can write the coupling matrix of TDDFT as

\[
K_{ai\sigma,bj\tau}(r', r'', \omega) = [\phi_{a\sigma}^* \phi_{i\sigma} | \phi_{b\tau} \phi_{j\tau}^*] + \int_{-\infty}^{\infty} e^{i\omega(t'-t'')} f_{ai\sigma,bj\tau}^{xc}(r', r'', \omega) d(t' - t'') \quad (G.88)
\]

\[
f_{ai\sigma,bj\tau}^{xc}(r', r'', \omega) = \int dr' \int dr'' \phi_{a\sigma}^*(r') \phi_{i\sigma}(r') \frac{\delta^2 E_{xc}[\rho]}{\delta \rho_{a}(r', t') \delta \rho_{b}(r'', t'')} \phi_{b\tau}(r'') \phi_{j\tau}^*(r'') \quad (G.89)
\]

Where we used the shorthand notation for the two-electron Coulomb integral (see Ref. 565, Table 2.2 on page 68) contribution to the coupling matrix, Eq. G.79. From Eq. G.88 we see that

\[
K_{ai\sigma,bj\tau}(r', r'', \omega) = [K_{bj\tau,ai\sigma}(r', r'', -\omega)]^* \quad (G.90)
\]

This notation means that we substitute \(\omega \rightarrow -\omega\) and take a complex conjugate, such that the exponential part of the Fourier transform remains unchanged. Also, for real orbitals, the TDDFT coupling matrix (for non-hybrid functionals) possesses symmetry

\[
K_{ai\sigma,bj\tau}(r', r'', \omega) = K_{ai\sigma,jb\tau}(r', r'', \omega) = K_{ia\sigma,jb\tau}(r', r'', \omega) = K_{ia\sigma,bj\tau}(r', r'', \omega) \quad (G.91)
\]

In the case of TDHF, because the coupling matrix is frequency-independent, we have (not assuming real orbitals)

\[
K_{ai\sigma,bj\tau}(r', r'') = K_{ia\sigma,jb\tau}(r', r'') \quad (G.92)
\]
If we then assume real orbitals, in TDHF

\[ K_{ai\sigma, bj\tau}(r', r'') \neq K_{ai\sigma, jib\tau}(r', r'') \]  

(Eq. G.93)

Eqs. G.91 and G.93 show that it is computationally simpler to do calculations with TDDFT (for non-hybrid functionals) than doing the calculation with TDHF. Often the accuracy for TDDFT is comparable or better than TDHF, depending on the user’s choice of functional. Choosing a functional contributed to by a nonlocal potential (exact exchange) results in a problem that loses the symmetry of the coupling matrix in TDDFT, which contributes to the added time required to solve the TDDFT equations when doing a calculation.

As discussed in Section 2.5 of Ref. 566, a general problem related to the coupling matrix is the dimensions of the matrix, which is \( N_{occ}^2 \cdot N_{virt}^2 \). For molecules with \( \geq 10^3 \) basis functions the matrix becomes too large to store in memory, and it would take significant CPU time to get excitation energies and oscillator strengths. Because we usually only need the lowest excitations of a molecule, it is possible to solve the TDDFT equation is solved iteratively such that the full coupling matrix isn’t calculated. A more detailed discussion dealing with solving the TDDFT equations can be found in Ref. 566 (which is available on the ADF website).

Based on Eq. G.85, the linear response equations are defined only when \( n_{b\tau} - n_{j\tau} \neq 0 \). In other words, assuming Aufbau occupations (\( n_{b\tau} \) is either 0 or 1), this means that only particle-hole and hole-particle contributions to the linear response of the density matrix are nonzero according to Eq. G.83. Let \( i, j \) refer to occupied orbitals, while \( a, b \) refer to virtual orbitals, where \( i < a \) and \( j < b \). Hence, \( \delta P_{ia\sigma} (\delta \nu_{ia\sigma}^{ext}) \) is an occupied-virtual (particle-hole) block and \( \delta P_{ai\sigma} (\delta \nu_{ai\sigma}^{ext}) \) is an virtual-occupied (hole-particle) block. Using Eq. G.85, the hole-particle block \( \delta \nu_{ai\sigma}^{ext} \) is given by
\[
\delta u_{\text{ext}}^{\text{ia\sigma}}(\omega) = \sum_{b,j,\tau} \left[ \left( \delta_{\sigma\tau} \delta_{ab} \delta_{ij} \frac{\omega - (\epsilon_{b\sigma} - \epsilon_{j\sigma})}{n_{j\sigma} - n_{b\sigma}} - K_{a\sigma,b\tau}(r', r'', \omega) \right) \delta P_{b\tau}(\omega) \right] - \sum_{b,j,\tau} K_{a\sigma,j\tau}(r', r'', \omega) \delta P_{j\tau}(\omega)
\]

\[
= \sum_{b,j,\tau} \left\{ - K_{a\sigma,j\tau}(r', r'', \omega) \delta P_{j\tau}(\omega) + \left[ \delta_{\sigma\tau} \delta_{ab} \delta_{ij} \left( \frac{\epsilon_{b\sigma} - \epsilon_{j\sigma}}{n_{b\sigma} - n_{j\sigma}} - K_{a\sigma,b\tau}(r', r'', \omega) \right) \delta P_{b\tau}(\omega) + \omega \left( \frac{\delta_{\sigma\tau} \delta_{ab} \delta_{ij}}{n_{b\sigma} - n_{j\sigma}} \right) \delta P_{b\tau}(\omega) \right\}
\]

and the particle-hole block \(\delta u_{\text{ext}}^{\text{ia\sigma}}\) is

\[
\delta u_{\text{ext}}^{\text{ia\sigma}}(\omega) = \sum_{b,j,\tau} \left[ \left( \delta_{\sigma\tau} \delta_{ab} \delta_{ij} \frac{\omega - (\epsilon_{j\sigma} - \epsilon_{b\sigma})}{n_{j\sigma} - n_{b\sigma}} - K_{i\sigma,j\tau}(r', r'', \omega) \right) \delta P_{j\tau}(\omega) \right] - \sum_{b,j,\tau} K_{i\sigma,b\tau}(r', r'', \omega) \delta P_{b\tau}(\omega)
\]

\[
= \sum_{b,j,\tau} \left\{ - K_{i\sigma,j\tau}(r', r'', \omega) \delta P_{j\tau}(\omega) + \left[ \delta_{\sigma\tau} \delta_{ab} \delta_{ij} \left( \frac{\epsilon_{j\sigma} - \epsilon_{b\sigma}}{n_{j\sigma} - n_{b\sigma}} - K_{i\sigma,b\tau}(r', r'', \omega) \right) \delta P_{b\tau}(\omega) - K_{a\sigma,j\tau}(r', r'', \omega) \delta P_{b\tau}(\omega) - \omega \left( \frac{\delta_{\sigma\tau} \delta_{ab} \delta_{ij}}{n_{b\sigma} - n_{j\sigma}} \right) \delta P_{b\tau}(\omega) \right\}
\]

The additional sums for Eqs. (G.94) and (G.95) account for the missed terms when the sums are restricted such that \(b > j\). Simplification to each expression was performed under the assumption that we are worked with non-hybrid DFT, where the coupling matrix is very symmetric. Exchange of the indices of the coupling matrix is not as straightforward when a hybrid functional is used. Both Eqs. (G.94) and (G.95) can be verified by looking at a system where it is possible to enumerate the combinations of orbitals, such as a system with 2 occupied and 2 virtual orbitals, and restricting the summation. Let
\[ A_{ai\sigma,bj\tau}(\omega) = \delta_{\sigma\tau} \delta_{ab} \delta_{ij} \left( \epsilon_{i\sigma} - \epsilon_{j\sigma} \right) \frac{n_{b\sigma} - n_{j\sigma}}{n_{b\sigma} - n_{j\sigma}} - K_{ai\sigma,bj\tau}(r', r'', \omega) \] (G.96)

\[ B_{ai\sigma,bj\tau}(\omega) = -K_{ai\sigma,jb\tau}(r', r'', \omega) \] (G.97)

\[ C_{ai\sigma,bj\tau} = \delta_{\sigma\tau} \delta_{ab} \delta_{ij} \] (G.98)

Eqs. G.94 and G.95 then reduce to

\[ \delta v_{ai\sigma}^{ext}(\omega) = \sum_{b,j,\tau} \left\{ B_{ai\sigma,bj\tau}(\omega)\delta P_{jb\tau}(\omega) + A_{ai\sigma,bj\tau}(\omega)\delta P_{bj\tau}(\omega) + \omega C_{ai\sigma,bj\tau}\delta P_{bj\tau}(\omega) \right\} \] (G.99)

\[ \delta v_{ia\sigma}^{ext}(\omega) = \sum_{b,j,\tau} \left\{ A_{ia\sigma,bj\tau}(\omega)\delta P_{jb\tau}(\omega) + B_{ai\sigma,bj\tau}(\omega)\delta P_{bj\tau}(\omega) - \omega C_{ai\sigma,bj\tau}\delta P_{jb\tau}(\omega) \right\} \] (G.100)

In this form, it is clear that we may write the two expressions in a single matrix equation

\[
\begin{bmatrix}
A(\omega) & B(\omega) \\
B(\omega) & A(\omega)
\end{bmatrix}
- \omega
\begin{bmatrix}
C & 0 \\
0 & -C
\end{bmatrix}
\begin{bmatrix}
\delta \vec{P}(\omega) \\
\delta \vec{P}^*(\omega)
\end{bmatrix}
= \begin{bmatrix}
\delta \vec{v}_{ext}(\omega) \\
\delta \vec{v}_{ext}^*(\omega)
\end{bmatrix}
\] (G.101)

Eq. G.101 are sometimes called the Casida equations. The top row of the matrices in brackets is identified with the particle-hole part of the equations, and the bottom row is the hole-particle part. It is important to note that the equations are solved using matrices, where the row is indexed by \((ia\sigma)\) (with \(n_i > n_a\)) and the column is indexed by \((jb\tau)\) (with \(n_j > n_b\)). Letting \(\delta P_{jb\tau}(\omega)\) define the Fourier transform of \(\delta P_{jb\tau}(t)\), by definition \(\delta P_{jb\tau}(\omega) = \delta P_{bj\tau}^*(\omega)\). Casida stresses, however, that the order of taking the Fourier transform and performing the complex conjugation does matter,
so $\delta P_{j\tau}(\omega) = \delta P^{*}_{b\tau}(\omega)$ (i.e. the expressions are equal when the Fourier transform is taken of the complex conjugate, not when the complex conjugate is taken of the Fourier transform). This discussion is also true for the external potential $\delta \nu^e_{ia\sigma}$. Alternatively the TDDFT equations can be written to look more (notationally) similar to the TDHF equations

$$\begin{pmatrix} A(\omega) & B(\omega) \\ B(\omega) & A(\omega) \end{pmatrix} - \omega \begin{pmatrix} C & 0 \\ 0 & -C \end{pmatrix} \begin{pmatrix} \tilde{X}(\omega) \\ \tilde{Y}(\omega) \end{pmatrix} = \begin{pmatrix} \tilde{V}(\omega) \\ \tilde{W}(\omega) \end{pmatrix} \quad \text{(G.102)}$$

Here we define

$$X_{b\tau}(\omega) = \delta P_{j\tau}(\omega), \quad Y_{b\tau}(\omega) = \delta P_{b\tau}(\omega) \quad \text{(G.103)}$$

$$V_{ia\sigma}(\omega) = \delta \nu^e_{i\sigma}(\omega), \quad W_{ai\sigma}(\omega) = \delta \nu^e_{i\sigma}(\omega) \quad \text{(G.104)}$$

We’ll assume the dependence of $A, B, \tilde{X}, \tilde{Y}, \tilde{V}$ and $\tilde{W}$ on the frequency $\omega$ for the rest of the section for notational convenience.

Employing the unitary transformation,

$$U = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}, \quad UU^\dagger = 1 \quad \text{(G.105)}$$

allows for the separation of the real/symmetric and imaginary/antisymmetric parts of the linear response of the density matrix. Substitution of $UU^\dagger = 1$ between $(\tilde{X}, \tilde{Y})^T$ and the term in square brackets, along with left multiplication by $U \cdot \sqrt{2}$ gives (see Section G.3.2 for explicit work)

$$\begin{pmatrix} A + B & 0 \\ 0 & A - B \end{pmatrix} + \omega \begin{pmatrix} 0 & C \\ C & 0 \end{pmatrix} \begin{pmatrix} \tilde{X} + \tilde{Y} \\ \tilde{Y} - \tilde{X} \end{pmatrix} = \begin{pmatrix} \tilde{V} + \tilde{W} \\ \tilde{W} - \tilde{V} \end{pmatrix} \quad \text{(G.106)}$$

These expressions can be written in terms of two linear equations
\[(\vec{X} + \vec{Y}) = (A + B)^{-1}[(\vec{V} + \vec{W}) - \omega C(\vec{Y} - \vec{X})]\]
\[(\vec{Y} - \vec{X}) = (A - B)^{-1}[(\vec{W} - \vec{V}) - \omega C(\vec{X} + \vec{Y})]\]  
\[(G.107)\]

We can find the real and imaginary parts of the linear response of the density matrix by substitution. These are given below

\[
[(A + B) - \omega^2 C(A - B)^{-1}C](\vec{X} + \vec{Y}) = (\vec{V} + \vec{W}) - \omega C(A - B)^{-1}(\vec{W} - \vec{V})
\]
\[
[(A - B) - \omega^2 C(A + B)^{-1}C](\vec{Y} - \vec{X}) = (\vec{W} - \vec{V}) - \omega C(A + B)^{-1}(\vec{V} + \vec{W})
\]  
\[(G.108)\]

or alternatively

\[
[(A + B) - \omega^2 C(A - B)^{-1}C]\text{Re}\delta\vec{P}(\omega) = \text{Re}\delta\vec{v}_{ext}(\omega) + i\omega C(A - B)^{-1}\text{Im}\delta\vec{v}_{ext}(\omega)
\]
\[
[(A - B) - \omega^2 C(A + B)^{-1}C]\text{Im}\delta\vec{P}(\omega) = \text{Im}\delta\vec{v}_{ext}(\omega) - i\omega C(A + B)^{-1}\text{Re}\delta\vec{v}_{ext}(\omega)
\]  
\[(G.109)\]

For a real perturbation (i.e. an electric field) of the molecule, \(\vec{V} = \vec{W}\) and the real part of the \(\delta\vec{P}(\omega)\) is

\[
[(A + B) + \omega^2 S](\vec{X} + \vec{Y}) = 2\vec{V}
\]  
\[(G.110)\]

where

\[
S = -C(A - B)^{-1}C
\]  
\[(G.111)\]

A particular element, \(S_{\alpha\beta,\lambda\tau}\), is given by (only in non-hybrid DFT)
\[ S_{ai\sigma,bj\tau} = -\frac{\delta_{\sigma\tau}\delta_{ab}\delta_{ij}}{n_{a\sigma} - n_{i\sigma}} \left( \delta_{\sigma\tau}\delta_{ab}\delta_{ij} \left( \frac{\epsilon_{b\sigma} - \epsilon_{j\sigma}}{n_{b\sigma} - n_{j\sigma}} \right) - K_{ai\sigma,bj\tau}(r', r'', \omega) \right) + K_{ai\sigma,jb\tau}(r', r'', \omega) \left( \frac{\delta_{\sigma\tau}\delta_{ab}\delta_{ij}}{n_{b\tau} - n_{j\tau}} \right)^{-1} \]

\[ = \frac{\delta_{\sigma\tau}\delta_{ab}\delta_{ij}}{(n_{b\sigma} - n_{j\sigma})(\epsilon_{j\sigma} - \epsilon_{b\sigma})} \] (G.112)

The matrix elements of \( S \) are guaranteed to be positive, because the difference \( n_{b\sigma} - n_{j\sigma} \) is negative and \( \epsilon_{j\sigma} - \epsilon_{b\sigma} \) is negative also. Consequently, the matrix \( S \) is positive definite and invertible also. This is not guaranteed in TDHF (and hybrid DFT) due to the reduced symmetry of the coupling matrix.

To identify excitation energies, we insert \( 1 = S^{-1/2}S^{1/2} \) between \( (A + B) + \omega^2 S \) and \( (\vec{X} + \vec{Y}) \) in Eq. G.110 and multiply the equation on the left by \( S^{-1/2} \)

\[ S^{-1/2}[(A + B) + \omega^2 S]S^{-1/2}S^{1/2}(\vec{X} + \vec{Y}) = 2S^{-1/2}\vec{V} \]
\[ [S^{-1/2}(A + B)S^{-1/2} + \omega^2 1]S^{1/2}(\vec{X} + \vec{Y}) = 2S^{-1/2}\vec{V} \] (G.113)

Where the \( \Omega \) matrix is defined

\[ \Omega = -S^{-1/2}(A + B)S^{-1/2} \] (G.114)

We can solve Eq. G.113 for the real part of the first order change in the density matrix, \( (\vec{X} + \vec{Y}) \),

\[ (\vec{X} + \vec{Y}) = S^{-1/2}[\omega^2 1 - \Omega]^{-1}2S^{-1/2}\vec{V} \] (G.115)

Based on this equation, we can determine the excitation energies of the system. As long as \( S \) is positive definite (which is guaranteed in non-hybrid TDDFT), the only singularity occurs when \( [\omega^2 1 - \Omega] \) is zero. In order to find the excitation energies, it is necessary to solve the eigenvalue problem
\[ \Omega \vec{F}_I = \omega_{I_0}^2 \vec{F}_I \]  

(G.116)

Here, \( \vec{F}_I \) is the eigenvector associated with excitation \( I \leftarrow 0 \) (going from the ground state to excited state \( I \)), and \( \omega_{I_0} \) are the electronic excitation energies. By solving Eq. G.116 it is also possible to find the oscillator strengths (and transition dipole moments), along with \( (\vec{X} + \vec{Y}) \). See Chapter 3 of Ref. 567 for information on evaluating those quantities.

Because the eigenvalue problem Eq. G.116 has a large dimension, it is usually not possible to solve using the entire matrix \( \Omega \). Instead, since we’re usually interested in the lowest energy excitations of the molecule, it is possible to use an iterative procedure such as the Davidson algorithm to solve the equation. In circumstances when it is possible to compute all excitations (all of the vectors \( \vec{F}_I \)), the calculation is called \textit{exact}. Calculating all excitations allows for the study of the polarizability using the sum-over-states formula.

**G.2.4 Connection of the TDDFT Equations and Polarizability**

For this section, we’re interested in a specific external perturbation, which will be used to calculate a component of the frequency-dependent polarizability tensor. Let the external perturbation be defined

\[ \delta \nu_{ext}(t) = \dot{\varepsilon}_z(t) \]  

(G.117)

If we’re interested in the \( xz \)-component of the polarizability tensor, \( \alpha_{xz}(t - t') \), we can expand the \( x \)-component of the dipole moment to first order in the time-dependent function \( \varepsilon_z(t) \),

\[ \mu_x(t) = \mu_x^{perm} + \delta \mu_x(t) + \ldots \]

\[ = \mu_x^{perm} + \int_{-\infty}^{\infty} \alpha_{xz}(t - t') \varepsilon_z(t') dt' + \ldots \]  

(G.118)

Here, \( \delta \mu_x(t) \) is the linear response of the dipole moment (induced dipole in the presence of one electric field). The Fourier convolution theorem can be used to write this equation in the frequency-domain instead.
\[ \mu_x(\omega) = \mu_x^{\text{perm}} + \delta \mu_x(\omega) + \ldots = \mu_x^{\text{perm}} + \alpha_{xz}(\omega) \epsilon_z(\omega) + \ldots \] (G.119)

We now need to relate the linear response of the dipole moment to the linear response of the density matrix. If we introduce the x-component of the dipole operator, \( \hat{\mu}_x = -e \hat{x} \), into Eq. G.51 and integrate over all space

\[
\delta \mu_x(\omega) = \sum_{a \sigma} \langle \phi_{ia} | \hat{\mu}_x | \phi_{ia} \rangle \delta P_{a \sigma}(\omega) = \sum_{a \sigma} \mu_{x,iaa} \delta P_{a \sigma}(\omega) = - \sum_{a \sigma} x_{iaa} \delta P_{a \sigma}(\omega)
\]
\[
= - \sum_{a \sigma, bj \tau} x_{iaa} \chi_{ai \sigma, bj \tau}(\omega) \delta v_{bj \tau}^{\text{ext}}(\omega) = - \sum_{a \sigma, bj \tau} x_{iaa} \chi_{ai \sigma, bj \tau}(\omega) z_{bj \tau} \epsilon_z(\omega)
\]

(G.120)

Here we work in atomic units (\( e = 1 \)) for convenience. Comparing Eq. G.119 and G.120, we see that the frequency-dependent polarizability is defined as

\[
\alpha_{xz}(\omega) = \frac{\delta \mu_x(\omega)}{\epsilon_z(\omega)} = - \sum_{a \sigma, bj \tau} x_{iaa} \chi_{ai \sigma, bj \tau}(\omega) z_{bj \tau}
\]

(G.121)

Using Eq. G.51 with \( a > i \), we have (note that \( x_{iaa} = x_{ai \sigma} \))

\[
\delta \mu_x(\omega) = - \sum_{a \sigma} n_{i}^{a} - n_{a}^{i} > 0 \left( x_{iaa} \delta P_{a \sigma}(\omega) + x_{iaa} \delta P_{a \sigma}(\omega) \right)
\]
\[
= - \sum_{a \sigma} x_{iaa} \left( \delta P_{a \sigma}(\omega) + \delta P_{a \sigma}(\omega) \right) = 2 \bar{D}^{T} (\bar{X} + \bar{Y})
\]

(G.122)

where \( \bar{D} \) is a vector containing electric dipole matrix elements. Thus, it is clear that finding \( (\bar{X} + \bar{Y}) \) is related to determining the frequency-dependent polarizability

\[
\alpha_{xz}(\omega) = -2 \sum_{a \sigma} n_{i}^{a} - n_{a}^{i} > 0 \frac{x_{iaa} (X_{a \sigma}(\omega) + Y_{a \sigma}(\omega))}{\epsilon_z(\omega)}
\]

(G.123)
G.3 Davidson Algorithm

G.3.1 Matrices are too big? No problem!

As described above, most users of TDDFT are only interested in the lowest few excitations of the molecule. Iterative solution to the TDDFT equations involve application of the Davidson algorithm, which has been outlined by several authors.\textsuperscript{36,568,569} This section aims to demonstrate what happens in a TDDFT calculation, referencing what is observed in an NWChem output to clarify certain aspects of the algorithm when possible.

The excitation energies of a molecule are associated with the poles of the linear response function, which are identified in Eq. G.68 when the denominator becomes zero (when $\omega = E_I - E_0$ for $\eta = 0$, $\omega$ is the excitation energy for state $I$). In relation to Eq. G.102, the poles are identified when the matrix on the left side has a zero eigenvalue. This gives (we don’t write the explicit dependence of matrices and vectors on $\omega$ for convenience)

\[
\left[ \begin{array}{cc} A & B \\ B & A \end{array} \right] - \omega \left[ \begin{array}{cc} C & 0 \\ 0 & -C \end{array} \right] \left[ \begin{array}{c} \vec{X} \\ \vec{Y} \end{array} \right] = 0 \quad (G.124)
\]

Using the unitary transformation, Eq. G.105, by inserting $U^\dagger U$ between the matrix and vector yields

\[
\left[ \begin{array}{cc} A + B & 0 \\ 0 & A - B \end{array} \right] + \omega \left[ \begin{array}{cc} 0 & C \\ C & 0 \end{array} \right] \left[ \begin{array}{c} \vec{X} + \vec{Y} \\ \vec{X} - \vec{Y} \end{array} \right] = 0 \quad (G.125)
\]

Note that $C = -1$ (negative identity matrix), since by definition we always have $n_{ba} - n_{ja} = -1$ by our definitions of occupied $(i, j)$ and virtual $(a, b)$ orbitals and the Kronecker deltas in Eq. G.98 dictate that off-diagonal elements are zero. This expression is alternatively written

\[
\left( \begin{array}{cc} A + B & 0 \\ 0 & A - B \end{array} \right) \left( \begin{array}{c} \vec{X} + \vec{Y} \\ \vec{X} - \vec{Y} \end{array} \right) = \omega \left( \begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array} \right) \left( \begin{array}{c} \vec{X} + \vec{Y} \\ \vec{X} - \vec{Y} \end{array} \right) \quad (G.126)
\]

which leads to
\[(A + B)(\vec{X} + \vec{Y}) = \omega(\vec{X} - \vec{Y}) \quad \text{(G.127)}\]

\[(A - B)(\vec{X} - \vec{Y}) = \omega(\vec{X} + \vec{Y})\]

Solving for \((\vec{X} - \vec{Y})\) and inserting into the first linear equation gives

\[(A - B)(A + B)(\vec{X} + \vec{Y}) = \omega^2(\vec{X} + \vec{Y}) \quad \text{(G.128)}\]

Eq. G.128 is a non-Hermitian eigenvalue problem, which may be solved using the Davidson algorithm (although in general this type of problem is difficult to solve). It is possible to make this expression easier to solve if \((A - B)\) is positive definite. This is guaranteed when a pure DFT exchange-correlation functional is used, but is not always true when hybrid functionals are employed. The vectors, \(\vec{R}_i^{\text{true}} = (\vec{X} + \vec{Y})_i\) and \(\vec{L}_i^{\text{true}} = (\vec{X} - \vec{Y})_i\), are the right and left eigenvectors of the matrix product shown on the left side of Eq. G.128 (the \(i\) here refers to the eigenvalue a particular eigenvector corresponds with). Assuming that \((A - B)\) is positive definite, both sides of Eq. G.128 may be left multiplied by \((A - B)^{-1/2}\) and we can insert \((A - B)^{1/2}(A - B)^{-1/2} = 1\) between the matrix and vector on the left side to get

\[(A - B)^{-1/2}(A - B)(A + B)(A - B)^{1/2}(A - B)^{-1/2}(\vec{X} + \vec{Y}) \quad \text{(G.129)}\]

\[= \omega^2(A - B)^{-1/2}(\vec{X} + \vec{Y})\]

\[(A - B)^{1/2}(A + B)(A - B)^{1/2}\vec{T} = \omega^2\vec{T} \quad \text{(G.130)}\]

with

\[\vec{T} = (A - B)^{-1/2}(\vec{X} + \vec{Y}) \quad \text{(G.131)}\]

Eq. G.129 is a Hermitian eigenvalue problem, which is also solvable by the Davidson algorithm. However, it is easier to solve Hermitian eigenvalue problems and preferable to use this form of the equation when possible. Hermitian matrices also guarantee real
eigenvalues, which is another benefit.

The goal of this section now shifts to solving the (non-)Hermitian eigenvalue problem. In general, we want an approach that will work for small and large molecules. Larger molecules pose the problem that it becomes impractical to store the entire sum and difference between the \( A \) and \( B \) matrices in memory. This demands that a direct procedure be used, where the particular elements of matrices and vectors are calculated and used as needed and stored in memory.

For the problem at hand, assume we want the lowest \( k \) excitations (eigenvalues of Eq. G.128 or Eq. G.129) of a large molecule. At this point, we also set a convergence threshold for the eigenvalues of the problem (NWChem uses \( 1 \times 10^{-4} \) a.u. for the excitation energies). The dimension (maximum number of distinct eigenvalues) of the problem is \( N = N_{\text{occ}} \times N_{\text{virt}} \), where \( N_{\text{occ}} \) is the number of occupied MOs and \( N_{\text{virt}} \) is the number of virtual MOs. The remainder of this section is written similarly with Ref. 36, which describes the Davidson algorithm in an algorithmic way. See also Ref. 570 for more information on the Davidson algorithm (and diagonalizing matrices).

**Step 1**: Select an orthonormal basis, \( \vec{b}_1, \vec{b}_2, \ldots, \vec{b}_l \) (\( l \geq k \)) that spans the left and right eigenvectors. It seems likely that most codes would choose the standard (canonical) basis for the trial vectors. For example, say we want the lowest 3 excitations for a molecule with 3 occupied and 3 virtual orbitals (shown in Figure G.1). Clearly this is example is not for a large molecule, but it is easy to enumerate all possible transitions.

The first thing the program (NWChem, for instance) determines is the MO energy differences to estimate which orbitals are involved in the lowest \( k \) excitations of the molecule. In our example, \( 3 \rightarrow 4 \) (HOMO \( \rightarrow \) LUMO), \( 3 \rightarrow 5 \) (HOMO \( \rightarrow \) LUMO+1), and \( 2 \rightarrow 4 \) (HOMO–1 \( \rightarrow \) LUMO) correspond to the 3 lowest energy differences/excitations. To form the orthonormal basis, the easiest choice is the standard basis of unit vectors. The trial vectors spanning the right eigenvectors for the lowest 3 excitations are given in Eq. G.132, where the vector on the left side of the expression shows the association between the occupied-virtual orbital pairs and the 1’s and 0’s in the unit vectors. At this point, it is also worthwhile to note that the left and right eigenvectors are bi-orthogonal, which is defined by the dot product in Eq. G.133. In the basis of trial vectors chosen for our example, we see that the initial trial vector subspace spanning the left eigenvectors are just transposes of vectors spanning the right eigenvectors. Since we use the Hermitian form of the problem, the left and right eigenvectors are always transposes of each other.
### Energy | Index
---|---
0.15 | 6
-0.15 | 5
-0.45 | 4
-0.85 | 3
-1.20 | 2
-1.60 | 1

| Transition | $\Delta E$ |
---|---|
1→4 | 1.15 |
1→5 | 1.45 |
1→6 | 1.75 |
2→4 | 0.75 |
2→5 | 1.05 |
2→6 | 1.35 |
3→4 | 0.40 |
3→5 | 0.70 |
3→6 | 1.00 |

**Figure G.1.** Example ground state electronic structure for a molecule with 3 occupied and 3 virtual orbitals. Energies and indices are shown and referred to in the text. The table indicates the energy differences for all possible electronic transitions (single excitations only).

\[
\begin{pmatrix}
1 \rightarrow 4 \\
1 \rightarrow 5 \\
1 \rightarrow 6 \\
2 \rightarrow 4 \\
2 \rightarrow 5 \\
2 \rightarrow 6 \\
3 \rightarrow 4 \\
3 \rightarrow 5 \\
3 \rightarrow 6
\end{pmatrix}
= 
\begin{pmatrix}
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
0
\end{pmatrix},
\begin{pmatrix}
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
0
\end{pmatrix},
\begin{pmatrix}
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
0
\end{pmatrix}
\Rightarrow 
\begin{pmatrix}
0, 0, 0 \\
0, 0, 1 \\
0, 0, 0 \\
1, 0, 0 \\
0, 1, 0 \\
0, 0, 0
\end{pmatrix}
\tag{G.132}
\]

\[
\left((\vec{X} - \vec{Y})_i^*, (\vec{X} + \vec{Y})_j\right) = \delta_{ij}
\tag{G.133}
\]

**Step 2:** Form the matrix-vector products, \((A + B)\vec{b}_i\) and \((A - B)\vec{b}_i\), for \(i = 1, \ldots, l\). I have no experience in calculating this part alone, but every author involved in implementing TDHF/TDDFT (excitations or polarizability) claims that this is the most CPU intensive step in the entire procedure.\cite{36,571} In particular, the paper by Weiss et al. demonstrates how the vectors associated with a particular excitation, from occupied orbital \(i\)
to virtual orbital a, are calculated at the level of TDHF. To write similar equations for TDDFT, we would clearly need to include the contribution from the exchange-correlation kernel, and a mixing coefficient for the exact-exchange in the case of a hybrid functional.

Step 3: Form the reduced dimension matrices, $\tilde{M}^+_ij = (\tilde{b}_i, (A + B)\tilde{b}_j)$ and $\tilde{M}^-ij = (\tilde{b}_i, (A - B)\tilde{b}_j)$, for $i, j = 1, \ldots, l$. The + and − superscripts on the matrices are meant to remind the reader of the association of the reduced matrices with the $A + B$ and $A - B$ matrices. Again, for two vectors, the notation $(\tilde{e}, \tilde{f}) = \sum_i e_i f_i$ indicates an inner product (dot product). The reason these are reduced dimension matrices is that they now contain $l \times l$ elements, instead of the original problem which contained $N^2 = (N_{\text{occ}} \times N_{\text{virt}})^2$ elements.

Step 4: The procedure at this point depends on whether the $A - B$ matrix is positive definite. If the $A - B$ matrix is not positive definite, we would need to form the non-Hermitian matrix product:

$$\tilde{M}^{nh} = \sum_j \tilde{M}^-ij \tilde{M}^+_jk = \sum_j \left[ \tilde{b}_i^T \cdot (A - B)\tilde{b}_j \right] \left[ \tilde{b}_j^T \cdot (A + B)\tilde{b}_k \right]$$

This expression is the analogue of Eq. G.128, in the reduced dimension. Most codes (NWChem, ADF, ...) are implemented in terms of the Hermitian matrix product:

$$\tilde{M}^{nh} = \sum_{j,k} \left( \tilde{M}^-ij \right)^{1/2} \left( \tilde{M}^+_jk \right) \left( \tilde{M}^-km \right)^{1/2} = \sum_{j,k} \left[ \tilde{b}_i^T \cdot (A - B)\tilde{b}_j \right]^{1/2} \left[ \tilde{b}_j^T \cdot (A + B)\tilde{b}_k \right] \left[ \tilde{b}_k^T \cdot (A - B)\tilde{b}_m \right]^{1/2}$$

which is the analogue of Eq. G.129 in the reduced dimension. Using the Hermitian form of the problem is guaranteed to work if the matrix $A - B$ is positive definite (when LDA or any GGA is used for the exchange-correlation functional). When hybrid functionals, including exact exchange, are used the matrix is not guaranteed to be positive definite, so the algorithm will check if this is true. In NWChem, when a hybrid functional is used and $A - B$ is not positive definite, the code outputs the error “tdflt_diagon: A-B is not positive-definite; try TDA”. The Tamm-Dancoff approximation (TDA) amounts to setting the matrix $B$ and vector $\tilde{Y}$ equal to zero, which has the net effect of making the
problem a Hermitian eigenvalue problem without any extra manipulation.

Step 5: Diagonalize $\tilde{M}_{mn}^h$ to find its eigenvalues and eigenvectors. The eigenvalues are written in this notation as $\tilde{\omega}_n$ (the best guess for the $n$th eigenvalue), and the best guess left and right eigenvectors are $\tilde{L}_n$ and $\tilde{R}_n$, respectively. Using these eigenvectors allows us to obtain the best approximation to the true $N$-dimensional left ($\tilde{L}_n$) and right ($\tilde{R}_n$) eigenvectors as a set of linear combinations of the trial vectors

\begin{equation}
\tilde{L}_n = \sum_{i=1}^{l} \tilde{L}_{in} \tilde{b}_i
\end{equation}

\begin{equation}
\tilde{R}_n = \sum_{i=1}^{l} \tilde{R}_{in} \tilde{b}_i
\end{equation}

It is necessary at this step to impose the bi-orthogonality condition, Eq. G.133, such that the inner product of the left and right eigenvectors corresponding to the same eigenvalue is one.

Step 6: Based on Eq. G.127, calculate the residual vectors $\tilde{W}_n$ for the left and right eigenvectors

\begin{equation}
\tilde{W}^L_n = (A + B)\tilde{R}_n - \tilde{\omega}_n \tilde{L}_n
\end{equation}

\begin{equation}
\tilde{W}^R_n = (A - B)\tilde{L}_n - \tilde{\omega}_n \tilde{R}_n
\end{equation}

At this point, we are able to determine whether any of the excitation energies are converged compared to the threshold. This is accomplished by taking the norm of the left and right residual vectors, determining which norm is larger, and comparing the larger norm to the threshold. If the larger norm is less than the threshold, that particular eigenvalue is converged. When all of the norms of all residual vectors fall below the threshold, the calculation is finished. However, if some of the norms are not below the threshold, we continue onward in the algorithm.

Step 7: If at least one norm of a residual vector is not below the threshold, we augment the basis of trial vectors with $2(k - m)$ new basis vectors, where $k$ is the number
of eigenvalues we want and \( m \) is the number of converged eigenvalues. These new vectors are preconditioned vectors, which we will denote \( \vec{q}_n \), are defined using the residual vectors

\[
q_{in} = (\tilde{\omega}_n - D_i)^{-1}W_{in}, \quad i = 1, \ldots, N
\]  

(G.140)

Again, \( N = N_{\text{occ}} \times N_{\text{virt}} \). The matrix elements \( D_i \) are the approximate diagonal elements of the non-Hermitian matrix we are trying to find eigenvalues for. These may be taken as \( \epsilon_{a\sigma} - \epsilon_{i\sigma} \) (each element of the vector \( \vec{q}_n \) corresponds to a particular occupied-virtual orbital pair, as in Eq. G.132).

Step 8: The \( \vec{q}_n \) vectors are orthonormalized against each other and the original set of \( l \) trial vectors, giving a set of \( l + 2(k - m) \) trial vectors. All vectors in this trial set are still denoted \( \vec{b}_i \).

Step 9: Repeat step 2 by forming and saving the vectors \((A + B)\vec{b}_i\) and \((A - B)\vec{b}_i\), for \( i = l + 1, \ldots, l + 2(k - m) \). Keep in mind we already have the corresponding matrix-vector products from the original trial set of \( l \) vectors. In all steps replace \( l \) by \( l + 2(k - m) \). Go to step 3 and repeat this process until all excitation energies are converged.

G.3.2 Separation of Real and Imaginary Parts of \( \delta \vec{P} \)

Starting from Eq. G.101 and using Eq. G.105, we obtain

\[
\sqrt{2}U \begin{pmatrix} A & B \\ B & A \end{pmatrix} - \omega \begin{pmatrix} C & 0 \\ 0 & -C \end{pmatrix} U^\dagger U \begin{pmatrix} \delta \vec{P}(\omega) \\ \delta \vec{P}^*(\omega) \end{pmatrix} = \sqrt{2}U \begin{pmatrix} \delta \vec{\upsilon}_{\text{ext}}(\omega) \\ \delta \vec{\upsilon}_{\text{ext}}^*(\omega) \end{pmatrix}
\]  

(G.141)

The left hand side of the equation is given by
\[
\frac{1}{2} \left( \begin{array}{cc} 1 & 1 \\ -1 & 1 \\ \end{array} \right) \left[ \left( \begin{array}{cc} A & B \\ B & A \\ \end{array} \right) - \omega \left( \begin{array}{cc} C & 0 \\ 0 & -C \\ \end{array} \right) \right] \left( \begin{array}{cc} 1 & -1 \\ 1 & 1 \\ \end{array} \right) \left( \begin{array}{cc} \delta \tilde{P}(\omega) \\ \delta \tilde{P}^*(\omega) \\ \end{array} \right) \\
= \frac{1}{2} \left[ \left( \begin{array}{cc} A + B & B + A \\ -A + B & -B + A \\ \end{array} \right) - \omega \left( \begin{array}{cc} C & -C \\ -C & C \\ \end{array} \right) \right] \left( \begin{array}{cc} 1 & -1 \\ 1 & 1 \\ \end{array} \right) \\
\times \begin{pmatrix} \delta \tilde{P}(\omega) + \delta \tilde{P}^*(\omega) \\ \delta \tilde{P}^*(\omega) - \delta \tilde{P}(\omega) \end{pmatrix}
\]

Combining this with the right side of the equation gives

\[
\left[ \left( \begin{array}{cc} A & 0 \\ 0 & A - B \end{array} \right) - \omega \left( \begin{array}{cc} 0 & -C \\ -C & 0 \end{array} \right) \right] \left( \begin{array}{cc} \delta \tilde{P}(\omega) + \delta \tilde{P}^*(\omega) \\ \delta \tilde{P}^*(\omega) - \delta \tilde{P}(\omega) \end{array} \right)
\]

\[
(G.142)
\]

Because the real and complex parts of a complex number \( x \) are defined

\[
\text{Re}(x) = \frac{x + x^*}{2}, \\
\text{Im}(x) = \frac{x - x^*}{2i}
\]

\[
\left[ \left( \begin{array}{cc} A & 0 \\ 0 & A - B \end{array} \right) + \omega \left( \begin{array}{cc} 0 & C \\ C & 0 \end{array} \right) \right] \left( \begin{array}{cc} \text{Re} \delta \tilde{P}(\omega) \\ -i \text{Im} \delta \tilde{P}(\omega) \end{array} \right) = \left( \begin{array}{cc} \text{Re} \delta \tilde{u}_{ext}(\omega) \\ -i \text{Im} \delta \tilde{u}_{ext}(\omega) \end{array} \right)
\]

\[
(G.143)
\]

If we choose to write the response equations in the notation used for TDHF, \( \text{Re} \delta \tilde{P}(\omega) = \tilde{X} + \tilde{Y} \), \( -i \text{Im} \delta \tilde{P}(\omega) = \tilde{Y} - \tilde{X} \), \( \text{Re} \delta \tilde{u}_{ext}(\omega) = \tilde{V} + \tilde{W} \), \( -i \text{Im} \delta \tilde{u}_{ext}(\omega) = \tilde{W} - \tilde{V} \). This gives Eq. G.106.
H.1 Initial Details

H.1.1 Equivalence of Notations

Up front, it is necessary to define some conventions in notation (most of these are standard):

1. Indices $i, j, k, l, \ldots$ are for occupied molecular orbitals (MOs)
2. Indices $a, b, c, d, \ldots$ are for virtual MOs
3. Indices $p, q, r, s, \ldots$ are for arbitrary MOs (can be occupied or virtual, depending on the situation)
4. Indices $\sigma, \tau, \nu$ are for spin
5. Indices $\alpha, \beta, \kappa, \lambda, \mu, \nu$ refer to atomic orbitals (AOs)

We always assume that an MO, $\phi_{p\sigma}(r)$, can be written as a linear combination of AOs

$$\phi_{p\sigma}(r) = \sum_{\mu} C_{\mu p\sigma} \chi_{\mu}(r) \quad \text{(H.1)}$$

In general, the TDDFT equations may be written in the form of a non-Hermitian eigenvalue problem
The matrices $A$ and $B$, which are sometimes called orbital rotation Hessians, have the following matrix representation

$$A_{ia\sigma j\beta r} = \delta_{\sigma\tau}\delta_{ab}\delta_{ij}(\epsilon_{i\sigma} - \epsilon_{i\alpha}) + (ia\sigma|j\beta\tau) + f^{xc}_{ia\alpha j\beta r} - c_x\delta_{\sigma\tau}(ab\sigma|ij\sigma) \quad (H.3)$$

$$B_{ia\alpha j\beta r} = (ia\sigma|j\beta\tau) + f^{xc}_{ia\alpha j\beta r} - c_x\delta_{\sigma\tau}(ja\sigma|ib\sigma) \quad (H.4)$$

In both expressions, $f^{xc}_{\sigma\tau}$ is the exchange-correlation (XC) kernel

$$f^{xc}_{\sigma\tau} = \frac{\delta^2 E^{xc}}{\delta\rho_{\sigma}(r')\delta\rho_{\tau}(r)} \quad (H.5)$$

The XC-kernel is implicitly dependent on the parameter $c_x$ which determines how much exact exchange to include in calculation. If $c_x$ is used to set the amount of exact exchange, $(1 - c_x)$ sets the amount of exchange from the XC-functional (making this explicit in the equation requires writing separate exchange and correlation kernels, so I choose not to do it here). The definitions of the orbital rotation Hessians rely on solving the TDDFT equations for the negative of the external potential, in contrast to my notes on linear response TDDFT. It seems like this is the more common method for writing the equations.

If Eq. H.2 is left multiplied by the vector $(\vec{X}^T \; \vec{Y}^T)$, the expression can also be written

$$\left( \begin{array}{cc} A & B \\ B & A \end{array} \right) \left( \begin{array}{c} \vec{X} \\ \vec{Y} \end{array} \right) = \omega \left( \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right) \left( \begin{array}{c} \vec{X} \\ \vec{Y} \end{array} \right) \quad (H.6)$$

An alternative notation, used in several references on TDDFT such as Refs. 64 and 572, uses a superoperator notation for the equation and casts the expression in terms of a
functional, $G[\vec{X},\vec{Y},\omega]$. This functional is written

$$G[\vec{X},\vec{Y},\omega] = \langle \vec{X},\vec{Y} | \Lambda | \vec{X},\vec{Y} \rangle - \omega \left( \langle \vec{X},\vec{Y} | \Delta | \vec{X},\vec{Y} \rangle - 1 \right) \quad (H.7)$$

The superoperators, $\Lambda$ and $\Delta$, are the matrices

$$\Lambda = \begin{pmatrix} A & B \\ B & A \end{pmatrix} \quad (H.8)$$

$$\Delta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (H.9)$$

The vectors involved in the evaluation of $G[\vec{X},\vec{Y},\omega]$ can be written in more explicit notation

$$| \vec{X},\vec{Y} \rangle = \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} \quad (H.10)$$

Here, we see the similarity between the definition of the TDDFT equations in Eqs. H.6 and H.7. The extra factor of $-\omega$ in the second term of $G[\vec{X},\vec{Y},\omega]$ accounts for the bi-orthogonality condition of the left and right eigenvectors of the problem. The functional $G[\vec{X},\vec{Y},\omega]$ may also be written in a more explicit form

$$G[\vec{X},\vec{Y},\omega] = \begin{pmatrix} \vec{X}^T & \vec{Y}^T \end{pmatrix} \begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} - \omega \left[ \begin{pmatrix} \vec{X}^T & \vec{Y}^T \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} - 1 \right] \quad (H.11)$$

H.1.2 Simplifying $G[\vec{X},\vec{Y},\omega]$

A $2 \times 2$ unitary transformation can be used to reduce the dimension of the equation by half (i.e. go from $2N_{\text{occ}} \times N_{\text{virt}}$ eigenvalues to $N_{\text{occ}} \times N_{\text{virt}}$ eigenvalues). This transformation has the form
\[
U = \frac{1}{\sqrt{2}} \begin{pmatrix}
1 & -1 \\
1 & 1
\end{pmatrix}
\]  
(H.12)

Inserting the product \(UU^\dagger = 1\) into the expression, we can perform this reduction of dimension. This is shown explicitly in the Appendix. The functional \(G[\vec{X}, \vec{Y}, \omega]\) may be written

\[
G[\vec{X}, \vec{Y}, \omega] = \frac{1}{2} \left[ (\vec{X} + \vec{Y})^T (A + B)(\vec{X} + \vec{Y}) + (\vec{X} - \vec{Y})^T (A - B)(\vec{X} - \vec{Y}) \right] \\
- \omega \left[ (\vec{X} + \vec{Y})^T (\vec{X} - \vec{Y}) - 1 \right]
= \frac{1}{2} \sum_{ia\sigma,jb\tau} \left[ (X + Y)_{ia\sigma}(A + B)_{ia\sigma,jb\tau}(X + Y)_{jb\tau} \\
+ (X - Y)_{ia\sigma}(A - B)_{ia\sigma,jb\tau}(X - Y)_{jb\tau} \right] \\
- \omega \left[ \sum_{ia\sigma} (X + Y)_{ia\sigma}(X - Y)_{ia\sigma} - 1 \right]
\]

(H.13)

The linear combinations of the orbital rotation Hessians are defined

\[
(A + B)_{ia\sigma,jb\tau} = \delta_{\sigma\tau}\delta_{ab\delta_{ij}}(\epsilon_{a\sigma} - \epsilon_{i\sigma}) + 2(ia\sigma|jb\tau) + 2f_{ia\sigma,jb\tau}^{xc} \\
- c_x\delta_{\sigma\tau} [(ab\sigma|ij\sigma) + (ja\sigma|ib\sigma)]
\]

(H.14)

and

\[
(A - B)_{ia\sigma,jb\tau} = \delta_{\sigma\tau}\delta_{ab\delta_{ij}}(\epsilon_{a\sigma} - \epsilon_{i\sigma}) + c_x\delta_{\sigma\tau} [(ja\sigma|ib\sigma) - (ab\sigma|ij\sigma)]
\]

(H.15)

By explicitly taking derivatives of \(G[\vec{X}, \vec{Y}, \omega]\) with respect to \((\vec{X} \pm \vec{Y})\), it is possible to derive the TDDFT equations in matrix form (since \(G\) is required to be stationary with respect to its parameters)
\[
\sum_{jb\tau}(A + B)_{ia\sigma}jb\tau(X + Y)_{jb\tau} = \omega(X - Y)_{ia\sigma} \\
\sum_{jb\tau}(A - B)_{ia\sigma}jb\tau(X - Y)_{jb\tau} = \omega(X + Y)_{ia\sigma}
\]  \(\text{(H.16)}\)

Differentiation with respect to \(\omega\) instead results in the normalization condition of the left and right eigenvectors

\[
\sum_{ia\sigma}(X + Y)_{ia\sigma}(X - Y)_{ia\sigma} = 1
\]  \(\text{(H.17)}\)

This illustrates the rationale behind the form of the functional, and that it is indeed possible to obtain the correct form of the TDDFT equations from this functional. It is very nonstandard to write the TDDFT equations in terms of a functional however. Also, it may not be obvious by inspection, but \(G\) defines the excitation energy (i.e. \(\omega = G[\vec{X}, \vec{Y}, \omega]\)). This is important for understanding the rationale of the expression.

Using Eq. H.6 along with the unitary transformation in Eq. H.12, we obtain

\[
\omega \left[(\vec{X} + \vec{Y})^T(\vec{X} - \vec{Y})\right] = \frac{1}{2} \left[ (\vec{X} + \vec{Y})^T(A + B)(\vec{X} + \vec{Y}) + (\vec{X} - \vec{Y})^T(A - B)(\vec{X} - \vec{Y}) \right]
\]  \(\text{(H.18)}\)

The latter expression uses that the left and right eigenvectors for a given excitation are normalized.

**H.1.3 The Lagrangian Functional**

The rationale in this section is defining the method of Furche and Ahlrichs \(^{64}\) for evaluating TDDFT gradients without derivatives of the MO coefficients. The assumption that the canonical Kohn-Sham (KS) MOs are used is not required, but will be used to be consistent with Ref. 64. This amounts to rewriting the combinations of orbital rotation Hessians as
\[(A + B)_{ia\sigma, jb\tau} = \delta_{\sigma\tau}(F_{ab\sigma}\delta_{ij} - F_{ij\sigma}\delta_{ab}) + 2(ia\sigma|jb\tau) + 2f_{ia\sigma, jb\tau}^{xc}
- c_x\delta_{\sigma\tau}[(ab\sigma|i\j) + (ja\sigma|i\b)]\]  
\hspace{1cm} (H.19)

and

\[(A - B)_{ia\sigma, jb\tau} = \delta_{\sigma\tau}(F_{ab\sigma}\delta_{ij} - F_{ij\sigma}\delta_{ab}) + c_x\delta_{\sigma\tau}[(ja\sigma|i\b) - (ab\sigma|i\j)] \]  
\hspace{1cm} (H.20)

where the Fock matrix, in the basis of canonical KS MOs, is written: \(F_{pq\sigma} = \delta_{pq}\epsilon_{p\sigma}\).

Written out more explicitly, the Fock matrix is given by

\[F_{pq\sigma} = h_{pq\sigma} + \sum_{\i\j}[((pq\sigma|i\i\j) - c_x\delta_{\sigma\tau}(pi\sigma|iq\sigma)] + V_{pq\sigma}^{xc}\]  
\hspace{1cm} (H.21)

In Eq. H.21, \(h\) is the core Hamiltonian, the second term is a Coulomb integral, the third term is the exact exchange part, and the XC-potential is

\[V_{pq\sigma}^{xc} = \langle p\sigma|V_{\sigma}^{xc}|q\sigma\rangle = \int d\mathbf{r}\phi_{p\sigma}(\mathbf{r})\frac{\delta E_{xc}}{\delta \rho_\sigma(\mathbf{r})}\phi_{q\sigma}(\mathbf{r})\]  
\hspace{1cm} (H.22)

Following from Ref. 64, the Lagrangian functional is defined

\[L[\mathbf{X}, \mathbf{Y}, \omega, \mathbf{C}, \mathbf{Z}, \mathbf{W}] =
\frac{1}{2} \sum_{ia\sigma, jb\tau} [(X + Y)_{ia\sigma}(A + B)_{ia\sigma, jb\tau}(X + Y)_{jb\tau}
+ (X - Y)_{ia\sigma}(A - B)_{ia\sigma, jb\tau}(X - Y)_{jb\tau}]
- \omega \sum_{ia\sigma}(X + Y)_{ia\sigma}(X - Y)_{ia\sigma} - 1]
+ \sum_{ia\sigma} Z_{ia\sigma} F_{ia\sigma} - \sum_{pq\sigma, p \leq q} W_{pq\sigma}(S_{pq\sigma} - \delta_{pq})
= G[\mathbf{X}, \mathbf{Y}, \omega] + \sum_{ia\sigma} Z_{ia\sigma} F_{ia\sigma} - \sum_{pq\sigma, p \leq q} W_{pq\sigma}(S_{pq\sigma} - \delta_{pq})\]  
\hspace{1cm} (H.23)

Based on the assumption of canonical orbitals and understanding of the overlap matrix elements, it should be obvious that we are effectively adding zero to the \(G\) functional.
when \( L \) is defined. Hence, the excitation energy \( \omega \) is equivalent to the \( L \), much like it was equivalent to \( G \) in Eq. H.18. The Lagrangian functional is required to be stationary with respect to its dependent variables. Differentiation with respect to \( \vec{X} \pm \vec{Y} \) and \( \omega \) yields the TDDFT equations described above. The Lagrange multiplier \( \vec{Z} \) enforces that the MOs satisfy the ground state KS equations, while the Lagrange multiplier \( \vec{W} \) enforces that the MOs are orthonormal:

\[
\frac{\partial L}{\partial Z_{pq\sigma}} = F_{pq\sigma} = 0 \quad p \neq q \quad (H.24)
\]

\[
\frac{\partial L}{\partial W_{pq\sigma}} = S_{pq\sigma} - \delta_{pq} = 0 \quad (H.25)
\]

By enforcing that the ground state KS equations are satisfied, the MO coefficients \( \vec{C} \) are held constant because they were variationally optimized, and thus

\[
\frac{\partial L}{\partial C_{\mu\sigma}} = 0 \quad (H.26)
\]

This requirement is necessary to derive the the forms of the Lagrange multipliers \( \vec{Z} \) and \( \vec{W} \). The major goal from this point is to evaluate the derivative in Eq. H.26, which can be written explicitly as shown in Eq. H.27.

\[
\frac{\partial L}{\partial C_{\mu\sigma}} = 0 = \frac{\partial G}{\partial C_{\mu\sigma}} + \sum_{i\alpha\tau} Z_{i\alpha\tau} \frac{\partial F_{i\alpha\tau}}{\partial C_{\mu\sigma}} - \sum_{r\sigma, s, r \\leq s} W_{r\tau s} \frac{\partial S_{r\tau s}}{\partial C_{\mu\sigma}} \quad (H.27)
\]

Because the Lagrange multipliers \( \vec{Z} \) and \( \vec{W} \) enforce that the ground state KS equations are satisfied, derivatives of those with respect to the MO coefficients are zero (the ground state energy is variationally optimized, or stationary, with respect to the MO coefficients).

In the final term on the right hand side, the indices of the summation are changed such that no terms in the general expression are lost when the derivative is taken.

Eq. H.27 is the requirement that \( L \) is stationary with respect to the MO coefficients. Mathematically, the equivalence of the derivative with zero allows us to perform any operations we want on both sides of the equation, and have the resulting expression equal
zero as well. We choose to multiply both sides of the equation with the MO coefficient $C_{\mu q\sigma}$ and sum both sides of the equation over the AO indices, $\mu$. The result is

$$
\sum_{\mu} \frac{\partial G}{\partial C_{\mu p\sigma}} C_{\mu q\sigma} + \sum_{\mu} \sum_{i\alpha\tau} Z_{i\alpha\tau} \frac{\partial F_{i\alpha\tau}}{\partial C_{\mu p\sigma}} C_{\mu q\sigma} - \sum_{\mu} \sum_{r_{st},r\leq s} \frac{W_{rst}}{C_{\mu p\sigma}} C_{\mu q\sigma} = 0
$$

In Section H.2, we will differentiate each term of Eq. H.28 from right to left. The derivative of $G$ is nontrivial compared to the other terms. I’ve numbered the terms to make it easier to discuss them in Section H.2.

**H.2 Derivatives of the Lagrangian Functional (MO Coefficients)**

As stated above, the goal of this section is to evaluate the derivative of the Lagrangian with respect to the MO coefficients. For all derivatives, the MO coefficient $C_{\mu p\sigma}$ can be either occupied or virtual. This can have very subtle effects on the equations, especially for the derivatives of the $G$ functional. We will wait until after all derivatives are evaluated to show the final form of the equations, with indices corresponding to occupied and/or virtual orbitals, which are required to find the Lagrange multipliers $\vec{Z}$ and $\vec{W}$.

**H.2.1 Derivative of the Overlap Matrix (Term 3)**

Resulting from its simple form, the derivative of the overlap matrix $S_{rst}$ with respect to the MO coefficients is straightforward. The derivative can be evaluated easily

$$
\frac{\partial S_{rst}}{\partial C_{\mu p\sigma}} = \frac{\partial}{\partial C_{\mu p\sigma}} [\langle \phi_{r\tau} | \phi_{s\tau} \rangle] = \frac{\partial}{\partial C_{\mu p\sigma}} \left[ \sum_{\alpha\beta} C_{\alpha r\tau} C_{\beta s\tau} \langle \chi_\alpha | \chi_\beta \rangle \right]
$$

$$
= \sum_{\alpha\beta} \delta_{\mu\alpha} \delta_{pr} \delta_{\sigma\tau} C_{\beta s\tau} \langle \chi_\alpha | \chi_\beta \rangle + \sum_{\alpha\beta} C_{\alpha r\tau} \delta_{\mu\beta} \delta_{ps} \delta_{\sigma\tau} \langle \chi_\alpha | \chi_\beta \rangle
$$

$$
= \sum_{\beta} \delta_{pr} \delta_{\sigma\tau} C_{\beta s\tau} \langle \chi_\mu | \chi_\beta \rangle + \sum_{\alpha} C_{\alpha r\tau} \delta_{ps} \delta_{\sigma\tau} \langle \chi_\alpha | \chi_\mu \rangle
$$

(H.29)

Hence, if we multiply by $C_{\mu p\sigma}$ and sum over $\mu$. 

\[
\sum_{\mu} \frac{\partial S_{rst}}{\partial C_{\mu p\sigma}} C_{\mu q\sigma} = \sum_{\mu \beta} \delta_{pr} \delta_{\sigma \tau} C_{\mu q\sigma} C_{\beta \sigma \tau} \langle \chi_{\mu} | \chi_{\beta} \rangle + \sum_{\alpha \mu} C_{\alpha \tau \sigma} \delta_{ps} \delta_{\sigma \tau} C_{\mu q\sigma} \langle \chi_{\alpha} | \chi_{\mu} \rangle \\
= \delta_{pr} \delta_{\sigma \tau} \langle \phi_{q\sigma} | \phi_{s\sigma} \rangle + \delta_{ps} \delta_{\sigma \tau} \langle \phi_{r\sigma} | \phi_{q\sigma} \rangle \\
= \delta_{pr} \delta_{\sigma \tau} S_{qs\sigma} + \delta_{ps} \delta_{\sigma \tau} S_{rq\sigma} \\
\] (H.30)

This is simplified as much as possible, such that we can calculate the general form of Term 3:

\[
\sum_{\mu} \sum_{rst, r \leq s} W_{rst} \frac{\partial S_{rst}}{\partial C_{\mu p\sigma}} C_{\mu q\sigma} = \sum_{rst, r \leq s} W_{rst} (\delta_{pr} \delta_{\sigma \tau} S_{qs\sigma} + \delta_{ps} \delta_{\sigma \tau} S_{rq\sigma}) \\
= \sum_{rst, r \leq s} W_{rst} (\delta_{pr} \delta_{\sigma \tau} \delta_{qs} + \delta_{ps} \delta_{\sigma \tau} \delta_{rq}) \\
= \sum_{rst, r \leq s} W_{rst} (\delta_{pr} \delta_{\sigma \tau} \delta_{qs} + \delta_{ps} \delta_{\sigma \tau} \delta_{rq}) \\
= \sum_{s} W_{ps\sigma} \delta_{qs} + \sum_{r} W_{rp\sigma} \delta_{rq} \\
\] (H.31)

If \( p = r \) and \( q = s \) (but \( p \neq s \) and/or \( q \neq r \)), we obtain a nondiagonal term where the third term is equal to \( W_{pq\sigma} \). If \( p = r \) and \( q = s \), and \( p = s \) and \( q = r \), we obtain a diagonal term where the value is \( 2W_{pq\sigma} \). Hence, the general form of the equation for Term 3 is

\[
\sum_{\mu} \sum_{rst, r \leq s} W_{rst} \frac{\partial S_{rst}}{\partial C_{\mu p\sigma}} C_{\mu q\sigma} = (1 + \delta_{pq}) W_{pq\sigma} \\
\] (H.32)

This confirms the expressions in the erratum of Ref. 64.

**H.2.2 Derivative of the Fock Matrix (Term 2)**

The derivative of the Fock matrix \( F_{\mu \tau \sigma} \) in Term 2 is more complicated than the derivative of the overlap matrix in Section H.2.1. Note that although we are using the canonical orbitals \( (F_{pq\sigma} = \delta_{pq} \epsilon_{p\sigma}) \), this equivalence should not be employed until after the derivative is taken. The explicit form for the derivative of the Fock matrix is (with the summation over \( \mu \) and multiplication by \( C_{\mu q\sigma} \))
\[
\sum_{\mu} \frac{\partial F_{i\alpha \tau}}{\partial C_{\mu \rho \sigma}} C_{\mu \rho \sigma} = \sum_{\mu} \frac{\partial}{\partial C_{\mu \rho \sigma}} \left[ h_{i\alpha \tau} + \sum_{j\upsilon} \{(i\alpha \tau | j\upsilon) - c_{\xi \delta \tau \upsilon} (i\jmath \tau | j\upsilon)\} + V_{i\alpha \tau}^{\text{xc}} \right] C_{\mu \rho \sigma}
\]  

(H.33)

It is convenient to evaluate the derivatives of each term separately. Here, each contribution (core Hamiltonian, Coulomb integral, exchange integral, XC-potential matrix elements) are written in terms of the AO basis

\[ h_{i\alpha \tau} = \sum_{\alpha \beta} C_{\alpha \rho \tau} C_{\beta \rho \tau} h_{\alpha \beta} \]  

(H.34)

\[ (i\alpha \tau | j\upsilon) = \sum_{\alpha \beta \kappa \lambda} C_{\alpha \rho \tau} C_{\beta \rho \tau} C_{\kappa \upsilon \tau} C_{\lambda \upsilon \tau} (\alpha \beta | \kappa \lambda) \]  

(H.35)

\[ (i\jmath \tau | j\alpha \tau) = \sum_{\alpha \beta \kappa \lambda} C_{\alpha \rho \tau} C_{\beta \rho \tau} C_{\kappa \upsilon \tau} C_{\lambda \upsilon \tau} (\alpha \beta | \kappa \lambda) \]  

(H.36)

\[ V_{i\alpha \tau}^{\text{xc}} = \sum_{\alpha \beta} C_{\alpha \rho \tau} C_{\beta \rho \tau} (\alpha | V_{\tau}^{\text{xc}} | \beta) \]  

(H.37)

The individual derivatives of each term are straightforward to evaluate

\[ \sum_{\mu} \frac{\partial}{\partial C_{\mu \rho \sigma}} \left[ h_{i\alpha \tau} \right] C_{\mu \rho \sigma} = \delta_{\sigma \tau} \delta_{ip} h_{q\alpha \sigma} + \delta_{\tau \sigma} \delta_{ap} h_{iq \sigma} \]  

(H.38)

\[ \sum_{\mu} \frac{\partial}{\partial C_{\mu \rho \sigma}} \left[ (i\alpha \tau | j\upsilon) \right] C_{\mu \rho \sigma} = \delta_{\sigma \tau} \delta_{ip} (q\alpha \tau | j\upsilon) + \delta_{\tau \sigma} \delta_{ap} (i\alpha \tau | j\upsilon) + 2\delta_{\sigma \upsilon} \delta_{jp} (q\alpha \tau | q\upsilon) \]  

(H.39)
\[
\sum_\mu \frac{\partial}{\partial C_{\mu p \sigma}} [(ij|ja\tau)] C_{\mu q \sigma} = \delta_{\sigma \tau} \delta_{ip} (q j|ja\tau) + \delta_{\sigma \tau} \delta_{jq} (i j|q a\tau) + \delta_{\sigma \tau} \delta_{ap} (i j|q a\tau)
\]

(H.40)

\[
\sum_\mu \frac{\partial}{\partial C_{\mu p \sigma}} [V_{i a\tau}^{xc}] C_{\mu q \sigma} = \delta_{\sigma \tau} \delta_{ip} V_{i a\tau}^{xc} + \delta_{\sigma \tau} \delta_{jp} V_{i q\tau}^{xc} + \sum_\mu \int dr \phi_{i \tau}(r) \frac{\partial}{\partial C_{\mu p \sigma}} \left[ \frac{\delta E^{xc}}{\delta \rho_{\sigma}(r)} \right] \phi_{a\tau}(r) C_{\mu q \sigma}
\]

(H.41)

The final term in the derivative of the XC-potential matrix elements can be determined using the chain rule for functional derivatives (see Appendix A of Ref. 45). The chain rule is used to write

\[
\frac{\partial}{\partial C_{\mu p \sigma}} \left[ \frac{\delta E^{xc}}{\delta \rho_{\sigma}(r)} \right] = \int dr' \frac{\partial}{\partial \rho_{\sigma}(r')} \left[ \frac{\delta E^{xc}}{\delta \rho_{\sigma}(r)} \right] \frac{\partial \rho_{\sigma}(r')}{\partial C_{\mu p \sigma}}
\]

\[
= \int dr' \frac{\delta^2 E^{xc}}{\delta \rho_{\sigma}(r') \delta \rho_{\sigma}(r)} \left[ \frac{\partial \rho_{\sigma}(r')}{\partial C_{\mu p \sigma}} \right]
\]

\[
= \int dr' f_{\sigma \tau}^{xc} \left[ \frac{\partial \rho_{\sigma}(r')}{\partial C_{\mu p \sigma}} \right]
\]

(H.42)

The XC-kernel is defined in Eq. H.5. The electron density is written

\[
\rho_{\sigma}(r') = \sum_j |\phi_{j\sigma}(r')|^2 = \sum_j \sum_{\alpha \beta} C_{\alpha j \sigma} C_{\beta j \sigma} \chi_{\alpha}(r') \chi_{\beta}(r')
\]

(H.43)

It is assumed that the AO basis functions are real, hence we drop the complex conjugation in writing the final form of the density. The derivative of the electron density with respect to MO coefficients is trivial to evaluate

\[
\frac{\partial \rho_{\sigma}(r')}{\partial C_{\mu p \sigma}} = \sum_j \sum_{\alpha \beta} \left[ \delta_{\alpha \mu} \delta_{j p} C_{\beta i \sigma} \chi_{\alpha}(r') \chi_{\beta}(r') + C_{\alpha j \sigma} \delta_{\beta \mu} \delta_{j p} \chi_{\alpha}(r') \chi_{\beta}(r') \right]
\]

\[
= \sum_j \delta_{j p} \left[ \sum_{\beta} C_{\beta p \sigma} \chi_{\mu}(r') \chi_{\beta}(r') + \sum_{\alpha} C_{\alpha p \sigma} \chi_{\alpha}(r') \chi_{\mu}(r') \right]
\]

(H.44)
Hence, the derivative in Eq. H.42 can be simplified by including the summation over $\mu$ and multiplying by $C_{\mu q \sigma}$

$$\sum_{\mu} \frac{\partial}{\partial C_{\mu q \sigma}} \left[ \frac{\delta E^{xc}}{\delta \rho_\tau(r)} \right] C_{\mu q \sigma} = \sum_j \delta_{jp} \int dr' f^{xc}_{\sigma \tau}(\phi_{q \sigma}(r') \phi_{p \sigma}(r') + \phi_{p \sigma}(r') \phi_{q \sigma}(r'))$$

$$= 2 \sum_j \delta_{jp} \int dr' \phi_{p \sigma}(r') f^{xc}_{\sigma \tau} \phi_{q \sigma}(r')$$  \hspace{1cm} (H.45)

The derivative of the XC-potential matrix elements can then be written

$$\sum_{\mu} \frac{\partial}{\partial C_{\mu q \sigma}} \left[ V^{xc}_{ia \tau} \right] C_{\mu q \sigma} = \delta_{\sigma \tau} \delta_{ip} V^{xc}_{qa \tau} + \delta_{\sigma \tau} \delta_{ap} V^{xc}_{iq \tau}$$

$$+ 2 \int dr \int dr' \phi_{p \sigma}(r') \phi_{q \sigma}(r') \frac{\delta^2 E^{xc}}{\delta \rho_\sigma(r) \delta \rho_\tau(r)} \phi_{i \tau}(r) \phi_{a \tau}(r)$$  \hspace{1cm} (H.46)

$$= \delta_{\sigma \tau} \delta_{ip} V^{xc}_{qa \tau} + \delta_{\sigma \tau} \delta_{ap} V^{xc}_{iq \tau} + 2 \sum_j \delta_{jp} f^{xc}_{pq \sigma i a \tau}$$

At this point, the equations look much more complicated than the one we started with, so now we want to simplify the expression as much as possible. The best strategy seems to be inspecting the individual derivatives and noticing that many of the terms have identical Kronecker deltas. Based on that, we can collect the terms based on the deltas. The derivative of the Fock matrix, including the summation over $\mu$ and multiplication by $C_{\mu q \sigma}$, is
\[
\sum_{\mu} \frac{\partial F_{i\alpha\tau}}{\partial C_{\mu\rho\sigma}} C_{\mu q \sigma} = \delta_{\sigma \tau} \left[ \delta_{i p} \left( h_{q a \sigma} + \sum_{j v} [(q a \tau | j j v) - c_x \delta_{\tau v} (q j \tau | j a \tau)] + V^{xc}_{q a \tau} \right) + \delta_{a p} \left( h_{i q \sigma} + \sum_{j v} [(i q \tau | j j v) - c_x \delta_{\tau v} (i j \tau | j q \tau)] + V^{xc}_{i q \tau} \right) \right] \\
+ \sum_{j v} \left[ 2 \delta_{\sigma \nu} \delta_{j p} (i a \tau | j q v) - c_x \delta_{\tau v} \delta_{\sigma \tau} \delta_{j p} \{(i q \tau | j a \tau) + (i j \tau | q a \tau)\} \right] + 2 \sum_{j} \delta_{j p} f_{p q \sigma i \alpha \tau}^{xc} \\
= \delta_{\sigma \tau} \delta_{i p} F_{q a \sigma} + \delta_{\sigma \tau} \delta_{a p} F_{i q \sigma} + \sum_{j} \delta_{j p} \left\{ 2 (i a \tau | q p \sigma) + 2 f_{p q \sigma i \alpha \tau}^{xc} - c_x \delta_{\sigma \nu} [(i q v | p a v) + (i p v | q a v)] \right\} \\
\text{(H.47)}
\]

This is much simpler looking, and can be used to find Term 2:

\[
\sum_{i a \tau} Z_{i a \tau} \sum_{\mu} \frac{\partial F_{i a \tau}}{\partial C_{\mu \rho \sigma}} C_{\mu q \sigma} \\
= \sum_{i a \tau} (\delta_{\sigma \tau} \delta_{i p} F_{q a \sigma} + \delta_{\sigma \tau} \delta_{a p} F_{i q \sigma}) Z_{i a \tau} \\
+ \sum_{j} \delta_{j p} \sum_{i a \tau} \left[ 2 (i a \tau | q p \sigma) + 2 f_{p q \sigma i \alpha \tau}^{xc} - c_x \delta_{\sigma \nu} [(i q v | p a v) + (i p v | q a v)] \right] Z_{i a \tau} \\
= \sum_{i a \tau} (\delta_{\sigma \tau} \delta_{i p} \delta_{q a} + \delta_{\sigma \tau} \delta_{a p} \delta_{i q}) \epsilon_{q a} Z_{i a \tau} + \sum_{j} \delta_{j p} H_{p q \sigma i a \tau}^{+} [\bar{Z}] \\
\text{(H.48)}
\]

Here, the linear transformation is

\[
H_{p q \sigma i a \tau}^{+} [\bar{Z}] = \sum_{r s \tau} \left[ 2 (r s \tau | q p \sigma) + 2 f_{p q \sigma r s \tau}^{xc} - c_x \delta_{\sigma \nu} [(r q v | p s v) + (r p v | q s v)] \right] Z_{r s \tau} \\
\text{(H.49)}
\]

Note that the final expression in Eq. H.48 implicitly defines that \( Z_{i j \tau} = Z_{a b \tau} = 0 \). Also, the linear transformation is only applied if \( p \) refers to an occupied orbital index, as indicated by the Kronecker delta.
H.2.3 Derivative of the $G$ Functional (Term 1)

Due to its complexity, we remind the reader of the form of the functional $G$ here (indices are changed from Eq. H.13, but the correspondence to occupied/virtual orbitals is still the same)

$$G[\vec{X}, \vec{Y}, \omega] = \frac{1}{2} \sum_{kcrldv} (X + Y)_{kcr} (A + B)_{kcrldv} (X + Y)_{ldv} + \frac{1}{2} \sum_{kcrldv} (X - Y)_{kdr} (A - B)_{kcrldv} (X - Y)_{ldv} - \omega \left[ \sum_{kcr} (X + Y)_{kcr} (X - Y)_{kcr} - 1 \right]$$  \hspace{1cm} (H.50)

Clearly, $G$ is a sum of three terms which can have their derivatives evaluated independently. To simplify the equations in Section H.3, use the following definition

$$Q_{pq\sigma} = \sum_{\mu} \frac{\partial G[\vec{X}, \vec{Y}, \omega]}{\partial C_{\mu p\sigma}} C_{\mu q\sigma}$$

$$= \sum_{\mu} \frac{\partial}{\partial C_{\mu p\sigma}} \left[ \frac{1}{2} \sum_{kcrldv} (X + Y)_{kcr} (A + B)_{kcrldv} (X + Y)_{ldv} \right] C_{\mu q\sigma}$$  \hspace{1cm} (H.51)

$$+ \sum_{\mu} \frac{\partial}{\partial C_{\mu p\sigma}} \left[ \frac{1}{2} \sum_{kcrldv} (X - Y)_{kdr} (A - B)_{kcrldv} (X - Y)_{ldv} \right] C_{\mu q\sigma}$$

$$- \sum_{\mu} \frac{\partial}{\partial C_{\mu p\sigma}} \left[ \omega \left[ \sum_{kcr} (X + Y)_{kcr} (X - Y)_{kcr} - 1 \right] \right] C_{\mu q\sigma}$$

For Term III, we can make use of Eq. H.17 and eliminate the derivative with respect to $C_{\mu p\sigma}$ entirely, because the excitation vectors $(\vec{X} \pm \vec{Y})$ are assumed to be the solution to the TDDFT equations (in other words, we’re taking the derivative of 0). We’re not so fortunate for the other two terms, which are more complicated. The remainder of this section is divided into multiple parts which attempt to explicitly tackle the derivatives.
H.2.3.1 Preliminary work-up of Terms I and II

Owing to the orbital stationarity condition (Eq. H.26) and that the Lagrangian is dependent on the excitation vectors ($\vec{X}$ and $\vec{Y}$), the derivative of term I is given by the derivative of the orbital rotation Hessian

$$\sum_{\mu} \frac{\partial}{\partial C_{\mu p q}} \left[ \frac{1}{2} \sum_{kerc \ell d v} (X + Y)_{ker} (A + B)_{kerld v} (X + Y)_{ld v} \right] C_{mp q} = \frac{1}{2} \sum_{kerc \ell d v} (X + Y)_{ker} \left\{ \sum_{\mu} \frac{\partial}{\partial C_{\mu p q}} \left[ (A + B)_{kerld v} \right] C_{mp q} \right\} (X + Y)_{ld v}$$

Likewise, the derivative of term II is the derivative of its orbital rotation Hessian

$$\sum_{\mu} \frac{\partial}{\partial C_{\mu p q}} \left[ \frac{1}{2} \sum_{kerc \ell d v} (X - Y)_{ker} (A - B)_{kerld v} (X - Y)_{ld v} \right] C_{mp q} = \frac{1}{2} \sum_{kerc \ell d v} (X - Y)_{ker} \left\{ \sum_{\mu} \frac{\partial}{\partial C_{\mu p q}} \left[ (A - B)_{kerld v} \right] C_{mp q} \right\} (X - Y)_{ld v}$$

H.2.3.2 Derivative of the (A+B) matrix (Term I)

We need the derivative of the $(A + B)$ matrix to complete the expression for Term I. The focus of this section is mainly the derivatives, we will multiply the excitation vectors into the equation later, when we also have the derivatives of the $(A - B)$ matrix. Recall that the $(A + B)$ matrix, in the basis of canonical KS orbitals, can be written

$$(A + B)_{kerld v} = \delta_{r_{uv}} (F_{cd \ell} \delta_{kl} - F_{k\tau r} \delta_{cd}) + 2 (k\tau r | l\ell v) + 2 f_{kerld v}^{\varepsilon\varepsilon} - c_{r} \delta_{r_{uv}} [(c\ell \tau | k\ell r) + (k\tau r | l\ell r)]$$

Therefore the derivative can be written more explicitly

$$\sum_{\mu} \frac{\partial}{\partial C_{\mu p q}} \left[ \frac{1}{2} \sum_{kerc \ell d v} (X + Y)_{ker} (A + B)_{kerld v} (X + Y)_{ld v} \right] C_{mp q}$$
\[ \sum_{\mu} \frac{\partial}{\partial C_{\mu \sigma}} \left[ (A + B)_{kcl \ld \nu} \right] C_{\mu \sigma} \]

\[ = \sum_{\mu} \frac{\partial}{\partial C_{\mu \sigma}} \left[ \delta_{\tau \nu} \left( F_{cd\tau} \delta_{kl} - F_{k\tau c \ld \nu} \right) + 2 (k \tau | l \nu) + 2 f_{kcl \ld \nu}^{xc} \right] \]

\[ - c_x \delta_{\tau \nu} \left\{ (cd \tau | kl \tau) + (k \tau | l \nu) \right\} \]

\( (H.55) \)

The derivative is a sum of six terms. The terms, \( ApB1 \) and \( ApB2 \) can be evaluated based on the work we did for Term 2 above, where the derivative of the Fock matrix was given in Eq. H.47. We rewrite the derivative of the Fock matrices in \( ApB1 \) and \( ApB2 \) here for convenience:

\[ \sum_{\mu} \frac{\partial}{\partial C_{\mu \sigma}} \left[ F_{cd\tau} \delta_{kl} \delta_{\tau \nu} \right] C_{\mu \sigma} \]

\[ = \delta_{kl} \delta_{\tau \nu} \left[ \delta_{\sigma \tau} \delta_{cp} F_{q \sigma} + \delta_{\sigma \tau} \delta_{dp} F_{c \sigma} + \sum_{i} \delta_{ip} \left\{ 2 (cd \tau | qp \sigma) + 2 f_{pq \sigma cd \tau}^{xc} \right\} \right] \]

\[ - c_x \delta_{\sigma \nu} \left\{ (cq | pd \nu) + (cp | qd \nu) \right\} \]

\( (H.56) \)

\[ \sum_{\mu} \frac{\partial}{\partial C_{\mu \sigma}} \left[ \delta_{cd} \delta_{\tau \nu} \right] C_{\mu \sigma} \]

\[ = -\delta_{cd} \delta_{\tau \nu} \left[ \delta_{\sigma \tau} \delta_{kp} F_{q \sigma} + \delta_{\sigma \tau} \delta_{ip} F_{k \sigma} + \sum_{i} \delta_{ip} \left\{ 2 (k \tau | q \sigma) + 2 f_{pq \sigma k \tau}^{xc} \right\} \right] \]

\[ - c_x \delta_{\sigma \nu} \left\{ (kq | p \tau \nu) + (kp | q \nu) \right\} \]

\( (H.57) \)

The derivative of the Coulomb term, \( ApB3 \), is
\[
\sum_{\mu} \frac{\partial}{\partial C_{\mu\sigma}} \left[ 2 (k_c\tau|ldv) \right] C_{\mu\sigma}
\]
\[
= 2 \left[ \delta_{\sigma\tau} \delta_{kp} (q_c\sigma|ldv) + \delta_{\sigma\tau} \delta_{cp} (k_q\sigma|ldv) + \delta_{\sigma\tau} \delta_{lp} (k_c\tau|q_d\sigma) + \delta_{\sigma\tau} \delta_{dp} (k_c\tau|l_q\sigma) \right] \tag{H.58}
\]

The derivative of the XC-kernel term, \( A_{pB4} \), is
\[
\sum_{\mu} \frac{\partial}{\partial C_{\mu\sigma}} \left[ 2 f_{kcrldv}^{xc} \right] C_{\mu\sigma}
\]
\[
= 2 \left[ \delta_{\sigma\tau} \delta_{kp} f_{qcrldv}^{xc} + \delta_{\sigma\tau} \delta_{cp} f_{kqrldv}^{xc} + \delta_{\sigma\tau} \delta_{lp} f_{kcrqd\sigma}^{xc} + \delta_{\sigma\tau} \delta_{dp} f_{kcrtlq\sigma}^{xc} \right]
+ \int dr' \int dr'' \phi_{k\tau}(r') \phi_{c\tau}(r') \left\{ \sum_{\mu} \frac{\partial}{\partial C_{\mu\sigma}} \left[ \frac{\delta^2 E_{xc}}{\delta \rho_{\tau}(r') \delta \rho_{\tau}(r'')} \right] C_{\mu\sigma} \right\} \phi_{l\upsilon}(r'') \phi_{d\upsilon}(r'') \tag{H.59}
\]

For the final term, we can use the chain rule for functional derivatives
\[
\frac{\partial}{\partial C_{\mu\sigma}} \left[ \frac{\delta^2 E_{xc}}{\delta \rho_{\tau}(r') \delta \rho_{\upsilon}(r'')} \right] = \int dr \frac{\delta^3 E_{xc}}{\delta \rho_{\sigma}(r) \delta \rho_{\tau}(r') \delta \rho_{\upsilon}(r'')} \left( \frac{\partial \rho_{\sigma}(r)}{\partial C_{\mu\rho}} \right)
= \int dr g_{\sigma\tau\upsilon}^{xc} \left( \frac{\partial \rho_{\sigma}(r)}{\partial C_{\mu\rho}} \right)
= 2 \sum_{m} \delta_{mp} \int dr \phi_{m\sigma}(r) g_{\sigma\tau\upsilon}^{xc} \phi_{\upsilon}(r) \tag{H.60}
\]

Here, we used Eqs. H.44 and H.45 to evaluate the derivative of the electron density. The Kronecker delta is kept, however, because it reminds us that the general index \( p \) must be an occupied orbital to yield a nonzero derivative of the electron density. This is the reason that the third-order functional derivatives only appear in specific terms of the \( Q_{\mu\sigma} \) vector, described in Ref. 64. The derivative of the XC-kernel is
\[
\sum_{\mu} \frac{\partial}{\partial C_{\mu\rho\sigma}} \left[ 2 f_{k\tau\nu\sigma}^{\rho\rho} \right] C_{\mu\rho\sigma} \\
= 2 \left[ \delta_{\sigma\tau} \delta_{kp} f_{\sigma\tau\nu\delta}^{\rho\rho} + \delta_{\sigma\tau} \delta_{cp} f_{\sigma\tau\nu\delta}^{\rho\rho} + \delta_{\sigma\tau} \delta_{lp} f_{\sigma\tau\nu\delta}^{\rho\rho} + \delta_{\sigma\tau} \delta_{dp} f_{\sigma\tau\nu\delta}^{\rho\rho} \right]
+ 2 \sum_{m} \delta_{mp} g_{m\nu\delta}^{k\tau\nu\sigma} \right] \] (H.61)

Finally, the exact exchange terms \( ApB5 \) and \( ApB6 \) are calculated similarly to the Coulomb term above:

\[
\sum_{\mu} \frac{\partial}{\partial C_{\mu\rho\sigma}} \left[ -c_x \delta_{\tau\nu} (cd|kl\tau) \right] C_{\mu\rho\sigma} \\
= -c_x \delta_{\tau\nu} \left[ \delta_{\sigma\tau} \delta_{cp} (q\sigma|kl\sigma) + \delta_{\sigma\tau} \delta_{lp} (c\sigma|kl\sigma) + \delta_{\sigma\tau} \delta_{kp} (cd\sigma|q\sigma) \right]
+ \delta_{\sigma\tau} \delta_{lp} (cd\sigma|q\sigma) \] (H.62)

\[
\sum_{\mu} \frac{\partial}{\partial C_{\mu\rho\sigma}} \left[ -c_x \delta_{\tau\nu} (lc|kd\tau) \right] C_{\mu\rho\sigma} \\
= -c_x \delta_{\tau\nu} \left[ \delta_{\sigma\tau} \delta_{lp} (qc\sigma|kd\sigma) + \delta_{\sigma\tau} \delta_{cp} (lq\sigma|kd\sigma) + \delta_{\sigma\tau} \delta_{kp} (lc\sigma|q\sigma) \right]
+ \delta_{\sigma\tau} \delta_{dp} (lc\sigma|q\sigma) \] (H.63)

We can now write the derivative in Eq. H.55 explicitly. We do some variable replacements at this step to make sure spin indices are consistent with the Kronecker deltas.
\[
\sum_{\mu} \frac{\partial}{\partial C_{\mu p}} [(A + B)_{kclvdv}] C_{\mu q}\n\]
\[
= \delta_{\sigma\tau} \delta_{\nu p} \left[ \delta_{kl} \delta_{\tau v} F_{q d r} + 2 (k q r | l d v) + 2 f_{k q r l d v}^{\text{exc}} - c_x^{\delta_{\tau v}} [(q d | l k r) + (l q r | k d)] \right] \\
+ \delta_{\sigma\tau} \delta_{dp} \left[ \delta_{kl} \delta_{\tau r} F_{c q r} + 2 (k c r | l q v) + 2 f_{k c r l q v}^{\text{exc}} - c_x^{\delta_{\tau r}} [(c q | l k r) + (l c | k q r)] \right] \\
+ \delta_{\sigma\tau} \delta_{kp} \left[ - \delta_{cd} \delta_{\tau r} F_{q k r} + 2 (q c r | l d v) + 2 f_{q k r l d v}^{\text{exc}} - c_x^{\delta_{\tau r}} [(c d | l q r) + (l c | q d)] \right] \\
+ \delta_{\sigma\tau} \delta_{lp} \left[ - \delta_{cd} \delta_{\tau r} F_{k q r} + 2 (k c r | q d v) + 2 f_{k c r q d v}^{\text{exc}} - c_x^{\delta_{\tau r}} [(c d | q r k) + (q c | k d)] \right] \\
+ \delta_{kl} \delta_{\tau r} \sum_{m} \delta_{mp} \left\{ 2 (c d | q p | l) - f_{p q r c d r}^{\text{exc}} - c_x^{\delta_{\tau r}} \{ (c q | p d v) + (c p | q d v) \} \right\} \\
- \delta_{cd} \delta_{\tau r} \sum_{m} \delta_{mp} \left\{ 2 (k l | q p | r) - f_{q p r k l r}^{\text{exc}} - c_x^{\delta_{\tau r}} \{ (k q | p l r) + (k p | q l r) \} \right\} \\
+ 4 \sum_{m} \delta_{mp} g_{m q p k c l r d v}^{\text{exc}} \right] \cdot C_{\mu q} \n\]

(H.64)

In order to understand the derivative of the $G$ functional, it is required that we also evaluate the derivatives of the $(A - B)$ matrix as well.

**H.2.3.3 Derivative of the (A-B) matrix (Term II)**

This section is devoted to evaluating the derivative of the $(A - B)$ matrix. Recall that this is written

\[
(A - B)_{kclvdv} = \delta_{\tau v} (F_{c d r} \delta_{kl} - F_{k l r} \delta_{cd}) + c_x^{\delta_{\tau v}} [(l c | k d r) - (c d | k l r)] \n\]

(H.65)

Therefore, the derivatives of this matrix are

\[
\sum_{\mu} \frac{\partial}{\partial C_{\mu p}} [(A - B)_{kclvdv}] C_{\mu q} \n\]
\[
= \sum_{\mu} \frac{\partial}{\partial C_{\mu p}} \left[ \delta_{\tau v} (F_{c d r} \delta_{kl} - F_{k l r} \delta_{cd}) + c_x^{\delta_{\tau v}} [(l c | k d r) - (c d | k l r)] \right] C_{\mu q} \n\]

(H.66)

H.63), \( ApB6 \leftrightarrow -AmB3 \) (Eq. H.62). To avoid redundancy, we don’t redefine the expressions in this section, but note that the \((A + B)\) matrix is associated with \((\vec{X} + \vec{Y})\), and the \((A - B)\) matrix is associated with \((\vec{X} - \vec{Y})\), so the derivatives are multiplied by different vectors. The final form of this derivative is

\[
\sum_{\mu} \frac{\partial}{\partial C_{\mu\sigma}} [(A - B)_{kcld\nu}] C_{\mu\sigma} = \frac{\delta_{\sigma\tau}}{2} \sum_{kl} \delta_{cp} \left\{ 2 (A - B)_{kcld\nu} C_{\mu\sigma} \right\} (X - Y)_{ld\nu} \tag{H.67}
\]

H.2.4 Simplifying Derivatives of \( G \) (Term 1)

By combining Eqs. H.52 and H.53, we can write the total derivative of \( G \)

\[
Q_{pq\sigma} = \sum_{\mu} \frac{\partial G}[\vec{X}, \vec{Y}, \omega] C_{\mu\sigma}
\]

\[
= \frac{1}{2} \sum_{kcld\nu} (X + Y)_{kcl} \left\{ \sum_{\mu} \frac{\partial}{\partial C_{\mu\sigma}} [(A + B)_{kcld\nu}] C_{\mu\sigma} \right\} (X + Y)_{ld\nu} \tag{H.68}
\]

Sections H.2.4.1 through H.3 attempt to collect similar terms in order to derive other parts of the expressions of Appendix A in Ref. 64. Using the derivatives with respect to the MO coefficients, it is possible to write four separate equations with four combinations of the indices \( p \) and \( q \):

1. \( p = i \leq q = j \) (occupied-occupied block)
2. \( p = i \) and \( q = a \) (occupied-virtual block)
3. \( p = a \) and \( q = i \) (virtual-occupied block)

4. \( p = a \leq q = b \) (virtual-virtual block)

**H.2.4.1 Occupied-Occupied Block of Q**

For the occupied-occupied block, Eq. H.64 yields

\[
\delta_{\sigma\tau} \delta_{ki} \left[ - \delta_{cd} \delta_{\tau v} F_{j\ell v} + 2 (j c \tau | j d v) + 2 f_{j c r \ell d v}^{xc} - c_x \delta_{\tau v} [(c d \tau | j l \tau) + (l c \tau | j d \tau)] \right] \\
+ \delta_{\sigma\tau} \delta_{li} \left[ - \delta_{cd} \delta_{\tau v} F_{k j \tau} + 2 (k c \tau | j d v) + 2 f_{k c r q d v}^{xc} - c_x \delta_{\tau v} [(c d \tau | k j \tau) + (j c \tau | k d \tau)] \right] \\
+ \delta_{kl} \delta_{\tau v} \sum_m \delta_{mi} \left\{ 2 (c d \tau | j i \sigma) + 2 f_{ij \sigma \delta \tau v}^{xc} - c_x \delta_{\sigma v} \{(c j v | i d v) + (c i v | j d v)\} \right\} \\
- \delta_{cd} \delta_{\tau v} \sum_m \delta_{mi} \left\{ 2 (k l \tau | j i \sigma) + 2 f_{ij \sigma k l \tau}^{xc} - c_x \delta_{\sigma v} \{(k j v | i l v) + (k i v | j l v)\} \right\} \\
+ 4 \sum_m \delta_{mi} g_{m j \sigma k c r l d v}^{xc}
\]

\[(H.69)\]

Eq. H.67 gives

\[
\delta_{\sigma\tau} \delta_{ki} \left[ - \delta_{cd} \delta_{\tau v} F_{j\ell v} + c_x \delta_{\tau v} [(l c \tau | j d v) - (c d \tau | j l \tau)] \right] \\
+ \delta_{\sigma\tau} \delta_{li} \left[ - \delta_{cd} \delta_{\tau v} F_{k j \tau} + c_x \delta_{\tau v} [(j c \tau | k d \tau) - (c d \tau | k j \tau)] \right] \\
+ \delta_{kl} \delta_{\tau v} \sum_m \delta_{mi} \left\{ 2 (c d \tau | j i \sigma) + 2 f_{ij \sigma \delta \tau v}^{xc} - c_x \delta_{\sigma v} \{(c j v | i d v) + (c i v | j d v)\} \right\} \\
- \delta_{cd} \delta_{\tau v} \sum_m \delta_{mi} \left\{ 2 (k l \tau | j i \sigma) + 2 f_{ij \sigma k l \tau}^{xc} - c_x \delta_{\sigma v} \{(k j v | i l v) + (k i v | j l v)\} \right\}
\]

\[(H.70)\]

Inspection of these equations allows us to do some redefinitions of the various terms. For instance, the first term in Eq. H.69 as

\[
\delta_{\sigma\tau} \delta_{ki} \left[ \delta_{ji} \delta_{\tau v} F_{c d r} - \delta_{cd} \delta_{\tau v} F_{j\ell v} + 2 (j c \tau | l d v) + 2 f_{j c r \ell d v}^{xc} - c_x \delta_{\tau v} [(c d \tau | j l \tau) + (l c \tau | j d \tau)] \right] - \delta_{\sigma\tau} \delta_{ki} \delta_{ji} \delta_{\tau v} F_{c d r}
\]

\[(H.71)\]

We can therefore rewrite Eqs. H.69 and H.70
\[
\begin{align*}
\delta_{\sigma\tau}\delta_{ki}[(A + B)_{jcrldv} - \delta_{jl}\delta_{\tau v}F_{c\tau r}] + \delta_{\sigma\tau}\delta_{ki}[(A + B)_{kcrjdv} - \delta_{jk}\delta_{\tau v}F_{c\tau r}] \\
+ \delta_{kl}\delta_{\tau v}\left\{2 (cd\tau|i\sigma) + 2 f^{xc}_{ij\sigma cd\tau} - c_x\delta_{\sigma v}\{(cjv|idv) + (civ|jdv)\}\right\} \\
- \delta_{ld\tau v}\left\{2 (kl\tau|ji\sigma) + 2 f^{xc}_{ij\sigma kl\tau} - c_x\delta_{\sigma v}\{(kiv|ilv) + (kiv|jlv)\}\right\} \\
+ 4 g^{xc}_{ij\sigma kl\tau rdv}
\end{align*}
\]

(H.72)

\[
\begin{align*}
\delta_{\sigma\tau}\delta_{ki}[(A - B)_{jcrldv} - \delta_{jl}\delta_{\tau v}F_{c\tau r}] + \delta_{\sigma\tau}\delta_{ki}[(A - B)_{kcrjdv} - \delta_{jk}\delta_{\tau v}F_{c\tau r}] \\
+ \delta_{kl}\delta_{\tau v}\left\{2 (cd\tau|i\sigma) + 2 f^{xc}_{ij\sigma cd\tau} - c_x\delta_{\sigma v}\{(cjv|idv) + (civ|jdv)\}\right\} \\
- \delta_{ld\tau v}\left\{2 (kl\tau|ji\sigma) + 2 f^{xc}_{ij\sigma kl\tau} - c_x\delta_{\sigma v}\{(kiv|ilv) + (kiv|jlv)\}\right\}
\end{align*}
\]

(H.73)

The first term in Eq. H.72 can be evaluated based on the Kronecker deltas and the TDDFT equations (Eq. H.16).

\[
\begin{align*}
\frac{1}{2} \sum_{kerldv} (X + Y)_{kcr} \delta_{\sigma\tau}\delta_{ki}[(A + B)_{jcrldv}] (X + Y)_{ldv} \\
-\frac{1}{2} \sum_{kerldv} (X + Y)_{kcr} \delta_{\sigma\tau}\delta_{ki}\delta_{jl}\delta_{\tau v}F_{c\tau r} (X + Y)_{ldv} \\
+\frac{1}{2} \sum_{ec} (X + Y)_{ic\tau} \sum_{ldv} (A + B)_{jcrldv} (X + Y)_{ldv} \\
+ \frac{1}{2} \sum_{kced} (X + Y)_{kcr} \delta_{ki}\delta_{jl}\delta_{c\tau d}\epsilon_{c\tau} (X + Y)_{ld\sigma} \\
=\frac{1}{2} \sum_{c} (X + Y)_{ic\tau} (X - Y)_{jcr} + \frac{1}{2} \sum_{c} \epsilon_{c\tau}(X + Y)_{ic\sigma} (X + Y)_{jcr}
\end{align*}
\]

(H.74)

The third and fourth terms in Eqs. H.72 and H.73 can be combined to yield
\[
\frac{1}{2} \sum_{k\in \mathcal{d}uv} (X + Y)_{k\epsilon r} \left[ \delta_{\epsilon\delta} \delta_{\tau\nu} \left\{ 2 (cd\tau|ji\sigma) + 2 f_{ij\sigma\epsilon \tau}^{\epsilon\tau} \right. \\
- c_x \delta_{\epsilon\tau} [(cj\nu|id\nu) + (ci\nu|jd\nu)] \right\} \\
- \delta_{\epsilon \delta} \delta_{\tau \nu} \left\{ 2 (kl\tau|ji\sigma) + 2 f_{ij\sigma k\tau}^{x\tau} \right. \\
- c_x \delta_{\epsilon \sigma} [(kj\nu|il\nu) + (ki\nu|jl\nu)] \left. \right\} (X + Y)_{l\nu}
\]

\[
\frac{1}{2} \sum_{k\in \mathcal{d}uv} (X - Y)_{k\epsilon r} \left[ \delta_{\epsilon\delta} \delta_{\tau\nu} \left\{ 2 (cd\tau|ji\sigma) + 2 f_{ij\sigma\epsilon \tau}^{\epsilon\tau} \right. \\
- c_x \delta_{\epsilon\tau} [(cj\nu|id\nu) + (ci\nu|jd\nu)] \right\} (X - Y)_{l\nu}
\]

\[
\frac{1}{2} \sum_{k\in \mathcal{d} \epsilon r} (X + Y)_{k\epsilon r} \left\{ 2 (cd\tau|ji\sigma) + 2 f_{ij\sigma\epsilon \tau}^{\epsilon\tau} \right. \\
= c_x \delta_{\epsilon \sigma} [(cj\nu|id\nu) + (ci\nu|jd\nu)] \right\} (X + Y)_{k\epsilon r}
\]

\[
\frac{1}{2} \sum_{k\in \mathcal{r} \epsilon l} (X + Y)_{k\epsilon r} \left\{ 2 (kl\tau|ji\sigma) + 2 f_{ij\sigma k\tau}^{x\tau} \right. \\
= c_x \delta_{\epsilon \sigma} [(kj\nu|il\nu) + (ki\nu|jl\nu)] \right\} (X + Y)_{l\epsilon r}
\]

\[
+ \frac{1}{2} \sum_{k\in \mathcal{d} \epsilon r} (X - Y)_{k\epsilon r} \left\{ 2 (cd\tau|ji\sigma) + 2 f_{ij\sigma\epsilon \tau}^{\epsilon\tau} \right. \\
= c_x \delta_{\epsilon \sigma} [(cj\nu|id\nu) + (ci\nu|jd\nu)] \right\} (X - Y)_{k\epsilon r}
\]

\[-\frac{1}{2} \sum_{k\in \mathcal{r} \epsilon l} (X - Y)_{k\epsilon r} \left\{ 2 (kl\tau|ji\sigma) + 2 f_{ij\sigma k\tau}^{x\tau} \right. \\
= c_x \delta_{\epsilon \sigma} [(kj\nu|il\nu) + (ki\nu|jl\nu)] \right\} (X - Y)_{l\epsilon r}
\]

If we associate the terms with identical sums (first term and third term, second term and fourth term), Eq. H.76 can be written
\[ \sum_{c d r} \left\{ 2 (c d r | j i o) + 2 f_{i j o}^{c e} c_d r - c_x \delta_{o r} [(c j o | i d o) + (c i o | j d o)] \right\} \]
\[ \times \frac{1}{2} \sum_{k} \left\{ (X + Y)_{k c r} (X + Y)_{k d r} + (X - Y)_{k c r} (X - Y)_{k d r} \right\} \]
\[ + \sum_{k l r} \left\{ 2 (k l r | j i o) + 2 f_{i j o k l r}^{c e} c_x \delta_{o r} [(k j o | i l o) + (k i o | j l o)] \right\} \]
\[ \times - \frac{1}{2} \sum_{c} \left\{ (X + Y)_{k c r} (X + Y)_{l c r} + (X - Y)_{k c r} (X - Y)_{l c r} \right\} \]

(H.77)

The components of the equation, right of the sum with a single index, are vectors that we will identify as

\[ T_{a b r} = \frac{1}{2} \sum_{i} \left\{ (X + Y)_{i a r} (X + Y)_{i b r} + (X - Y)_{i a r} (X - Y)_{i b r} \right\} \] (H.78)

\[ T_{i j r} = -\frac{1}{2} \sum_{a} \left\{ (X + Y)_{i a r} (X + Y)_{j a r} + (X - Y)_{i a r} (X - Y)_{j a r} \right\} \] (H.79)

\[ T_{i a r} = T_{a i r} = 0 \] (H.80)

\[ \vec{T} \] is known as the unrelaxed difference density matrix. Thus, Eq. H.77 is

\[ H_{i j o}^{\uparrow} [\vec{T}] = \sum_{c d r} \left\{ 2 (c d r | j i o) + 2 f_{i j o c d r}^{c e} - c_x \delta_{o r} [(c j o | i d o) + (c i o | j d o)] \right\} T_{c d r} \]
\[ + \sum_{k l r} \left\{ 2 (k l r | j i o) + 2 f_{i j o k l r}^{c e} c_x \delta_{o r} [(k j o | i l o) + (k i o | j l o)] \right\} T_{k l r} \] (H.81)

We note in passing that the combination of occupied and virtual orbital indices for the vector \[ \vec{T}, T_{i a r}, \] is zero. This allows us to write Eq. H.81 in terms of the general linear transformation (defined in Eq. H.49) because particular indices of \[ \vec{T} \] are zero.

Combining several of the equations together allows us to define the occupied-occupied
block of $Q$.

$$Q_{ij\sigma} = \omega \sum_a \{(X + Y)_{i\sigma}(X - Y)_{j\sigma} + (X - Y)_{i\sigma}(X + Y)_{j\sigma}\}$$

$$- \sum_a \varepsilon_{i\sigma} \{ (X + Y)_{i\sigma}(X + Y)_{j\sigma} + (X - Y)_{i\sigma}(X - Y)_{j\sigma} \} + H_{ij\sigma}^T[\tilde{T}] \tag{H.82}$$

$$+ 2 \sum_{kcrldv} \left[ g_{ij\sigma kcrldv}^{xe} \right] (X + Y)_{kcr}(X + Y)_{ldv}$$

**H.2.4.2 Occupied-Virtual Block of $Q$**

For the occupied-virtual block, we again start from Eqs. H.64 and H.67.

$$\delta_{\sigma\tau} \delta_{ki} \left[ 2 (ac\tau|ldv) + 2 f_{acrlvdv}^{xe} - c_x \delta_{\tau\nu} \left[ (cd\tau|al\tau) + (lc\tau|ad\tau) \right] \right]$$

$$+ \delta_{\sigma\tau} \delta_{li} \left[ 2 (kc\tau|adv) + 2 f_{kc\tauadv}^{xe} - c_x \delta_{\tau\nu} \left[ (cd\tau|ka\tau) + (ac\tau|kd\tau) \right] \right]$$

$$+ \delta_{kl} \delta_{\tau\nu} \left\{ 2 (cd\tau|ai\sigma) + 2 f_{i\sigma ac\tau}^{xe} - c_x \delta_{\sigma\nu} \left\{ (cav|idv) + (civ|adv) \right\} \right\} \tag{H.83}$$

$$- \delta_{cd} \delta_{\tau\nu} \left\{ 2 (kl\tau|ai\sigma) + 2 f_{i\sigma kl\tau}^{xe} - c_x \delta_{\sigma\nu} \left\{ (kav|ilv) + (kiv|alv) \right\} \right\}$$

$$+ 4 g_{i\sigma ac\tau kcrldv}^{xe}$$

$$\delta_{\sigma\tau} \delta_{ki} \left[ c_x \delta_{\tau\nu} \left[ (lc\tau|ad\tau) - (cd\tau|al\tau) \right] \right]$$

$$+ \delta_{\sigma\nu} \delta_{li} \left[ c_x \delta_{\tau\nu} \left[ (ac\tau|kd\tau) - (cd\tau|ka\tau) \right] \right]$$

$$+ \delta_{kl} \delta_{\tau\nu} \left\{ 2 (cd\tau|ap\sigma) + 2 f_{p\sigma ac\tau}^{xe} - c_x \delta_{\sigma\nu} \left\{ (cav|pdv) + (civ|adv) \right\} \right\} \tag{H.84}$$

$$- \delta_{cd} \delta_{\tau\nu} \left\{ 2 (kl\tau|ap\sigma) + 2 f_{p\sigma kl\tau}^{xe} - c_x \delta_{\sigma\nu} \left\{ (kav|plv) + (kiv|alv) \right\} \right\}$$

Most terms are straightforwardly related to those in Section H.2.4.1. The first two lines in Eq. H.83 are related to the linear transformation in Eq. H.49.
The first two lines in Eq. H.84 allow for the definition of another linear transformation that is specific to calculations including Hartree-Fock exchange.

\[
\frac{1}{2} \sum_c (X + Y)_{ic\sigma} \sum_{ld\nu} \left[ 2(ac\sigma|ld\nu) + 2f_{ac\sigma ld\nu}^{xc} \right. \\
\left. - c_x \delta_{\sigma\nu} [(cd\sigma|al\sigma) + (lc\sigma|ad\sigma)] \right] (X + Y)_{ld\nu}
\]

\[
\frac{1}{2} \sum_d (X + Y)_{id\sigma} \sum_{kcr} \left[ 2(kcr|ad\sigma) + 2f_{kcr ad\sigma}^{xc} \right. \\
\left. - c_x \delta_{\sigma\nu} [(cd\tau|ka\tau) + (ac\tau|kd\tau)] \right] (X + Y)_{kcr}
\]

\[
= \frac{1}{2} \sum_c (X + Y)_{ic\sigma} H_{ac\sigma}^+ [(\vec{X} + \vec{Y})] + \frac{1}{2} \sum_d (X + Y)_{id\sigma} H_{ad\sigma}^+ [(\vec{X} + \vec{Y})]
\]

\[
= \sum_b (X + Y)_{ib\sigma} H_{ab\sigma}^+ [(\vec{X} + \vec{Y})]
\]

(H.85)

Here we used the linear transformation \( H_{pq\sigma} [\vec{V}] \) defined below

\[
H_{pq\sigma} [\vec{V}] = \sum_{rs\tau} \left\{ c_x \delta_{\sigma\tau} \left[ (rq\sigma|ps\sigma) - (qs\sigma|pr\sigma) \right] \right\} V_{rst}
\]

(H.87)

We can now write the occupied-virtual block of \( Q \).
\[ Q_{ia\sigma} = H_{ia\sigma}^+ [\vec{T}] + \sum_b \left\{ (X + Y)_{iba\sigma} H_{aba\sigma}^+ [\vec{X} + \vec{Y}] + (X - Y)_{iba\sigma} H_{aba\sigma}^- [\vec{X} - \vec{Y}] \right\} \]
\[ + 2 \sum_{kcrldu} \left[ g_{ia\sigma kcrldu}^e (X + Y)_{kcr} (X + Y)_{ldu} \right] \]

(H.88)

**H.2.4.3 Virtual-Occupied Block of \( Q \)**

For the virtual-occupied block, we again start from Eqs. H.64 and H.67.

\[ \delta_{\sigma\tau} \delta_{ca} \left[ 2 (k\tau | l\nu) + 2 f_{kcrldu}^e \delta_{\tau\nu} \{(id\tau | k\ell\tau) + (li\tau | k\nu)\} \right] \]
\[ + \delta_{\sigma\tau} \delta_{da} \left[ 2 (k\nu | l\tau) + 2 f_{kcrldu}^e \delta_{\tau\nu} \{(ci\tau | k\ell\tau) + (lc\tau | k\nu)\} \right] \]

(H.89)

\[ \delta_{\sigma\tau} \delta_{ca} \left[ c_x \delta_{\tau\nu} \{(li\tau | k\nu) - (id\tau | k\ell\tau)\} \right] \]
\[ + \delta_{\sigma\tau} \delta_{da} \left[ c_x \delta_{\tau\nu} \{(lc\tau | k\nu) - (ci\tau | k\ell\tau)\} \right] \]

(H.90)

All quantities needed to evaluate this block have been defined, so we can write the virtual-occupied block of \( Q \) as

\[ Q_{ai\sigma} = \sum_j \left\{ (X + Y)_{ja\sigma} H_{jia\sigma}^+ [\vec{X} + \vec{Y}] + (X - Y)_{ja\sigma} H_{jia\sigma}^- [\vec{X} - \vec{Y}] \right\} \]

(H.91)

**H.2.4.4 Virtual-Virtual Block of \( Q \)**

For the virtual-virtual block, we again start from Eqs. H.64 and H.67.

\[ \delta_{\sigma\tau} \delta_{ca} \left[ \delta_{kl} \delta_{\tau\nu} F_{b\nu\tau} + 2 (kb\nu | l\nu) + 2 f_{kbrldu}^e \delta_{\tau\nu} \{(bd\nu | k\ell\tau) + (lb\nu | k\nu)\} \right] \]
\[ + \delta_{\sigma\tau} \delta_{da} \left[ \delta_{kl} \delta_{\tau\nu} F_{c\nu\tau} + 2 (kc\nu | l\nu) + 2 f_{kcrldu}^e \delta_{\tau\nu} \{(cb\nu | k\ell\tau) + (lc\nu | k\nu)\} \right] \]

(H.92)

\[ \delta_{\sigma\tau} \delta_{ca} \left[ \delta_{kl} \delta_{\tau\nu} F_{b\nu\tau} + c_x \delta_{\tau\nu} \{(lb\nu | k\nu) - (bd\nu | k\ell\tau)\} \right] \]
\[ + \delta_{\sigma\tau} \delta_{da} \left[ \delta_{kl} \delta_{\tau\nu} F_{c\nu\tau} + c_x \delta_{\tau\nu} \{(lc\nu | k\nu) - (cb\nu | k\ell\tau)\} \right] \]

(H.93)
All quantities needed to evaluate this block have been defined, so we can write the virtual-virtual block of $Q$ as

\[
Q_{ab\sigma} = \omega \sum_i \{(X + Y)_{ia\sigma}(X - Y)_{ib\sigma} + (X - Y)_{ia\sigma}(X + Y)_{ib\sigma}\}
\]
\[
+ \sum_i \epsilon_{b\sigma} \{(X + Y)_{ia\sigma}(X + Y)_{ib\sigma} + (X - Y)_{ia\sigma}(X - Y)_{ib\sigma}\}
\]

\[\text{H.94}\]

**H.3 Final form of the Lagrangian functional derivatives**

This section summarizes the findings of Section H.2, in which the derivatives of the Lagrangian were written as a sum of three terms (Term 1, 2, and 3). For Term 1, recall that $Q_{\mu\nu\sigma}$ is defined as \(\sum_\mu \frac{\partial G}{\partial C_{\mu\nu\sigma}} C_{\mu\nu\sigma}\) in Eq. H.51. Term 2 involved the derivative of the Fock matrix with respect to the MO coefficients. This was written in simplified form in Eq. H.48, (we substitute $j \rightarrow i$ in the second term)

\[
\sum_\mu \frac{\partial F_{i\tau}}{\partial C_{\mu\rho\sigma}} C_{\mu\rho\sigma} = \sum_\mu \left( \delta_{\sigma\tau} \delta_{ip} \delta_{qa} + \delta_{\sigma\tau} \delta_{ap} \delta_{iq} \right) \epsilon_{q\sigma} Z_{i\tau} + \sum_i \delta_{ip} H_{pq\sigma}^+ [\bar{Z}] \]  

\[\text{H.95}\]

Term 3 involved the derivative of the overlap matrix with respect to the MO coefficients. This was simplified in Eq. H.32

\[
\sum_\mu \sum_{\tau, r \leq s} W_{r\sigma\tau} \frac{\partial S_{r\sigma\tau}}{\partial C_{\mu\rho\sigma}} C_{\mu\rho\sigma} = (1 + \delta_{pq}) W_{pq\sigma} 
\]

\[\text{H.96}\]

In order to evaluate the Lagrange multipliers $\bar{Z}$ and $\bar{W}$, we equate equations to uniquely express both multipliers. Using the derivatives with respect to the MO coefficients, it is possible to write four separate equations with four combinations of the indices $p$ and $q$:

1. $p = i \leq q = j$ (occupied-occupied block)
2. $p = i$ and $q = a$ (occupied-virtual block)
3. $p = a$ and $q = i$ (virtual-occupied block)
4. $p = a \leq q = b$ (virtual-virtual block)

For $p = i \leq q = j$, the sum of the derivatives with respect to the MO coefficients are written
\[ Q_{ij\sigma} + H_{ij\sigma}^+ [\vec{Z}] = (1 + \delta_{ij}) W_{ij\sigma} \quad \text{(H.97)} \]

\( Q_{ij\sigma} \) is defined in Eq. H.82. For \( p = i \) and \( q = a \), the sum of the derivatives with respect to the MO coefficients are written

\[ Q_{ia\sigma} + \epsilon_{a\sigma} Z_{ia\sigma} + H_{ia\sigma}^+ [\vec{Z}] = W_{ia\sigma} \quad \text{(H.98)} \]

\( Q_{ia\sigma} \) is defined in Eq. H.88. For \( p = a \) and \( q = i \), the sum of the derivatives with respect to the MO coefficients are written

\[ Q_{ai\sigma} + \epsilon_{i\sigma} Z_{ia\sigma} = W_{ai\sigma} = W_{ia\sigma} \quad \text{(H.99)} \]

\( Q_{ai\sigma} \) is defined in Eq. H.91. For \( p = a \leq q = b \), the sum of the derivatives with respect to the MO coefficients are written

\[ Q_{ab\sigma} = (1 + \delta_{ab}) W_{ab\sigma} \quad \text{(H.100)} \]

\( Q_{ab\sigma} \) is defined in Eq. H.94. At this point, it is imperative to compare the results of this section to Appendix A in Ref. 64. We see that all expressions are correct, so we can now proceed with determining the Lagrange multipliers.

To find the Z-vector equation, we subtract Eq. H.99 from Eq. H.98. This eliminates \( \vec{W} \) from the equation to give

\[ Q_{ia\sigma} + \epsilon_{a\sigma} Z_{ia\sigma} + H_{ia\sigma}^+ [\vec{Z}] - Q_{ai\sigma} - \epsilon_{i\sigma} Z_{ia\sigma} = 0 \]

\[ (\epsilon_{a\sigma} - \epsilon_{i\sigma}) Z_{ia\sigma} + H_{ia\sigma}^+ [\vec{Z}] = -(Q_{ia\sigma} - Q_{ai\sigma}) \quad \text{(H.101)} \]

Using the definition of the linear transformation (Eq. H.49), we may write the Z-vector equation as
\[(\epsilon_{a\sigma} - \epsilon_{i\sigma})Z_{ia\sigma} + \sum_{jbr} \left[ 2(jb\tau|ia\sigma) + 2f_{ia\sigma,jb\tau}^{xc} - c_{x}\delta_{\sigma\upsilon}([ja\upsilon|ib\upsilon) + (jiv|ab\upsilon)] \right] Z_{jbr} \]

\[= -(Q_{ia\sigma} - Q_{ai\sigma}) \]  

(H.102)

This can be simplified by writing the first term as: \[(\epsilon_{a\sigma} - \epsilon_{i\sigma})Z_{ia\sigma} = \sum_{jbr} \delta_{ij}\delta_{ab}\delta_{\sigma\tau}(\epsilon_{a\sigma} - \epsilon_{i\sigma})Z_{jbr} \]. The left hand side then becomes:

\[\sum_{jbr}(A + B)_{ia\sigma,jb\tau}Z_{jbr} = -(Q_{ia\sigma} - Q_{ai\sigma}) \]  

(H.103)

The right hand side vector, \(\vec{R} \), is defined as

\[R_{ia\sigma} = (Q_{ia\sigma} - Q_{ai\sigma}) \]

\[= H_{ia\sigma}^+[\vec{T}] + \sum_{b} \left\{ (X + Y)_{i\sigma} H_{a\sigma}^+[([\vec{X} + \vec{Y}] + (X - Y)_{i\sigma} H_{a\sigma}^-[([\vec{X} - \vec{Y}]) \right] \]

\[+ 2 \sum_{kcrldv} g_{ia\sigma,kcrldv}^{xc}(X + Y)_{k\sigma}(X + Y)_{l\upsilon} \]

\[\sum_{j} \left\{ (X + Y)_{ja\sigma} H_{j\sigma}^+[([\vec{X} + \vec{Y}] + (X - Y)_{ja\sigma} H_{j\sigma}^-[([\vec{X} - \vec{Y}]) \right] \}

(H.104)

And the Z-vector equation may be written

\[\sum_{jbr}(A + B)_{ia\sigma,jb\tau}Z_{jbr} = -R_{ia\sigma} \]  

(H.105)

Eq. H.105 is identical to Eq. 18 in Ref. 64, which confirms that some of the expressions in this section are correct. The Z-vector equation must be solved prior to finding the Lagrange multiplier \(\vec{W} \). With the Z-vector equation solved, we may find the occupied-occupied, virtual-virtual, and occupied-virtual blocks of \(\vec{W} \) using Eqs. H.97, H.100, and Eq. H.99:
\[ W_{ij\sigma} = \frac{1}{1 + \delta_{ij}} \left( Q_{ij\sigma} + H_{ij\sigma}^+ \langle \vec{Z} \rangle \right) \]  \hspace{1cm} (H.106)

\[ W_{ab\sigma} = \frac{1}{1 + \delta_{ab}} Q_{ab\sigma} \]  \hspace{1cm} (H.107)

\[ W_{ia\sigma} = Q_{ai\sigma} + \epsilon_{i\sigma} Z_{ia\sigma} \]  \hspace{1cm} (H.108)

**H.4 Gradient of the excitation energy**

In this section, the gradient of the excitation energy along each nuclear coordinate is shown. In similar notation to the ground state gradients, we will let the derivative of a property with respect to a nuclear coordinate be denoted: \( \xi \). For this part, we note the definitions of \((A \pm B)\) in Eqs. H.14 and H.15 (in terms of the MO energies, not the Fock matrices) and the Fock matrix in Eq. H.21. The derivative of the Langrangian \( L \) may be used to find the derivative of the excitation energy, as

\[
\omega^{\xi} = L^{\xi} [\vec{X}, \vec{Y}, \omega, \vec{C}, \vec{Z}, \vec{W}]
\]

\[
= \frac{1}{2} \sum_{i\alpha a j\beta r} \left[ (X + Y)_{i\alpha a (A + B)^{\xi}_{i\alpha a j\beta r}} (X + Y)_{j\beta r}
\right.
\]

\[
+ (X - Y)_{i\alpha a (A - B)^{\xi}_{i\alpha a j\beta r}} (X - Y)_{j\beta r}
\]

\[
+ \sum_{i\alpha a} Z_{i\alpha a} F_{i\alpha a}^{\xi} - \sum_{p\sigma, p \leq q} W_{p\sigma q} C_{p\sigma}^{\xi}
\]  \hspace{1cm} (H.109)

The superscript, \( (\xi) \), indicates that the derivative is taken with the MO coefficients, \( C_{\mu\nu\sigma} \), held constant at their variationally optimized values from solving the ground state KS equations. The conversion between MO and AO indices is important at this step. At this point, we note that
\[(A + B)_{\sigma j}^{(\xi)} = 2 (i\sigma | j\tau)^{(\xi)} + 2 f_{\sigma j}^{xc} \left[ (ab\sigma | ij\sigma)^{(\xi)} + (ja\sigma | ib\sigma)^{(\xi)} \right] - c_x \delta_{\sigma\tau} \left[ 2 \left( \frac{\mu\nu}{\kappa\lambda} \right)^{(\xi)} + f^{xc}_{\mu\nu\kappa\lambda} \right] \]

\[(A - B)_{\sigma j}^{(\xi)} = c_x \delta_{\sigma\tau} [(ja\sigma | ib\sigma) - (ab\sigma | ij\sigma)] = \sum_{\mu\nu\kappa\lambda} \left[ c_x \delta_{\sigma\tau} \left\{ C_{\mu\sigma\nu\sigma} C_{\kappa\tau\nu\tau} (\mu\nu | \kappa\lambda)^{(\xi)} \right. \right. \]

\[
\left. \left. - C_{\mu\sigma\nu\sigma} C_{\kappa\tau\nu\tau} (\mu\nu | \kappa\lambda)^{(\xi)} \right) \right]\]

The gradients of the MO energies with respective to the nuclear coordinates are: \( \epsilon^{(\xi)}_{\rho\sigma} = 0 \).

For the Fock matrix, we can write

\[ F_{i\sigma}^{(\xi)} = h_{i\sigma}^{(\xi)} + \sum_{j\tau} (i\sigma | j\tau)^{(\xi)} - c_x \delta_{\sigma\tau} (ij\sigma | ja\sigma)^{(\xi)} + V^{xc}_{i\sigma} \]

\[ = \sum_{\mu\nu} C_{\mu\sigma\nu\sigma} h_{\mu\nu}^{\xi} + \sum_{j\tau} \sum_{\mu\nu\kappa\lambda} \left[ C_{\mu\sigma\nu\sigma} C_{\kappa\tau\nu\tau} (\mu\nu | \kappa\lambda)^{\xi} - c_x \delta_{\sigma\tau} C_{\mu\sigma\nu\sigma} C_{\kappa\tau\nu\tau} (\mu\nu | \kappa\lambda)^{\xi} \right] + \sum_{\mu\nu} C_{\mu\sigma\nu\sigma} V^{xc}_{\mu\nu\sigma} \]

The gradient of the Fock matrix may also be written as.
\[ F_{ia\sigma}^{(\xi)} = h_{ia\sigma}^{(\xi)} + \sum_{j\tau} \left[ (ia\sigma | jj\tau)^{(\xi)} - \frac{1}{2} c_x \delta_{\sigma\tau} \left\{ (ij\sigma | ja\sigma)^{(\xi)} + (ij\sigma | aj\sigma)^{(\xi)} \right\} \right] + V_{ia\sigma}^{xc \ (\xi)} \]

\[ \begin{align*}
F_{ia\sigma}^{(\xi)} &= \sum_{\mu\nu} C_{\mu i\sigma} C_{\nu a\sigma} h^{\xi}_{\mu\nu} + \sum_{j\tau} \sum_{\mu\nu\kappa\lambda} \left[ C_{\mu i\sigma} C_{\nu a\sigma} C_{\kappa j\tau} C_{\lambda j\tau} (\mu\nu|\kappa\lambda)^{\xi} \\
&- \frac{1}{2} c_x \delta_{\sigma\tau} \left\{ C_{\mu i\sigma} C_{\nu j\sigma} C_{\kappa j\tau} C_{\lambda a\tau} (\mu\nu|\kappa\lambda)^{\xi} + C_{\mu i\sigma} C_{\nu j\sigma} C_{\kappa a\tau} C_{\lambda j\tau} (\mu\nu|\kappa\lambda)^{\xi} \right\} \right] \\
&+ \sum_{\mu\nu} C_{\mu i\sigma} C_{\nu a\sigma} V_{\mu\nu\sigma}^{xc \ (\xi)} \end{align*} \tag{H.113} \]

The latter form is used in Ref. 64, whereas the former is used in Ref. 529. We will use Eq. H.112, but will indicate the difference in the final equation if Eq. H.113 is used, also. The parts of the expression depending on the XC-functional are not separable from the electron density, and therefore the superscript \((\xi)\) must be kept for those terms.

Before taking the gradient, let the following MO to AO transformation be defined

\[ V_{\mu\nu\sigma} = \sum_{pq} C_{\mu p\sigma} V_{pq\sigma} C_{\nu q\sigma} \tag{H.114} \]

The vectors in Eq. H.114 are: \( \bar{P}, \bar{W}, (\bar{X} \pm \bar{Y}) \). The relaxed one-particle difference density matrix is given by \( \bar{P} = \bar{T} + \bar{Z} \). Based on Eq. H.109, the gradient of the excitation energy may now be written
\[ \omega^\xi = \frac{1}{2} \sum_{i\alpha j\beta} \left\{ \left( \sum_{\mu\nu,\kappa,\lambda} 2C_{\mu i\sigma}C_{\nu\alpha \sigma}C_{\kappa j\tau}C_{\lambda\mu\tau} (\mu\nu|\kappa\lambda)^\xi + 2\sum_{\mu\nu,\kappa,\lambda} C_{\mu i\sigma}C_{\nu\alpha \sigma}C_{\kappa j\tau}C_{\lambda\mu\tau} f_{\mu\sigma\kappa\lambda\tau}^{xc}(\xi) \right) \\
\quad - c_x \delta_{\sigma\tau} \sum_{\mu\nu,\kappa,\lambda} \left[ C_{\mu i\sigma}C_{\nu\alpha \sigma}C_{\kappa j\tau}C_{\lambda\mu\tau} (\mu\nu|\kappa\lambda)^\xi \right] \right\} (X + Y)_{i\alpha\sigma}(X + Y)_{j\beta} \]
\[ + \left\{ c_x \delta_{\sigma\tau} \sum_{\mu\nu,\kappa,\lambda} \left[ C_{\mu j\sigma}C_{\nu\alpha \sigma}C_{\kappa i\tau}C_{\lambda\mu\tau} (\mu\nu|\kappa\lambda)^\xi \right] \right\} (X - Y)_{i\alpha\sigma}(X - Y)_{j\beta} \]
\[ + \sum_{i\alpha\sigma} Z_{i\alpha\sigma} \left\{ \sum_{\mu\nu} C_{\mu i\sigma}C_{\nu\alpha \sigma} h_{\mu\nu}^\xi + \sum_{j\tau} \left\{ \sum_{\mu\nu,\kappa,\lambda} C_{\mu i\sigma}C_{\nu\alpha \sigma}C_{\kappa j\tau}C_{\lambda\mu\tau} (\mu\nu|\kappa\lambda)^\xi \right. \right. \]
\[ \quad - c_x \delta_{\sigma\tau} \sum_{\mu\nu,\kappa,\lambda} C_{\mu i\sigma}C_{\nu j\sigma}C_{\kappa\mu\tau}C_{\lambda\nu\tau} (\mu\nu|\kappa\lambda)^\xi \left. \left. \right\} + \sum_{\mu\nu} C_{\mu i\sigma}C_{\nu\alpha \sigma} V_{\mu\nu\sigma}^{xc}(\xi) \right\} \]
\[ - \sum_{p\rho q, p \leq q} W_{p\rho q} \sum_{\mu\nu} C_{\mu p\sigma}C_{\nu q\sigma} S_{\mu\nu}^{\xi} \]

(H.115)

If we use the transformation to AO indices by interchanging the summations, Eq. H.115 simplifies significantly to

\[ \omega^\xi = \frac{1}{2} \sum_{\mu\kappa,\lambda,\tau} \left\{ \left( \sum_{\mu\nu,\kappa,\lambda} 2(X + Y)_{\mu\nu\sigma}(X + Y)_{\kappa\lambda\tau} - c_x \delta_{\sigma\tau} \left[ (X + Y)_{\kappa\mu\sigma}(X + Y)_{\mu\lambda\tau} \right. \right. \right. \]
\[ \quad + (X + Y)_{\kappa\mu\sigma}(X + Y)_{\lambda\nu\tau} - (X - Y)_{\kappa\mu\sigma}(X - Y)_{\mu\lambda\tau} \right. \]
\[ + (X - Y)_{\kappa\mu\sigma}(X - Y)_{\lambda\nu\tau} \right\} \left( \mu\nu|\kappa\lambda \right)^\xi \]
\[ + \sum_{\mu\nu\sigma} Z_{\mu\nu\sigma} h_{\mu\nu}^\xi + \sum_{\mu\nu,\kappa,\lambda,\tau} Z_{\mu\nu\sigma} D_{\kappa\lambda\tau} (\mu\nu|\kappa\lambda)^\xi - \sum_{\mu\nu,\kappa,\lambda,\tau} c_x \delta_{\sigma\tau} Z_{\mu\kappa\sigma} D_{\nu\lambda\tau} (\mu\nu|\kappa\lambda)^\xi \]
\[ + \sum_{\mu\nu\sigma} Z_{\mu\nu\sigma} V_{\mu\nu\sigma}^{xc}(\xi) - \sum_{\mu\nu\sigma} W_{\mu\nu\sigma} S_{\mu\nu}^{\xi} + \sum_{\mu\nu,\kappa,\lambda,\tau} f_{\mu\nu\sigma\kappa\lambda\tau}^{xc}(\xi) (X + Y)_{\mu\nu\sigma}(X + Y)_{\kappa\lambda\tau} \]

(H.116)

Note that the ground state density matrix, \( D_{\mu\nu\tau} \), is defined
\[ D_{\mu\nu\tau} = \sum_p C_{\mu p \tau} C_{\nu p \tau} \]  

(H.117)

The final step in the derivation of the excitation energy gradients is to collect all terms related to the two-electron integrals. It should be stressed here that for all terms related to \( \vec{Z} \), we can write that \( P_{ia\sigma} = T_{ia\sigma} + Z_{ia\sigma} \) (or \( P_{\mu\nu\sigma} = T_{\mu\nu\sigma} + Z_{\mu\nu\sigma} = Z_{\mu\nu\sigma} \), since the MO to AO transformation is a linear map) because \( T_{ia\sigma} = 0 \). In AO indices, we use that substitution to write

\[
\omega^\xi = \sum_{\mu\sigma} h_{\mu\sigma}^\xi P_{\mu\sigma} - \sum_{\mu\sigma} S_{\mu\sigma}^\xi W_{\mu\sigma} + \sum_{\mu\sigma} V_{\mu\sigma}^{xc}(\xi) P_{\mu\sigma} + \sum_{\mu\nu\kappa\lambda\sigma\tau} \left[ \frac{1}{2} \left\{ 2(X + Y)_{\mu\sigma}(X + Y)_{\kappa\lambda\tau} + 2P_{\mu\sigma} D_{\kappa\lambda\tau} \right. \right.
\]
\[
- c_x \delta_{\sigma\tau} \left[ 2P_{\mu\sigma} D_{\nu\lambda\tau} + (X + Y)_{\kappa\nu\sigma}(X + Y)_{\mu\lambda\tau} + (X + Y)_{\kappa\nu\sigma}(X + Y)_{\mu\lambda\tau} - (X - Y)_{\kappa\nu\sigma}(X - Y)_{\mu\lambda\tau} \right.
\]
\[
+ (X - Y)_{\kappa\mu\sigma}(X - Y)_{\lambda\nu\tau} \right\} (\mu\nu|\kappa\lambda)\xi \right] + \sum_{\mu\nu\kappa\lambda\sigma\tau} f_{\mu\nu\sigma\kappa\lambda\tau}^{xc}(\xi) (X + Y)_{\mu\nu\sigma}(X + Y)_{\kappa\lambda\tau}
\]
\[
+ \sum_{\mu\nu\kappa\lambda\sigma\tau} f_{\mu\nu\sigma\kappa\lambda\tau}^{xc}(\xi) (X + Y)_{\mu\nu\sigma}(X + Y)_{\kappa\lambda\tau}
\]

(H.118)

Here, the effective two-particle difference density matrix \( \Gamma_{\mu\nu\sigma\kappa\lambda\tau} \) is given as

\[
\Gamma_{\mu\nu\sigma\kappa\lambda\tau} = \frac{1}{2} \left\{ 2(X + Y)_{\mu\nu\sigma}(X + Y)_{\kappa\lambda\tau} + 2P_{\mu\sigma} D_{\kappa\lambda\tau} \right. \right.
\]
\[
- c_x \delta_{\sigma\tau} \left[ 2P_{\mu\sigma} D_{\nu\lambda\tau} + (X + Y)_{\kappa\nu\sigma}(X + Y)_{\mu\lambda\tau} + (X + Y)_{\kappa\nu\sigma}(X + Y)_{\mu\lambda\tau} - (X - Y)_{\kappa\nu\sigma}(X - Y)_{\mu\lambda\tau} \right.
\]
\[
+ (X - Y)_{\kappa\mu\sigma}(X - Y)_{\lambda\nu\tau} \right\} (\mu\nu|\kappa\lambda)\xi \right] \right.
\]
\[
+ \sum_{\mu\nu\kappa\lambda\sigma\tau} f_{\mu\nu\sigma\kappa\lambda\tau}^{xc}(\xi) (X + Y)_{\mu\nu\sigma}(X + Y)_{\kappa\lambda\tau}
\]
\[
+ \sum_{\mu\nu\kappa\lambda\sigma\tau} f_{\mu\nu\sigma\kappa\lambda\tau}^{xc}(\xi) (X + Y)_{\mu\nu\sigma}(X + Y)_{\kappa\lambda\tau}
\]

(H.119)
If we had used Eq. H.113 for the Fock matrix instead, $\Gamma_{\mu\nu\sigma\kappa\lambda\tau}$ would instead be defined

$$
\Gamma_{\mu\nu\sigma\kappa\lambda\tau} = \frac{1}{2} \left\{ 2(X + Y)_{\mu\nu}(X + Y)_{\kappa\lambda\tau} + 2P_{\mu\nu\sigma}D_{\kappa\lambda\tau} 
\right.
$$

$$
- c_x \delta_{\sigma\tau} \left[ P_{\mu\nu\sigma}D_{\nu\lambda\tau} + P_{\mu\lambda\sigma}D_{\nu\kappa\tau} + (X + Y)_{\kappa\nu\sigma}(X + Y)_{\mu\lambda\tau} 
\right.
$$

$$
+ (X + Y)_{\kappa\mu\sigma}(X + Y)_{\lambda\nu\tau} - (X - Y)_{\kappa\nu\sigma}(X - Y)_{\mu\lambda\tau} 
$$

$$
\left. + (X - Y)_{\kappa\mu\sigma}(X - Y)_{\lambda\nu\tau} \right\} 
$$

(H.120)

Both forms are identical, so we will use Eq. H.119 (we show both to alleviate confusion).

It should be clear at this point that the gradient of the excitation energy requires knowledge of $\vec{P}/\vec{Z}$ and $\vec{W}$. These must be calculated first, then multiplied by several quantities calculated during the ground state geometry optimization (such as the gradient of the core Hamiltonian). There are also two distinct cases:

1. Hartree-Fock calculation: in this case, we set all terms related to the XC-functional to zero.

2. (Pure) DFT calculation: in this case, we set $c_x = 0$.

For Hartree-Fock (case 1), $\Gamma_{\mu\nu\sigma\kappa\lambda\tau}$ is defined in Eq. H.119 with $c_x = 1$, and the gradient of the excitation energy is

$$
\omega_{HF}^{\xi} = \sum_{\mu\sigma} h_{\mu\sigma}^\xi P_{\mu\sigma} - \sum_{\mu\sigma} S_{\mu\sigma}^\xi W_{\mu\sigma} + \sum_{\mu\nu\kappa\lambda\tau} (\mu\nu|\kappa\lambda)^\xi \Gamma_{\mu\nu\sigma\kappa\lambda\tau} 
$$

(H.121)

The Hartree-Fock result is particularly simple, being mindful that it avoids all derivatives of the XC-functional. For DFT (case 2), the excitation energy gradient is given by Eq. H.116, and $\Gamma_{\mu\nu\sigma\kappa\lambda\tau}$ becomes very simple

$$
\Gamma_{\mu\nu\sigma\kappa\lambda\tau}^{DFT} = \frac{1}{2} \left\{ 2(X + Y)_{\mu\nu}(X + Y)_{\kappa\lambda\tau} + 2P_{\mu\nu\sigma}D_{\kappa\lambda\tau} \right\} 
$$

(H.122)

The DFT result for the excitation energy gradient, however, is more complicated because of the XC-functional terms.
Finally, it is helpful to establish the forms of the gradients of the XC-potential and XC-kernel, since it may not be obvious how those are done. The gradient of the XC-potential,

\[ V_{\mu\nu\tau}^{\text{xc}}(\xi) = \sum_{pq} C_{\mu\rho\tau}^{\nu\sigma} V_{pq\tau}^{\text{xc}}(\xi) C_{\nu\rho\tau}, \]

is:

\[ V_{pq\tau}^{\text{xc}}(\xi) = \int dr' \phi_{p\tau}(r') \frac{\partial}{\partial \xi} \left[ \frac{\delta E_{\text{xc}}}{\delta \rho_{\tau}(r')} \right] C=C_0 \phi_{q\tau}(r') \]  

(H.123)

This can be calculated using the chain rule for functional derivatives:

\[ \frac{\partial}{\partial \xi} \left[ \frac{\delta E_{\text{xc}}}{\delta \rho_{\tau}(r')} \right] C=C_0 = \int dr \frac{\delta^2 E_{\text{xc}}}{\delta \rho_{\sigma}(r) \delta \rho_{\tau}(r')} \left( \frac{\partial \rho_{\sigma}(r)}{\partial \xi} \right) C=C_0 \]  

(H.124)

\[ = \int dr f_{\sigma\tau}^{\text{xc}}(\xi) (r) \]

The chain rule may also be used for the gradient of the XC-kernel, as shown below.

\[ f_{pq\tau\rho\sigma}^{\text{xc}}(\xi) = \int dr' \int dr'' \phi_{p\tau}(r') \phi_{q\sigma}(r') \frac{\partial}{\partial \xi} \left[ \frac{\delta^2 E_{\text{xc}}}{\delta \rho_{\tau}(r') \delta \rho_{\rho}(r'')} \right] C=C_0 \phi_{r\sigma}(r'') \phi_{s\tau}(r'') \]  

(H.125)

\[ = \int dr \frac{\delta^3 E_{\text{xc}}}{\delta \rho_{\sigma}(r) \delta \rho_{\tau}(r') \delta \rho_{\rho}(r'')} \left( \frac{\partial \rho_{\sigma}(r)}{\partial \xi} \right) C=C_0 \]  

(H.126)

Gradients of the electron density involve computing the derivative of the AO basis functions with respect to the nuclear coordinate \( \xi \). The gradients of AO basis functions are nonzero only when a basis function is centered on the nucleus associated with coordinate \( \xi \). For details, see Ref. 31 (pg. 342) for the expressions used for gradients of AO basis functions using Gaussian-type orbitals.
H.4.1 Reduction in dimension of $G[\vec{X}, \vec{Y}, \omega]$

For the first term in the function $G[\vec{X}, \vec{Y}, \omega]$, we employ the unitary transformation to write

\[
\frac{1}{2} \begin{pmatrix} \vec{X}^T & \vec{Y}^T \end{pmatrix} \begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \\ -1 \\ 1 \end{pmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix}
\]

\[
= \frac{1}{2} \begin{pmatrix} \vec{X}^T & \vec{Y}^T \end{pmatrix} \begin{pmatrix} A + B & -A + B \\ A + B & A - B \end{pmatrix} \begin{pmatrix} \vec{X} + \vec{Y} \\ -\vec{X} + \vec{Y} \end{pmatrix}
\]

\[
= \frac{1}{2} \begin{pmatrix} \vec{X}^T & \vec{Y}^T \end{pmatrix} \begin{pmatrix} (A + B)(\vec{X} + \vec{Y}) + (A - B)(\vec{X} - \vec{Y}) \\ (A + B)(\vec{X} + \vec{Y}) - (A - B)(\vec{X} - \vec{Y}) \end{pmatrix}
\]

\[
= \frac{1}{2} \begin{pmatrix} \vec{X}^T & \vec{Y}^T \end{pmatrix} \begin{pmatrix} \vec{X} + \vec{Y} \\ \vec{X} - \vec{Y} \end{pmatrix} + \vec{Y}^T(A + B)(\vec{X} + \vec{Y}) - \vec{Y}^T(A - B)(\vec{X} - \vec{Y})
\]

\[
= \frac{1}{2} \left[ (\vec{X} + \vec{Y})^T(A + B)(\vec{X} + \vec{Y}) + (\vec{X} - \vec{Y})^T(A - B)(\vec{X} - \vec{Y}) \right]
\]

The unitary transformation can also simplify the second term

\[
-\frac{1}{2} \omega \left[ \begin{pmatrix} \vec{X}^T & \vec{Y}^T \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \\ -1 \\ 1 \end{pmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} - 2 \right]
\]

\[
= -\frac{1}{2} \omega \left[ \begin{pmatrix} \vec{X}^T & \vec{Y}^T \end{pmatrix} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} \vec{X} + \vec{Y} \\ -\vec{X} + \vec{Y} \end{pmatrix} - 2 \right]
\]

\[
= -\frac{1}{2} \omega \left[ \begin{pmatrix} \vec{X}^T & \vec{Y}^T \end{pmatrix} \begin{pmatrix} 0 & + \vec{X} + \vec{Y} \\ (\vec{X} + \vec{Y}) + (\vec{X} - \vec{Y}) \end{pmatrix} - 2 \right]
\]

\[
= -\frac{1}{2} \omega \left[ \vec{X}^T(\vec{X} + \vec{Y}) + \vec{X}^T(\vec{X} - \vec{Y}) - \vec{Y}^T(\vec{X} + \vec{Y}) + \vec{Y}^T(\vec{X} - \vec{Y}) - 2 \right]
\]

\[
= -\frac{1}{2} \omega \left[ (\vec{X} - \vec{Y})^T(\vec{X} + \vec{Y}) + (\vec{X} + \vec{Y})^T(\vec{X} - \vec{Y}) - 2 \right]
\]

\[
= -\omega \left[ (\vec{X} + \vec{Y})^T(\vec{X} - \vec{Y}) - 1 \right]
\]
Bibliography


Vita

Daniel W. Silverstein

Education

2008–2013  Ph.D., Chemistry
The Pennsylvania State University, University Park, PA
2003–2007  B.S., Chemistry
University of Colorado at Denver — Anschutz Medical Campus, Denver, CO

Awards and Honors

2012  Braucher Award for outstanding research accomplishments
2010  Continuing Chemistry Graduate Student Research Award
2009  Dan H. Waugh Memorial Teaching Award (honorable mention)
2008  Incoming Class New Graduate Student Award
2008  Best Graduating Student in Chemistry
2007  Academic Excellence in Analytical Chemistry
2006  Academic Excellence in Organic Chemistry

Publications


