The Pennsylvania State University The Graduate School

INTERPRETING HIGH-RESOLUTION TIP-ENHANCED RAMAN SPECTROSCOPY IMAGES

A Dissertation in Chemistry by Pengchong Liu

@ 2020 Pengchong Liu

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The dissertation of Pengchong Liu was reviewed and approved by the following:

Lasse Jensen Professor of Chemistry Dissertation Advisor, Chair of Committee

Paul S. Cremer J. Lloyd Huck Chair in Natural Sciences Professor of Chemistry, Biochemistry and Molecular Biology

William G. Noid Professor of Chemistry

Adri C.T. van Duin Professor of Mechanical and Nuclear Engineering

Phillip C. Bevilacqua Distinguished Professor of Chemistry, Biochemistry and Molecular Biology Head of the Department of Chemistry

Abstract

Raman spectroscopy is one of the fundamental techniques in chemical characterization. It measures the amount of photons and their frequency shifts scattered by the molecule under a given laser beam. The frequency shifts originate from the molecule's vibrations, which are determined by its microscopic structure. Thus, a Raman spectrum is often regarded as the molecule's "fingerprint". When the molecule is placed on a noble metal surface with some curvature, the Raman signals are greatly enhanced by the plasmonic near field at the surface. This technique is called "surfaceenhanced Raman spectroscopy", or SERS. Because of the significantly improved sensitivity relative to regular Raman scattering, SERS has grown into a widely popular tool for chemical research and practical applications. Moreover, the molecule-metal interaction that lies in the center of the mechanism of SERS has been a hot topic of fundamental research since its discovery and has led to many variants in the development of spectroscopic techniques.

Tip-enhanced Raman spectroscopy (TERS) integrates the scanning probe microscopy and SERS. Similar to SERS, the enhancement of Raman scattering in TERS benefits from the inhomogeneous near field induced by the plasmonic resonance of the noble metal nanostructure. However, the TERS spectrum of a molecule is often found different than SERS, and it changes with the tip position. The combination of the chemical sensitivity and the spatial resolution makes TERS a promising technique for microscopic characterization. A comprehensive demonstration of these unique features is TERS imaging. A TERS image is a two-dimensional map of the Raman intensity at a certain frequency varying with the scanning tip. It exhibits a sub-nanometer resolution and is specific to the corresponding vibrational mode. TERS imaging is considered as a visualization of molecular vibrations and sets stage for a new way of understanding molecules. Therefore, it is necessary to develop theoretical interpretation of TERS images and their connections to the underlying molecular vibration. However, interpreting TERS images is challenging as the brightspot pattern does not always strictly align with the vibrating atoms and the signals are very sensitive to experimental conditions.

In this dissertation, three major aspects of TERS theory are explored: the effect of the plasmonic near field (electromagnetic mechanism), the plasmonic resonance inside a subnanometer cavity (gap plasmonics), and the quantum mechanical interactions between the molecule and the substrate (the chemical mechanism). In particular, the critical conditions of the near field to achieve atomic resolution are found. It is also illustrated that the locally integrated Raman polarizability density is the sub-molecular property probed by the confined near field in TERS. It provides an intuitive description of the TERS imaging mechanism, which is usually hidden in the self-consistent cycles of conventional calculations using the time-dependent density functional theory. The distinct feature of TERS is largely ascribed to the unique plasmonic properties of a sub-nanometer junction consisting of a flat metal substrate and an atomically sharp tip. At this length scale, atomistic electrodynamics is adopted to describe the nanostructure because it captures the microscopic structure and at the same time retains the efficiency of a classical model.

To study the charge-transfer plasmon due to quantum tunneling, a Hirshfeld partitioning scheme is developed to distinguish the plasmonic resonances within and across the coupled nanoparticles. Furthermore, this dissertation presents the development of a new theoretical method to better describe the substrate-molecule coupling, namely, exact frozen density embedding. The method to obtain the response properties of a molecule is derived based on the exact frozen density embedding within the framework of time-dependent density functional theory. Finally, a polarizable frozen density embedding method is developed to include the polarization effect due to the presence of a metal nanoparticle. The development of these theoretical tools is potentially applicable to the studies of the electronic structures of a TERS system.

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List of Symbols

Below are a list of the most common sub- and super-scripts:

- i, j Occupied orbitals
- a, b Virtual or unoccupied orbitals

 α,β,γ – Cartesian coordinates or atomic orbital index, depending on context

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

Angular frequency
Electric field
Near-field distribution
Electric dipole
Traceless electric quadrupole
Electric dipole-dipole polarizability
Electric dipole-quadrupole polarizability
Electric quadrupole-dipole polarizability
Electric quadrupole-quadrupole polarizability
General n th order response tensor
Kronecker delta
Kohn-Sham orbital energy
kth normal mode coordinates
nth order interaction tensor
Non-interacting kinetic energy
Non-additive kinetic potential
Electron density
Kohn-Sham orbital
Atomic orbital
Identity matrix
Overlap matrix
Coupling matrix
Vector in Cartesian coordinates

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Dedication

To my family, for their unconditional love, support, and trust so that I can fearlessly chase my dream.

Part I

Introductory Material

Chapter 1 Introduction

Raman spectroscopy, first reported in 1928¹, is a popular analytical technique for chemical characterizations. It measures shifts in the frequency of the light scattered by the molecule, which is determined by the molecule's vibrations. Specifically, the Raman process involves the absorption of incident light of frequency ω_{in} , excitation of molecular vibration at frequency ω_{vib} , and re-emission/scattering of the light of a different frequency $\omega_{in} \pm \omega_{vib}$, where the sum/difference represents the anti-Stokes/Stokes shift in frequency due to the molecular vibration. A typical Raman spectrum maps the intensity of the scattered light with respect to the corresponding shift in frequency ω_{vib} . Because the molecule's vibrational modes are unique to its microscopic structure, a Raman spectrum is usually regarded as the molecule's "fingerprint". However, the probability of regular Raman process is very low and hinders its practical applications in many fields.

In early 1970's, Fleishmann and co-workers first reported the strong Raman scattering of pyridine on roughened silver electrodes.² Later, the mechanism of electromagnetic enhancement from the surface was proposed by Jeanmaire and Van Duyne.³ An overall enhancement factor of about $10^5 - 10^6$ in comparison with regular Raman was suggested ^{3,4}. Nowadays, the enhancement in SERS is largely ascribed to the plasmon-induced near field, $E(\omega)$, on the surface of the metal structure, and it scales with $|E(\omega)|^4/|E_0|^4$, which is known as the electromagnetic mechanism (EMM). In addition, the presence of metal in the close vicinity of the molecule leads to reconfiguration of the molecule's electronic structure for both ground and excited states, and consequently gives rise to changes in the spectral features in various ways. This is known as the chemical mechanism (CM). SERS exhibits much higher sensitivity than regular Raman spectroscopy. It requires much less concentration for the sample molecule, sometime only a single molecule, in the measurement thanks to the enhanced intensity. Moreover, SERS spectrum of a species often has more number of peaks (different selection rules) and higher signal-to-noise ratio (narrower peak). Besides the wide applications as a sensitive analytical tool, SERS is now a fundamental phenomenon that involves studies of quantum mechanics, molecular dynamics, and electromagnetic theory, and has led to many variants of plasmon-enhanced spectroscopies⁵.

Tip-enhanced Raman spectroscopy (TERS) is among the techniques recently developed based on SERS, and has drawn enormous attention⁶. In short, TERS utilizes the state-of-the-art atomic force microscopy (AFM) or scanning tunneling microscopy (STM) as a platform to perform Raman scattering measurements. It harnesses the extremely enhanced and confined near field within the metal junction to significantly improves chemical sensitivity and spatial resolution. In the presence of the confined near field, the selection rules of TERS is drastically changed compared with SERS or conventional Raman spectroscopy.^{7,8} Moreover, the spectrum varies with the position of the tip. By mapping the changes in intensity at a certain vibrational frequency as the tip scans over the molecule, one obtains a two dimensional image that has a unique pattern of brightspot. Such an image is known as the TERS image for this vibrational mode. Over the years, size of the discrete brightspot in TERS images has become as small as a single atom due to the precise control over the tip and the confined near field.^{9–13} A TERS image is usually uniquely determined by the vibrational mode of the molecule. Therefore, the technique of TERS imaging simultaneously provides chemical and structural information of the sample molecule. It sets stage for a new way of "seeing" and understanding molecular vibrations, and thus is sometimes called the "chemiscope"¹⁴.

Along with the exciting experimental observations comes with the challenges on interpretation and prediction of TERS images. In other words, accurate theoretical modeling is required for us to understand the underlying mechanism of TERS. As a sister technique to SERS⁵, the EMM has been commonly recognized as the dominant mechanism for TERS, where the molecular properties are obtained in quantum mechanical models, e.g., the time-dependent density functional theory (TDDFT), under a near field with a narrow spatial distribution. Conventional TDDFT-based calculations with a modified external field $^{15-18}$, is limited by its computational cost, especially for simulating TERS images where a complete calculation is required for each tip position on the scanning grid. Also, to reproduce experimental results, one often needs to search in a large space of proper tip positions due to the sensitivity of the spectrum. These conditions pose substantial challenges to practical applications of existing theories to interpret experimental TERS measurements. Furthermore, most of existing TDDFT methods provide a physical quantity that is only on the molecular level such as the molecular polarizability. Molecular properties alone are not informative enough for TERS. For example, different vibrational modes with similar polarizability derivatives often give rise to distinct TERS images. In other words, only a part of molecule is probed locally at the tip position. Hence, a property that can be locally attributed to the vibrating atoms or chemical bonds is needed to explain the variation of TERS intensities.

In addition to the EMM, the CM is also of particular importance in TERS as suggested by experimental results¹³. On one hand, a strong binding that anchors the molecule on the substrate is key to the atomic resolution of TERS images; on the other hand, the STM setup actually injects electrons into/through the molecule. Both processes may lead to significant changes in the electronic structure of the molecule. Two areas that requires immediate investigation include 1) quantum mechanical treatment of the metal junction without sacrificing for the expensive computational cost; 2) the charge-transfer process across the plasmonic junction.

This dissertation aims to address both the EMM and the CM through the development of theoretical models and to interpret high-resolution TERS images recorded in experiments. We have employed a hybrid electrodynamics/quantum mechanics model to study single-molecule TERS imaging, and predicted the critical conditions to achieve atomic resolution. As an extension, we have developed a simplified theoretical model to approximate TERS qualitatively and significantly improve the computational efficiency. This model provides an approximate mechanism of TERS imaging process. It allows for intuitive interpretations of experimental results, where the sample molecule is usually far beyond the computational capacity of conventional TDDFT methods. Furthermore, the strong coupling of plasmonic between two metallic systems is studied systematically, with an emphasis on the quantum size regime where the gap between the two metallic systems is as small as a few Ångströms. Finally, early attempts to include part of the metal system into the quantum mechanical treatment are presented. In particular, an exact frozen density embedding (FDE) method is derived to describe the chemical interaction between the molecule and the metal in addition to the classical polarization interaction.

Chapter 2 Overview of Dissertation

This main body of the dissertation is presented in three parts. Part II focuses on the development and application of theoretical methods to interpret TERS images, with an emphasis on the effects of the plasmonic near field (EMM). In Part III, the unique properties of plasmons in a subnanometer gap is discussed, which is the fundamental model of a tip-substrate setup in TERS. Part IV presents recent efforts on a DFT-based method to include metal atoms into the quantum mechanical description, namely, the frozen density embedding method. In the following, a brief outline of each chapter is presented. Chapters 3 through 9, except for Chapter 8, are all adapted from published work.

Chapter 3 Single-Molecule Imaging Using Atomistic Near-Field Tip-Enhanced Raman Spectroscopy

A systematic study of TERS imaging using the hybrid electrodynamics/quantum mechanics method, which provides a consistent framework to treat both the plasmoninduced near field and the molecular properties. The conditions to achieve atomic resolution are presented, and the effect of near-field focal plane on TERS images is revealed.

Chapter 4 High-Resolution TERS Probes Sub-Molecular Density Changes

The theoretical model of locally integrated Raman polarizability density (LIRPD) is developed to intuitively and efficiently predict TERS images. It is found that the local sub-molecular changes of density induced by the confined near-field can qualitatively describe the TERS images. This method is also used to explain previous experimental results on a relatively large molecule.

Chapter 5 Resolving Molecular Structures with High-Resolution TERS Images The application of LIRPD model to the interpretation of experimental results. Thanks to the accuracy and efficiency of the LIRPD model, we discover the most likely molecular conformation underlying a set of experimental TERS images. The effect of the near-field localization is further elucidated in terms of multipole expansion.

Chapter 6 Atomistic Electrodynamics Simulations of Plasmonic Nanoparticles A review of the atomistic electrodynamics approach applied to the simulations of large plasmonic nanoparticles.

Chapter 7 Atomistic Characterization of Plasmonic Dimers in the Quantum Size Regime

A Hirshfeld partitioning scheme for atomic charges and polarizabilities to study the plasmonic dimers, focusing on the charge-transfer plasmons. The charge-transfer plasmon due to quantum tunneling is consistently separated from the local resonances in the individual plasmonic nanoparticles. It is found that the strengths of the charge-transfer plasmons can be limited by the widths of the charge-flow pathways.

Chapter 8 Exact Frozen Density Embedding for the Time-Dependent Density Functional Theory

An exact subsystem TDDFT theory using frozen density embedding theory with external orthogonality. The methods to calculate the molecular excitation energies, transition dipole moments, oscillator strengths, and static polarizabilities are derived.

Chapter 9 Polarizable Frozen Density Embedding with External Orthogonality

A polarizable subsystem DFT theory is presented for the description of molecular electronic properties. Specifically, the expensive freeze-and-thaw cycles are bypassed by a polarization term in the molecular Hamiltonion. And the combination of the polarization and EO embedding potential allows for calculations in the supermolecular basis set.

Chapter 10 Summary and Chapter 11 Outlook

The findings of this dissertation are summarized, and several potential future projects using the methods described within are proposed.

In addition to these chapters, there are five appendices.

- Appendix A Supporting Information for Single-Molecule Imaging Using Atomistic Near-Field Tip-Enhanced Raman Spectroscopy Supporting information for Chapter 3 is given.
- Appendix B Supporting Information for High-Resolution TERS Probes Sub-Molecular Density Changes Supporting information for Chapter 4 is given.
- Appendix C Supporting Information for Resolving Molecular Structures with High-Resolution TERS Images Supporting information for Chapter 5 is given.
- Appendix D Supplementary Information for Atomistic Characterization of Plasmonic Dimers in the Quantum Size Regime Supporting information for Chapter 7 is given.
- Appendix E Supplementary Information for Polarizable Frozen Density Embedding with External Orthogonality

Supporting information for Chapter 9 is given.

Part II

Interpreting Tip-Enhanced Raman Scattering Images

Chapter 3 Single-Molecule Imaging Using Atomistic Near-Field Tip-Enhanced Raman Spectroscopy

Liu, P.; Chulhai, D. V.; Jensen, L. Single-Molecule Imaging Using Atomistic Near-Field Tip-Enhanced Raman Spectroscopy. ACS Nano **2017**, 11, 5094–5102.*

Abstract

Advances in tip-enhanced Raman spectroscopy (TERS) have demonstrated ultrahigh spatial resolution so that the vibrational modes of individual molecules can be visualized. The spatial resolution of TERS is determined by the confinement of the plasmon-induced field in the junction; however, the conditions necessary for achieving the high spatial confinement required for imaging individual molecules are not fully understood. Here, we present a systematic theoretical study of TERS imaging of single molecules, using a hybrid atomistic electrodynamics-quantum mechanical method. This approach provides a consistent treatment of the molecule and the plasmonic near field under conditions where they cannot be treated separately. In our simulations, we demonstrate that TERS is capable of uniquely resolving intricate molecule vibrations with atomic resolution, although we find that TERS images are extremely sensitive to the near field in the junction. Achieving the atomic resolution requires the near field to be confined within a few Angstroms in diameter and the near-field focal plane to be in the molecule plane. Furthermore, we demonstrate that the traditional surface selection rule of Raman spectroscopy is altered due to the significant field confinement that leads to significant field-gradient effects in the Raman scattering. This work provides insights into single-molecule imaging based on TERS and Raman scattering of molecules in nanojunctions with atomic dimensions.

^{*}Author contributions: L.J. conceived the basic idea; P.L. carried out the calculation; D.V.C. contributed to early calculations as proof of concept. P.L. and L.J. wrote the manuscript.

3.1 Introduction

Tip-enhanced Raman spectroscopy (TERS) integrates the surface-enhanced Raman spectroscopy (SERS) with scanning probe microscopy (SPM)^{7,19,20}. The nanostructure of a noble metal SPM tip is optically excited to generate localized surface plasmon resonances (LSPR). The LSPR induces a strong electromagnetic field that is confined within the tip-substrate junction, which drastically enhances ($\sim 10^8$) the Raman scattering signals of the specimen located in the junction. Due to the extremely high sensitivity and spatial resolution, TERS is very promising for applications in numerous fields, including materials engineering,²¹⁻²⁵ electrochemistry and catalysis²⁶⁻³², and biotechnology³³⁻³⁷.

Precise control of the field within the SPM junction at cryogenic temperatures has led to higher and higher spatial resolution of TERS^{11,38–45}. Recently, TERS imaging of a single *meso*-tetrakis(3,5-di-tertiarybutylphenyl)-porphyrin molecule (H₂TBPP) with a sub-nanometer resolution was reported, where the structural profile of the molecule was visualized by mapping the TERS signals while scanning across the molecule¹⁰. Later, it was demonstrated that TERS is able to distinguish between different molecules with similar structures, adsorbed adjacent to each other.¹² Moreover, using a simultaneous TERS and STM imaging technique, it is possible to resolve subtle differences of adsorbates, such as conformational differences⁴⁶. In these studies, lateral resolutions of only a few Ångstroms have been achieved.

Along with the great strides in experiments comes an urgent need for in-depth investigations of the physical mechanism underlying the spatial resolution of TERS.^{12,46} Computer simulation is a necessary approach to rationalizing experimental findings and to a complete understanding of TERS imaging. Since the spatial resolution of TERS imaging is determined by the confinement of the field that is induced by the sharp tip^{39,47,48}, it is crucial for TERS theories to accurately describe this confined field in the junction.

One of the earliest efforts to model the TERS used an arbitrary Gaussian-confined near field and described its interaction with molecules using time-dependent density functional theory (TDDFT).^{10,15} This model was later employed to visualize the vibrational modes of water with sub-molecular features¹⁶. Although this model was successful in reproducing the TERS images obtained in experiments, it provides no mechanism for generating the highly confined fields necessary for the TERS resolution. Furthermore, in a typical TERS setup, the size of the junction is within the quantum effects regime where the plasmonic responses are significantly modified^{49–53}. Microscopic details of the metallic junction are needed for an accurate description of the plasmon-induced near field in the quantum size regime and thereby a complete and accurate description of TERS^{53–55}. Both quantum mechanical models⁵⁵ and classical models⁵⁶ have demonstrated that atomic features in the junctions can lead to such high field confinement. Quantum mechanical simulations have shown that such high resolution is possible based on a chemical enhancement mechanism but did not consider the localized near field which typically dominates the enhancement.⁵⁷ Atomistic electrodynamics represents each atom of a metallic nanoparticle by an atomic polarizability, and thus enables a precise control of the local environment of the nanoparticle $5^{5,59}$. As a result, the plasmonic properties due to quantum mechanical effects

in a sub-nanometer gap are accurately captured by the atomistic electrodynamics model^{54,60}. Therefore, atomistic electrodynamics combined with a TDDFT description of the molecules provides a consistent treatment of the molecules and the nanojunction, and thus is well-suited for describing high-resolution TERS.

Herein, we present a systematic study of single-molecule TERS imaging with atomic resolution using a hybrid atomistic electrodynamics-quantum mechanical approach.⁵⁴ We observe in simulations that the atomic resolution of TERS imaging arises from the extreme confinement of the near field, which is determined by the incident light energy. The field maximum height relative to the molecule plane, which we define as the near-field focal plane, is found to have significant effects on the TERS images, especially for non-planar molecules. We show that a field confinement of a few Ångstroms and a near-field focal plane in the molecule plane are necessary for generating high-resolution images in TERS. The highly confined field also results in strong local field-gradient, which changes the selection rule of Raman spectroscopy 61,62 . We are able to visualize these field-gradient enhanced vibrations in the simulated TERS images. For resonant Raman scattering, we are able to resolve different vibrational modes of one porphyrin molecule with atomic features, and to distinguish similar vibrations associated with two different porphyrins based on the transition dipole moment between electronic states.

3.2 Results and Discussion

3.2.1 TERS images of planar water molecule

In our simulation model (Fig. 3.1 a), a water molecule is placed flat on a silver plane (XY) with a vertical separation of 2.5 Å. Previous simulations¹⁶ demonstrated high-resolution TERS images for water and thus this system provides a good benchmark system. We consider the molecule plane to pass through the origin of Z axis ($Z_0 = 0.0$ Å). The SPM tip is represented by the vertex of a silver icosahedral nanoparticle (Ag_{561}) . In the specific case of Fig. 3.1, the tip of the nanoparticle is $Z^{\text{Tip}} = 2.5$ Å above the molecule plane, and is excited by an incident light of 3.09 eV. The effects of the incident light energy and the tip-to-sample height will be addressed later. The silver nanoparticle is moved by a small step size (0.2 Å) across an area covering the molecule. TERS intensities, represented by the differential cross sections ⁶³, are calculated at each step. Only the zz component of the polarizability tensor is used for the intensity calculations, as it resembles experimental setups of perpendicular plane-polarized light and back scattering, and sample molecules are assumed to exhibit no rotation. Mapping the intensities for each vibrational mode (see Fig. A.2 for full spectra), we obtain the TERS images of the water molecule, as shown in Fig. 3.1 (b~d). Our results qualitatively agree with the images presented in Ref. 16, but have a few non-trivial differences. For the bending mode, the hot-spots are roughly elliptical instead of the dumb-bell shape reported in Ref. 16. Also, the hot-spots are located in between the two hydrogen atoms, with no prominent feature around the oxygen atom. For the symmetric and anti-symmetric stretching modes, we observe slight symmetry breaking in the TERS images. This is likely due to the difference in the curvatures of tip along the X and Y axes. Along the Y axis, the edge of the icosahedron is in the +Y direction while the facet is in the -Y direction. Along the X axis both directions see an edge, but the projection line of these two edges onto the imaging plane is not parallel with the X axis. The variance in the tip curvature gives rise to asymmetry in the near-field distribution on the imaging plane, and consequently, asymmetric interactions with the molecule.



Figure 3.1. (a) Ag_{561} icosahedron with a diameter of 2.9 nm is used as the SPM tip, and a water molecule sits flat on the silver XY plane. Simulated TERS images of the water molecule at different vibrational modes: (b) bending mode at 1600 cm⁻¹; (c) symmetric stretching mode at 3676 cm⁻¹; (d) anti-symmetric stretching mode at 3776 cm⁻¹. The dimension of each TERS image is 6 Å × 6 Å. The plot dimension and the color scale bar are shared by all TERS images of water in this work unless otherwise stated.

3.2.2 Effects of near-field confinement

For the aforementioned junction structure, we examine the effect of field confinement on TERS spatial resolution by varying the energy of the incident light. Three energies are selected for case studies: 3.09 eV, 3.41 eV and 3.59 eV, which spans from the onset of the nanoparticle absorption band to the peak (Fig. A.1). The near-field intensity $(|E|^2/|E_0|^2)$ is calculated from induced atomic dipoles of the metal system on a numerical grid (step size 0.2 Å) with a probe radius of 1.50 Å.⁶⁰ To quantify the field confinement, the full widths at half maxima (FWHMs) of the field enhancement along X and Y axes are obtained directly from the field grid without any curve fitting (see Fig. A.3 for the line shapes of the field). For conciseness, only the symmetric stretching mode is shown in the following discussions on water, as the other modes exhibit the same trend (Fig. A.4 & A.5). As is shown in Fig. 3.2, the TERS image of the best resolution

is generated by the incident light of about 3.09 eV. The distribution of near-field intensity has FWHMs slightly less than 5 Å, and the field maximum is located exactly on the molecule plane $(Z_{\text{max}} = 0.0 \text{ Å})$. With the 3.41 eV incident light, the near field is less confined, of which FWHMs are about 6 Å. The TERS image is blurred, relatively speaking, compared to the 3.09 eV case, despite the fact that the field intensity is slightly higher. In the 3.59 eV case (plasmonic peak), the field is significantly less confined and the intensity decreases by an order of magnitude, which leads to the loss of atomic features in the corresponding TERS image.



Figure 3.2. TERS images of the symmetric stretching mode and field enhancement $(|E|^2/|E_0|^2)$ distributions with different incident light energies: (a ~ c) 3.09 eV, (d ~ f) 3.41 eV, (g ~ i) 3.59 eV. For the field enhancement map in the molecule plane (b, e, h), the FWHMs along the X and Y axes are noted in Ångstroms. For the field enhancement map in the YZ plane (c, f, i), the water molecule plane, $Z_0 = 0$ Å, is represented by the white dash line on the left side; the maximum positions of the field on the Z axis are represented by the dash line on the right side, noted as Z_{max} . The dimension of each field distribution plot is 20 Å × 20 Å.

An atomically sharp tip, as modeled in this work, is found experimentally to be able to trap

optical fields in a sub-nanometer cavity at cryogenic temperatures¹⁷. Such extreme confinement of the field is well reproduced in our model, represented by FWHMs in Fig. 3.2. For an isolated plasmonic nanoparticle, the enhanced field localized on the sharp points of the structure is caused by the plasmonic resonance⁶⁴. However, for a plasmonic dimer with a small gap (in this case, substrate and tip nanoparticle), the strongest field enhancement within the junction occurs at a lower energy than the single-nanoparticle plasmonic resonance⁵², which arises from a metallic screening in the junction ("lightning rod effect").^{55,65} When the dimer system is excited at the single-nanoparticle plasmon energy, the intensity of the induced near field within the tip-substrate junction decreases and the "effective localization area" enlarges (i.e., less confined)⁵⁵. Consequently, the obtained TERS images under the single-nanoparticle plasmonic resonance do not retain the desired resolution (Fig. 3.2 g). In short, the resolution of TERS is extremely sensitive to the confinement of the field. With a carefully controlled incident light energy, an atomically sharp tip is able to confine the field in an area of about 5 Å in diameter (FWHM), which suffices to unravel atomic features for TERS images. The confinement of the field cannot reach any significantly smaller area according to the atomistic electrodynamics model.

3.2.3 Effects of near-field focal plane

Also shown in Fig. 3.2, the height of the near-field maximum (Z_{max}) in addition to the confinement area changes with the incident light energy. For the TERS images of the best resolution, the near-field maximum is exactly in the molecule plane $(Z_{\text{max}} = 0 \text{ Å})$. To better understand this effect, we slightly retract the tip without breaking the junction (Fig. 3.3 a ~ f), and keep the incident energy of 3.09 eV for the same field confinement. We find that the height of the near-field maximum changes with the height of the nanoparticle tip (Fig. 3.3 c & f), and that the height of the field maximum determines the resolution of the TERS images. With $Z_{\text{max}} = 0.3 \text{ Å}$, the desired pattern of the TERS image can still be roughly preserved (Fig. 3.3 a). But at $Z_{\text{max}} = 0.7$ Å the resolution drops significantly (Fig. 3.3 d).



Figure 3.3. TERS images of the symmetric stretching mode and field distributions with a tip-to-sample height of $Z^{\text{Tip}} = 3.0$ Å (a ~ c) and $Z^{\text{Tip}} = 3.5$ Å (d ~ f). The same setup as in Fig. 3.1(a) is used for the first two rows. The bottom row (g ~ i) corresponds to the large nanoparticle (Ag₂₀₅₇), with $Z_{large}^{\text{Tip}} = 3.5$ Å.

In order to rule out the effect of the reduced field intensity in the molecule plane while retracting the tip, the size of the nanoparticle is increased to generate a stronger field. Using the large nanoparticle (Ag₂₀₅₇, 4.6 nm in diameter) that is also excited at 3.09 eV, we are able to increase the near-field intensity while keeping the tip curvature, field-confinement area, and field maximum height, unaltered (Fig. 3.2 h & i). In this regard, we find that the increased field intensity does not lead to better imaging resolution. Even for the stronger field, it still requires the field maximum to be in the molecule plane to achieve the atomic resolution (Fig. A.7). In the simulations presented above, the field maximum position is consistently in or higher than the molecule plane, which adheres to the presumption of no chemical bonding between the tip and the molecule. We also push the nanoparticle closer to the molecule to have the near-field maximum underneath the molecule plane ($Z_{max} = -0.2$ Å). The obtained TERS images retain the desired resolution (Fig. A.6). The field maximum height, Z_{max} , can be considered as the

plane of focus for the near field in TERS imaging apparatus. The sharpest resolution of TERS images is obtained in the focal plane, which is preferred to overlap with the molecule plane.



Figure 3.4. TERS images of the vertical water molecule. The oxygen atom is at the bottom, placed at $Z^O = 0.0$ Å, and the height of hydrogen atoms are both $Z^H = 0.60$ Å. Tip-to-oxygen distance is 2.5 Å (a ~ c, field maximum at $Z_{\text{max}} = 0.0$ Å), 3.0 Å (d ~ f, $Z_{\text{max}} = 0.3$ Å), and 3.5 Å (g ~ i, $Z_{\text{max}} = 0.7$ Å). The first column (a, d, g) corresponds to the bending mode; the 2nd column (b, e, h) corresponds to the symmetric stretching mode; the 3rd column (c, f, i) corresponds to the anti-symmetric stretching mode.

However, the molecule adsorbed on the metal substrate is very likely, in reality, to have a more complex structure than a simple plane. The focal plane height is then expected to affect the TERS images in other aspects than the resolution alone. We explore these aspects by simulating a water molecule placed perpendicular to the substrate, where the oxygen atom is in the original plane ($Z^O = 0.0$ Å) and the hydrogen atoms are closer to the tip ($Z^H = 0.60$ Å). Each of the aforementioned focal planes ($Z_{\text{max}} = 0.0, 0.3, 0.7$ Å) are located on the oxygen atom, in between

the oxygen and the hydrogen, or roughly on the hydrogen atoms. As is shown in Fig. 3.4, the three focal planes all lead to atomistically resolved TERS images. However, each normal mode of water behaves differently with respect to changes of focal plane height, and the identity of water by its TERS images is not as clear as it was in the parallel case. For the bending mode (Fig. 3.4 a, d & g), the hot-spots evolve from two overlapping ovals into a single oval as the focal plane is moved higher. The symmetric stretching mode has two separate lobes located in the vicinity of the H atoms when the focal plane is on the oxygen atom (Fig. 3.4 b). While elevating the focal plane, the two lobes expand towards the center and eventually merge into one ellipse on top of the projection of the molecule (Fig. 3.4 e & h). The anti-symmetric stretching mode has almost the same TERS image as the symmetric mode (Fig. 3.4 c) at first; however, rather than merging into one ellipse, the two lobes consistently expands outwards as the focal plane moves higher. The above analyses indicate that small changes in the focal plane height may exert dramatic effects on the TERS image patterns. To ensure the best resolution, the focal plane is kept on the molecule plane ($Z_{max} = 0.0$ Å) in the following discussions.

3.2.4 Field-gradient active modes

The highly confined field in the TERS junction brings about strong field-gradients (FG), which may change the selection rules for plasmon-enhanced Raman spectroscopies ^{66–70}. To explore the FG effects in TERS, we simulate the TERS images of benzene. Three FG active normal modes of benzene are selected in this study, which are associated with the symmetry type a_{2u} $(\nu_{11}, 664 \ cm^{-1}), e_{1g} \ (\nu_{10}, 835 \ cm^{-1}), and a_{1g} \ (\nu_1, 988 \ cm^{-1})$. In the first two modes, the molecule vibrations are out-of-plane. As reported in detail in Ref. 70, the induced dipoles of 664 $\ cm^{-1}$ mode arise from FG contributions through the electric dipole-quadrupole term $(|E'|^2 \cdot |\nabla E|^2 + |\nabla E'|^2 \cdot |E|^2, \text{ correlated field and FG enhancement mechanism}); the 835 \ cm^{-1}$ mode is enhanced by FG through the quadrupole-quadrupole term $(|\nabla E'|^2 \cdot |\nabla E|^2, \text{ pure FG}$ term); the 988 $\ cm^{-1}$ mode exhibits contributions from both the dipole-dipole term and the quadrupole-quadrupole term $(|E'|^2 \cdot |E|^2 + |\nabla E'|^2 \cdot |\nabla E|^2, \text{ separate field and FG contributions}).$ These three modes are explicitly depicted in Fig. 3.5 (a~c).



Figure 3.5. Selected normal modes and their respective TERS images of the benzene molecule: (a & d) 664 cm^{-1} , (b & e) 835 cm^{-1} , (c & f) 988 cm^{-1} . The carbon vibrations are not intense enough to be seen in (a) & (b). The schematics of molecular vibrations (a~c) are rotated slightly for a clearer view of out-of-plane motions. The dimension of each TERS image is 8 Å × 8 Å.

In the 664 cm^{-1} mode (Fig. 3.5 a & d), the six hydrogen atoms are symmetrically vibrating vertical to the carbon ring. The corresponding TERS image preserves the symmetry, where the hot-spots are six lobes located outside the molecule in close vicinity to the H atoms. The less prominent hot-spots in between two neighboring H atoms are ascribed to the relatively weak carbon motions that are coupled with the hydrogen motions but in the opposite direction. In the 835 cm^{-1} mode (Fig. 3.5 b & e), the H atoms are vibrating in two opposite directions, with the 1- and 4-H motions being the strongest. Meanwhile, each C atom is vibrating in the same direction as its attached H atom. As a result, the TERS image shows an overall dipolar pattern. As for the 988 cm^{-1} mode, the simulated TERS image captures the "ring breathing" feature of the vibration, leading to a continuous hexagonal pattern (Fig. 3.5 c & f). The hot-spots in the TERS images of benzene (as well as water) appear to be next to the atom projections on the XY plane rather than on top of them. Given that the maximum point of the near field in the imaging plane is at the exact spot of the tip atom (Fig. A.3), when the tip scans through the area surrounding a certain chemical bond, the bond itself sees a strong field gradient. We also note that the asymmetries of these TERS images are related to the tip curvature difference. The simulations of benzene clearly demonstrate that TERS is capable of detecting and uniquely visualizing FG active vibrational modes.

3.2.5 Resonant TERS images

To extend the study from non-resonant to resonant TERS, we carry out simulations of TERS imaging of simple porphyrin molecules. The two model molecules are porphin and zinc-porphin (ZnP). TDDFT calculations in vacuum show that the $Q_y(0,0)$ transition of the two molecules are both at 2.29 eV. Additionally, the $Q_x(0,0)$ transition of ZnP is degenerate with its $Q_y(0,0)$ transition. To match this excitation energy for resonant Raman while maintaining a highly confined field in the junction, we use an Au₂₀₅₇ icosahedron as the tip. The incident light energy of 2.29 eV corresponds to halfway on the low-energy edge of the absorption band of the gold nanoparticle (see Fig. A.1 for absorption spectrum). The induced near field is confined within about 5.6 Å in diameter (FWHM), while the maximum is at $Z_{max} = 0.1$ Å (Fig. A.8). The field-confinement conditions resemble those for the non-resonant TERS images of the best resolution (Fig. 3.2), and thereby suffices to resolve atomic features in the simulated TERS images.



Figure 3.6. Selected normal modes and their respective TERS images of porphyrin molecules: (a) 683 cm^{-1} for porphin, (b) 692 cm^{-1} for ZnP, (c) 1539 cm^{-1} for porphin, (d) 1538 cm^{-1} for ZnP, and (e) 678 cm^{-1} for porphin. (a) and (b), and (c) and (d) are pairs of similar vibrational modes in porphin and ZnP. The scanned area of each TERS image is 16 Å × 16 Å. The schematics of molecular vibrations (left side of each sub-figure) are rotated slightly for a clearer view of out-of-plane motions.

The experimental TERS images of different porphyrin (H₂TBPP) vibrational modes appeared similar to each other, with four lobes of hot-spots located symmetrically at the four phenyl groups¹⁰. However, our simulated TERS images of the porphin are clearly distinct from each other (Fig. 3.6 a, c, e). Moreover, similar vibrational modes shared by porphin and ZnP lead to very different patterns in the TERS images. Specifically, the 683 cm^{-1} mode of porphin and 692 cm^{-1} mode of ZnP correspond to the same symmetric out-of-plane motions of the outer hydrogen atoms (Fig. 3.6 a & b). Similarly, the 1539 cm^{-1} mode of porphin and the 1538 cm^{-1} mode of ZnP have the same pattern of in-plane atomic motions (Fig. 3.6 c & d). For each pair of vibrational modes, we find that the outline shape of the patterns in the TERS images remains the same, but the distribution of hot-spots differs. The TERS images of porphin exhibit an overall dipolar pattern along the Y direction, while ZnP gives rise to a four-fold symmetric pattern. As stated above, the transition dipole moment (TDM) of porphin under the specific resonance condition is completely along Y axis $[Q_v(0,0)]$, while the TDM of zinc-porphin has almost equal contributions from both X and Y directions $[Q_x(0,0)+Q_y(0,0)]$. Therefore, we ascribe the symmetry in resonant TERS images to the direction of the TDM. If the two central hydrogens of porphin were aligned on the X axis, one would expect the TERS image to be rotated accordingly. In fact, the hydrogen tautomerization of porphyrin molecules has been reported to take place in low-temperature STM experiments with a small bias (< 1.5 V), and the activation barrier depends on the specific chemical species and the substrate 71,72 . Therefore, we believe that hydrogen tautomerization is the root of the four-fold symmetry obtained in the experimental TERS imaging of H₂TBPP in Ref. 10. As for the vibrational mode associated with strong central hydrogen motions (Fig. 3.6 e), the TERS image has hot-spots inside the porphin ring and around the carbon atoms whose motions are coupled to the hydrogen vibrations. The clear distinction between vibrational modes with atomic details presented in this work has not been observed in previous experiments or theoretical simulations^{10,15}. These simulations demonstrate the ability of TERS imaging to atomistically resolve different vibrational modes under resonant Raman conditions.

3.3 Conclusion

In this work we simulated single-molecule TERS imaging with atomic resolution using a hybrid atomistic electrodynamics-quantum mechanical approach. We showed that an atomically sharp tip in a quantum size junction confines the plasmon-induced near field within a few Ångstroms in diameter (FWHM), and this confinement is closely related to the incident light energy. Using water as a simple model system, we observed that the resolution of TERS images is extremely sensitive to the field confinement. The field confinement of ~ 5 Å in FWHMs is narrow enough to resolve each vibrational mode of a single molecule with atomistic details. We also demonstrated the importance of the near-field focal plane of TERS, which is defined as the field maximum height. The focal plane is required, in principle, to overlap with the molecule plane to obtain the best resolution. For non-planar molecular geometries, the effect of focal plane height becomes intricate. A small change in the focal plane may lead to a significantly different TERS image, and this dependence varies from mode to mode. Moreover, by visualizing the field-gradient active modes of benzene, we conclude that field-gradient effects are implicated in the TERS images. Finally, it is illustrated in the porphyrin simulations that TERS imaging is also able to atomistically resolve different vibrational modes under resonant Raman conditions, where hot-spot distributions in the images are determined by the electronic transition dipole moments. In addition to the theoretical insights, this work highlights the necessity of accurately describing the near field in the quantum size junction for TERS simulations. The atomistic electrodynamics approach adopted in this work provides a mechanism to generate the plasmon-induced field and to describe plasmon-molecule interactions, which can be applied for more general TERS studies in the future.

Methods

A locally modified version of the Amsterdam Density Functional (ADF) program package^{73–75} was used to carry out the calculations. The Becke-Perdew (BP86)^{76,77} exchange-correlation functional and the triple- ζ polarized (TZP) Slater-type basis set from the ADF library were used. The geometries of the sample molecules were optimized with a small frozen-core in the absence of the plasmonic nanostructure. The vibrational frequencies and normal modes were calculated analytically without scaling. Differential cross sections ($d\sigma/d\Omega$) of Raman scattering represent the TERS intensities in this work. To resemble experimental setup, only the *zz* component of the polarizability tensor was used to calculate the differential cross section, which is given by ^{63,78}

$$\frac{d\sigma}{d\Omega} = \frac{\pi^2}{\epsilon_0^2} (\tilde{\nu}_{in} - \tilde{\nu}_p)^4 \cdot \frac{h}{8\pi^2 c \tilde{\nu}_p} \cdot \frac{|\alpha'_{zz,p}|^2}{1 - \exp(-hc \tilde{\nu}_p/k_B T)}$$
(3.1)

where $\tilde{\nu}_{in}$ is the frequency of incident light, and $\tilde{\nu}_p$ is the frequency of the *p*th vibrational mode. $\alpha'_{zz,p}$ is the *zz* component of molecular polarizability derivative with respect to the *p*th vibrational mode. The molecular polarizabilities were calculated using the AOResponse module implemented in ADF with a excited state lifetime of $\Gamma = 0.1 \text{ eV}^{78-82}$. The polarizability derivatives are obtained by numerical three-point differentiation. This is done by calculating the polarizabilities for molecular geometries in a plus and a minus directions of a certain normal mode. High numerical qualities for TDDFT calculations are recommended to obtain smooth TERS images. TERS cross sections are obtained assuming T = 298 K.

All metal atoms were treated with the discrete interaction model (DIM).^{58,59} The icosahedron nanoparticles were constructed using FCC unit cells. The substrates were constructed as a large block of silver (or gold) unit cells and molecules were placed on the (111) surface. The frequent-dependent complex dielectric functions of silver and gold were obtained from Johnson and Christy⁸³. The nanoparticle was moved across an area large enough to cover the sample molecule (6 Å × 6 Å for water, 8 Å × 8 Å for benzene, and 16 Å × 16 Å for porphyrins). The step size for scanning was 0.2 Å. Smaller step sizes such as 0.1 Å were found to have no significant effect on the TERS images other than smoothness. For the purpose of reducing computational cost of the porphyrin simulations, only one quadrant of each simulated image was calculated and then expanded to full size in accordance with the rotational symmetry of the molecule. The
asymmetry in the TERS images due to the tip curvature variation as is for water and benzene was consequently removed.

All molecular geometries and vibrations were rendered using the Visual Molecular Dynamics (VDM) 1.9.3 software⁸⁴. Molecular vibrations were visualized by atomic displacement vectors obtained from normal mode coordinates.

Chapter 4 High-Resolution TERS Probes Sub-Molecular Density Changes

Chen, X.[†]; Liu, P.[†]; Hu, Z.; Jensen, L. High-Resolution Tip-Enhanced Raman Scattering Probes Sub-Molecular Density Changes. *Nat. Commun.* **2019**, *10*, 2567.*

Abstract

Tip-enhanced Raman spectroscopy (TERS) exhibits new selection rule and sub-nanometer spatial resolution, which is attributed to the plasmonic near-field confinement. Despite recent advances in simulations of TERS spectra under highly confined fields, a simply physical mechanism has remained elusive. In this work we show that single-molecule TERS images can be explained by local sub-molecular density changes induced by the confined near-field during the Raman process. The local sub-molecular density changes determine the spatial resolution in TERS and the gradient-based selection rule. Using this approach we find that the four-fold symmetry of *meso*-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (H₂TBPP) TERS images observed in experiments arises from the combination of degenerate normal modes localized in the functional side groups rather than the porphyrin ring as previously considered. As an illustration of the potential of the method, we demonstrate how this new theory can be applied to microscopic structure characterization.

[†]Contributed equally.

^{*}L.J. conceived the basic idea. X.C., P.L., and Z.H. implemented the method. X.C. and P.L. carried out the simulations. X.C., P.L., and L.J. analyzed the results and wrote the manuscript.

4.1 Introduction

Many theoretical modeling works were carried out to simulate TERS images by calculating the molecular responses to narrowly distributed near fields^{10,15,17,18}. It was reported that atomic resolution can be achieved when the near-field confinement reaches a few Ångstroms in diameter, and each normal mode can be uniquely resolved^{16,85,86}. TERS images in both simulations and experiments suggested strong correlations between the hotspots distributions and the vibrating atoms. However, the molecular response is a non-local property and thus not easily localized on individual atoms. Therefore, despite the success in simulating TERS images, existing theories do not provide clear and consistent explanations on how the vibrating atoms locally affect the TERS intensities.

In this chapter, we address the question of what local property of a molecule is probed by the TERS tip. We demonstrate that sub-molecular density changes are probed by the confined near field in TERS and lead to the varying Raman intensities over normal modes and space. The probed density changes, which we define as Raman polarizability density, is a truly local property and is strongly correlated with the given vibrational mode. The density distribution is extracted from a small volume defined by the highly confined near field, leading to the spatially variant TERS intensities. This approach offers a clear explanation for the mode specificity and spatial variation of TERS signals. We show that the proposed mechanism accurately reproduces atomistic simulations and experimental results, and more importantly provides intuitive interpretations of TERS images. In the end we demonstrate how TERS imaging combined with the new theory can be applied to microscopic characterization and its potential to compete with scanning tunneling microscopy (STM).

4.2 Results and Discussion

4.2.1 Locally Integrated Raman Polarizability Density

The method was adopted in this work, namely locally integrated Raman polarizability density (LIRPD). All the molecular properties and the near field are dependent on the frequency of the external field, and are in tensor format. The explicit notations of frequency and the tensor subscripts are omitted for simplicity. A detailed justification of the method is provided in Supplementary Methods.

The concept of distributed polarizability density was first introduced by Maaskant and Oosterhoff in the theory of optical rotation⁸⁷, and was later generalized by Hunt^{88,89}. Briefly, the molecular polarizability α can be expressed as a spatial integration of a polarizability density $\rho^{(\alpha)}$,

$$\alpha = -\int \rho^{(\alpha)}(\mathbf{r}) \cdot d\mathbf{r} = -\int \hat{\mu}^{\text{eff}} \cdot \delta\rho(\mathbf{r}) \cdot d\mathbf{r} , \qquad (4.1)$$

where $\delta \rho(\mathbf{r})$ is the linear change in the electron density of a molecule due to an external electric field, $\hat{\mu}^{\text{eff}}$ is the effective dipole operator, and \mathbf{r} is a vector in space. The polarizability density,

 $\rho^{(\alpha)}(\mathbf{r})$, is a local property as it's derived from the electron density distribution, which is different from the definition in Ref. 88 and 89. However, the concept of "polarizability density" is similar as its spatial integral gives rise to the molecular polarizability.

In the linear-response time-dependent density functional theory, the induced electron density of the molecule due to an electric field perturbation is expressed as

$$\delta\rho(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') \hat{v}^{\text{pert}}(\mathbf{r}') d\mathbf{r}' , \qquad (4.2)$$

where $\chi(\mathbf{r}, \mathbf{r}')$ is the density-density linear response function ⁹⁰ and $\hat{v}^{\text{pert}}(\mathbf{r}')$ is the perturbation operator. Because the confined near field dominates the field distribution in the TERS junction, we can represent both the perturbation and effective dipole operators as the product of the near field distribution $\mathbf{F}(\mathbf{r} - \mathbf{R})$ centered at \mathbf{R} and a free-molecule operator in the unit external field,

$$\hat{\mu}^{\text{eff}}(\mathbf{r}) = -\mathbf{F}(\mathbf{r} - \mathbf{R}) \cdot \hat{\mu} ,$$

$$\hat{\nu}^{\text{pert}}(\mathbf{r}' - \mathbf{R}) = -\mathbf{F}(\mathbf{r}' - \mathbf{R}) \cdot \hat{\mu}(\mathbf{r}') .$$
(4.3)

Here $\hat{\mu}$ is the dipole operator, and the perturbation operator entails the plasmon-induced near field.

Combining the first three equations, we obtain the molecular polarizability that is now dependent on the tip position,

$$\begin{aligned} \alpha(\mathbf{R}) &= \int \hat{\mu}^{\text{eff}}(\mathbf{r}) \Big[\int \chi(\mathbf{r}, \mathbf{r}') \hat{v}^{\text{pert}}(\mathbf{r}') d\mathbf{r}' \Big] d\mathbf{r} \\ &= \int \mathbf{F}(\mathbf{r} - \mathbf{R}) \hat{\mu} \Big[\int \chi(\mathbf{r}, \mathbf{r}', \omega) \hat{\mu}(\mathbf{r}') \mathbf{F}(\mathbf{r}' - \mathbf{R}) d\mathbf{r}' \Big] d\mathbf{r} \end{aligned}$$
(4.4)

Because the near field is highly confined in high-resolution TERS, the induced density away from the near-field center diminishes quickly. Thus, we make a local approximation to the induced density perturbed by the near field, and take the near-field distribution out of the inner integral. Then we obtain the molecular polarizability in the form of locally integrated polarizability density,

$$\begin{aligned} \alpha(\mathbf{R}) &= \int \mathbf{F}(\mathbf{r} - \mathbf{R})\hat{\mu} \Big[\int \chi(\mathbf{r}, \mathbf{r}', \omega)\hat{\mu}(\mathbf{r}')\mathbf{F}(\mathbf{r}' - \mathbf{R})d\mathbf{r}' \Big] d\mathbf{r} \\ &\approx \int \mathbf{F}(\mathbf{r} - \mathbf{R})\hat{\mu} \Big[\int \chi^{\text{free}}(\mathbf{r}, \mathbf{r}', \omega)\hat{\mu}(\mathbf{r}')d\mathbf{r}' \Big] \mathbf{F}(\mathbf{r} - \mathbf{R})d\mathbf{r} \\ &= \int \mathbf{F}(\mathbf{r} - \mathbf{R}) \cdot \hat{\mu} \,\delta\rho^{\text{free}}(\mathbf{r}) \cdot \mathbf{F}(\mathbf{r} - \mathbf{R}) \cdot d\mathbf{r} \\ &= \int \mathbf{F}(\mathbf{r} - \mathbf{R}) \cdot \rho^{(\alpha)}(\mathbf{r}) \cdot \mathbf{F}(\mathbf{r} - \mathbf{R}) \cdot d\mathbf{r} \end{aligned}$$
(4.5)

Here $\rho^{(\alpha)}(\mathbf{r})$ is the free-molecule polarizability density as given in Equation 4.1. The validity of this local approximation will be verify by explicit comparison with the fully non-local response as shown below.

The Raman polarizability density, denoted as $\delta \rho^{(\alpha)} = \partial \rho^{(\alpha)} / \partial Q_k$, is the change of molecular polarizability density due to the vibrational mode k. It is calculated by the finite differentiation

of polarizability densities with respect to small atomic displacements in a given vibrational mode. In a TERS junction, the effective Raman polarizability density is then represented as the free-molecule Raman polarizability density distributed over the near-field distribution $(\mathbf{F}(\mathbf{r} - \mathbf{R}))$,

$$\delta \rho_{\rm loc}^{(\alpha)}(\mathbf{r}, \mathbf{R}) = \mathbf{F}(\mathbf{r} - \mathbf{R}) \cdot \delta \rho^{(\alpha)}(\mathbf{r}) \cdot \mathbf{F}(\mathbf{r} - \mathbf{R}) .$$
(4.6)

The TERS intensity of a certain vibrational mode is proportional to the square of integrated effective Raman scattering polarizability density, formulated as

$$I(Q_k) \propto \left[\int \delta \rho_{\rm loc}^{(\alpha)}(\mathbf{r}) \cdot d\mathbf{r} \right]^2 \,. \tag{4.7}$$

Due to the confinement of the near field, the integration over all space can be effectively approximated by local integration within a finite volume. This integration volume is determined by the full width at half maximum (FWHM) of the near-field distribution.

Here we have briefly summarized the method of LIRPD without explicitly writing down the element form of all matrices since only the zz component of the polarizability tensor is considered in calculating the Raman intensities (the long axis of the TERS junction aligns with the z direction). A detailed description of LIRPD in full tensor representation is provided in Supplementary Methods. The local approximation made in Equation 4.3 can be improved by including the densities of higher-order polarizability tensors, for example, the quadrupole-dipole polarizability (\mathcal{A} tensor)⁹¹ density. It is equivalent of applying multipole expansion to the effective dipole operator^{92,93}, which introduces a semi-local correction to the local approximation. Including \mathcal{A} -tensor densities slightly improves the accuracy when an atomically confined field is applied to a small molecule (benzene). But we find for larger systems, since the required near field is less confined, the contribution from \mathcal{A} -tensor densities becomes trivial. Therefore, all presented TERS images are calculated by considering only the dipole-dipole polarizability density. The TERS images with additional \mathcal{A} -tensor density contributions are provided for comparison in Fig. B.1.

Here we take a benzene molecule as an example to demonstrate how the LIRPD approach works for TERS imaging. The Raman polarizability density distribution is plotted on the right panel of Fig. 4.1. The positive value of density is colored blue and the negative value is in yellow. The near field is confined in a red sphere, which we call the effective integration volume. In this work the near-field distribution is expressed as a 3D Lorentzian function. Compared with the widely used Gaussian field model, Lorentzian distribution has slightly more pronounced tails, which better captures the background near field on the substrate away from the tip as is obtained from our atomistic electrodynamics calculations¹⁴. The diameter of the integration volume is the full width at half maximum (FWHM) of the field distribution. The Raman polarizability densities distributed within the red sphere are locally enhanced by the near field leading to the effective scattering polarizability densities, which are then integrated over all space to obtain Raman intensity that corresponds to the specific tip position recorded in the TERS image (Fig. 4.1 insert in the right panel). The imaging pattern is not sensitive to the field shape, which is shown in Fig. B.3. Without the confined near field, the integration of the Raman polarizability density



Figure 4.1. Schematic representation of locally integrated Raman polarizability density. The Raman polarizability density of the normal mode at 664 cm^{-1} of a benzene molecule is illustrated by isosurface (right panel). The density distributions in blue and in yellow hold the positive and negative signs, respectively. The red sphere denotes the confined near-field distribution at its FWHMs. The Raman polarizability densities in the red sphere are drastically enhanced and spatially integrated giving rise to a Raman intensity (symmetric bending) at 664 cm^{-1} (in insert). TERS image is generated from locally integrating Raman polarizability density by tip scanning over a benzene molecule (left panel).

over all space leads to the far-field Raman signals of the molecule. The mechanism of LIRPD explains the gradient-based selection rule in plasmon-enhanced Raman spectroscopy as well as the spatial localization of the TERS intensity.

4.2.2 TERS Imaging and Selection Rule

TERS images are obtained by scanning the tip over a sample molecule and simultaneously collecting the Raman signals. Atomically resolved TERS images were previously simulated, and the confinement of near field down to 5 Å in diameter was found necessary to achieve the ultrahigh resolution⁸⁵. However, the local properties probed by the highly confined near field, which is key to establish the dependence of high-resolution TERS images on molecular normal modes, was still not clear. For example, the simulated TERS images are drastically different between the symmetric and anti-symmetric bending modes of benzene, even though it is the same atoms that are vibrating in these two normal modes. Using the LIRPD method, we illustrate where such spatial variation originates and how it's affected by the atomic vibrations. The consistency of this model is evidenced by reproducing the TERS images calculated by the hybrid atomistic electrodynamics/quantum mechanics method (DIM/QM) in ref. 85 which include the fully non-local response. Here we use the same symmetric and anti-symmetric bending modes of benzene as examples.

The normal modes of the symmetric (Fig. 4.2 a) and anti-symmetric bending vibrations (Fig. 4.2 e) and the related Raman polarizability density distributions (Fig. 4.2 b and f) were calculated with the molecule-substrate mutual polarization taken into account. The spatial distributions of the Raman polarizability densities and the molecular vibrations are highly correlated. In the 664 cm^{-1} mode, all the hydrogen atoms symmetrically bend out of the molecular plane. The corresponding density distribution preserves the symmetry. The densities are largely localized



Figure 4.2. Normal modes, Raman polarizability densities, and TERS images of benzene. Normal modes (a-d) at 664 cm⁻¹ and (e-h) at 835 cm⁻¹. (a,e) Schematic representation of molecular vibrations. (b,f) Raman polarizability density (left column) and locally enhanced Raman polarizability density (right column) by a near field at the marked position (red asterisk) from the top view (top) and side view (bottom). The density is normalized and the absolute isovalue is set to 0.2 with the positive sign in blue and the negative sign in yellow. Simulated TERS images obtained by LIRPD in c and g, and the hybrid atomistic DIM/QM in d and h, respectively.

on the hydrogen atoms and benzene ring (top of Fig. 4.2 b). The distribution is symmetric, but the signs are opposite with respect to the molecular plane (bottom of Fig. 4.2 b). The large atomic displacement leads to the prominent density distributions on the hydrogen atoms. The densities distributed over the benzene ring come from the coupled motions of the carbon atoms. The 835 cm⁻¹ mode is featured by anti-symmetric out-of-plane vibrations (Fig. 4.2 e). The corresponding density distribution inherits the same anti-symmetry by having opposite signs in xy plane either above or below the molecular plane. The in-plane opposite signs stem from the para-hydrogen atoms coupled with the attached carbon atoms vibrating in opposite directions. Across the molecular plane, the densities also have opposite signs around the same atoms.

The near field is here represented by a 3D Lorentzian distribution with FWHMs of 1.3 Å centered at 1.0 Å above the benzene plane in our simulations. By using Equation 4.6, the Raman polarizability densities are enhanced within the Lorentzian peak, while the densities outside the peak are smeared out. In such way the Raman density distribution is extracted from a small volume defined by the confined near field. In other words, the Raman densities are locally selected by the confined near field. The selected densities are then integrated over space to obtain a Raman intensity. For the mode at 664 cm^{-1} , the densities at the near-field position rather than elsewhere are greatly boosted. The integrated density (local polarizability density) is largely due to the densities with the same sign being accumulated, resulting in a strong TERS signal. In contrast, the integrated density is close to zero in the integration volume above the center of benzene, because the local densities are distributed with opposite signs and thus are integrated to zero. We accordingly see a quite low intensity in the center of the TERS image at 835 cm⁻¹.

Using the LIRPD method to calculate Raman intensities while scanning the tip over a molecule, we are able to reproduce the high-resolution TERS images predicted by the DIM/QM method (Fig. 4.2 c, d, g, and h). In general, the TERS intensity is predominantly determined by two factors: the Raman polarizability density distribution and the local integration volume (near-field distribution) in terms of size and position. The Raman polarizability density distribution is dominated by the large atomic displacements in a normal mode, and governs the pattern of its TERS image. A narrow near-field distribution leads to the atomic resolution in TERS images. For instance, the image resolution is sensitive to field FWHMs of the x and y components rather than the z component. Moreover, the height from tip to molecular plane, which is similarly defined as the near-field focal plane in Ref. 85, plays a vital role in TERS imaging. A small change of tip height leads to a significantly different TERS image. These findings suggest that distributing the near fields within atomic dimensions over an appropriate imaging plane is the key to the atomic resolution in TERS images. (see Fig. B.4)

It is noted that the integration of the Raman polarizability density without the confined near field leads to the typical far-field property of the molecule. For the selected two modes of benzene, the Raman polarizability density distributions are symmetric with opposite signs so that integration over all space is zero. This means the Raman signals are silent for the specific modes, which is consistent with the traditional selection rules. However, the confined near field breaks the symmetry, and thus leads to non-zero values after the integration. It provides the explanation for the inactive Raman modes being evoked in plasmon-enhanced Raman spectra. This symmetry breaking of Raman polarizability density distribution aligns with the field-gradient effects typically invoked to explain the high spacial resolution^{14,70,85}. In TERS images, the hotspots indicate the tip positions locally break the symmetry.

4.2.3 Complex Raman Polarizability Density in Resonant TERS

The LIRPD model is naturally transferable to resonant TERS spectra. Contributions from both the electronic and the vibrational transitions are coherently included in the Raman polarizability, which now has a non-trivial imaginary part. We take free-base porphyrin as an example to explore the correlation between Raman polarizability densities and resonant TERS images. Two representative modes of porphyrin are selected: one out-of-plane vibrational mode at 678 cm⁻¹ and one in-plane mode at 1539 cm⁻¹. The 678 cm⁻¹ mode is characterized by the opposite out-of-plane bending of two hydrogen atoms attached to the para-nitrogens (Fig. 4.3 a). The applied excitation energy is at 2.29 eV corresponding to the $Q_u(0,0)$ transition of porphyrin.

As shown in Fig. 4.3 b and c, the real part of the density distribution reflects the dominant atomic displacement, and is symmetrically distributed with respect to the molecular plane with opposite signs. In the 678 cm⁻¹ mode, the atoms vibrate perpendicularly to the molecular plane. Similar to the benzene out-of-plane modes, the real Raman polarizability density here is distributed closely around the vibrating atoms, and has opposite signs above and below the molecular plane. In contrast, the imaginary density distribution is asymmetric with respect to the molecular plane, where most of the densities are distributed underneath the porphyrin



Figure 4.3. Normal modes, Raman polarizability densities, and TERS images of porphyrin. (a-c) Normal modes at 678 cm⁻¹ and (d-f) at 1539 cm⁻¹. (a,d) Schematic representation of molecular vibrations. (b,e) The Raman polarizability densities in real (left) and imaginary (right) parts of porphyrin on a Au(111) surface from the top view. (c, f) The Raman polarizability densities are distributed throughout the scanning volume with the thickness of 2 Å above porphyrin plane from the side view. The densities are normalized and the absolute isovalue is set to 0.2 with the positive sign in blue and the negative sign in yellow. Simulated TERS images of modes at 678 cm⁻¹ (g, h) and 1539 cm⁻¹ (i and j) obtained by LIRPD (g, i) and DIM/QM approaches (h and j), respectively.

molecule. However, the imaginary Raman density distribution preserves the same symmetry as in the vibrational mode underneath the molecule. Similar trend is also observed in the 1539 cm⁻¹ mode (Fig. 4.3 e and f). As 1539 cm⁻¹ mode is an in-plane mode, the real Raman polarizability densities are more broadly distributed in-plane. The direction from positive to negative values follows the overall trend of the atomic displacement.

By locally integrating the complex Raman polarizability densities enhanced by the near field, mode-specific resonant TERS images with atomic resolution are obtained (Fig. 4.3 g-j). The near fields with FWHMs of 2 Å are placed 1.5 Å above the molecular plane. The effective densities distributed in the scanning volume are illustrated in Fig. 4.3 c and f and the locally enhanced Raman polarizability densities by the given tips are given in Fig. B.2. We again see the strong resonant Raman intensities at the dominant atomic displacements, which is consistent with the atomistic simulation results (Fig. 4.3 g-j). The patterns in TERS images are mostly similar to the real Raman polarizability density distributions, which is attributed to the facts that the imaginary part of the density is overall much weaker than the real part and that the imaginary Raman densities are largely distributed underneath the molecule. The weak imaginary zz polarizability is expected, because the $Q_y(0,0)$ band has a very weak oscillator strength due to the transition dipole moment on the xy plane. The mutual polarization dominates the interaction between the molecule and the substrate, which explains the imaginary Raman polarizability densities underneath the molecule. The overall patterns in these Raman polarizability density distributions and the corresponding TERS images align with the electronic transition dipole moment, which is along y axis in this specific example. We note that the TERS image of the 1539 cm⁻¹ mode is not intuitively correlated to the real density distribution shown in Fig. 4.3 e. Actually, the maximal density corresponding to the brighter hotspots in the TERS image is 4-fold larger than the densities around the nitrogen atoms. This density value difference explains the contrast in the TERS image.

Self-consistent solutions^{15,16,85} of molecular property perturbed by a confined near field are considered the most accurate at the TDDFT level of theory, as they calculate the fully non-local response of the molecule to the near field (Equation 4.4). DIM/QM is regarded as benchmark in this work because it provides a consistent treatment of both the near-field distribution and the molecular properties. The local approximation made in Equation 4.5 qualitatively reproduces the results from DIM/QM, which is an evidence of the validity of LIRPD approach. The agreement between the LIRPD and DIM/QM results is qualitatively good. Because while the overall symmetry patterns of the benzene TERS images are reserved in LIRPD, the two key features for benzene are also captured: hotspots are slightly off the atoms, and Raman inactive modes are activated by strong field gradient (Fig. B.5). Because of this local treatment of the electronic density, the FWHM of the Lorentzian field has to be smaller than DIM/QM. The agreement between the LIRPD and DIM/QM results can be improved by considering the multipole expansion at the density level. In Fig. B.1, we have shown that for small molecules like benzene and porphyrin, the \mathcal{A} -tensor densities drives the hotspots slightly further away from the vibrating atoms, and the effective integration volume becomes closer to that in the DIM/QM simulations. However, the contribution from \mathcal{A} -tensor decreases when the near field confinement is beyond the atomic scale, which is the case for the following analysis regarding interpreting experimental results. Moreover, because the Raman polarizability density in LIRPD is independent on the tip position, the LIRPD calculation is order of magnitude (the total number of grids) faster than DIM/QM, which is advantageous for analyzing large molecules seen in experiments.

4.2.4 Interpreting Experimental TERS Images

In the pioneering work of TERS imaging¹⁰, a single molecule of *meso*-tetrakis(3,5-di-*tert*butylphenyl)porphyrin (H₂TBPP) was visualized with sub-nanometer resolution via precise tuning of the plasmon resonance coupled with molecular vibrations. The four-fold symmetry in both experimental and simulated TERS images are invariant across different normal modes, which was attributed to electronic resonance and tautomerization^{10,15}. Using the energetically favored concave configuration of H₂TBPP^{15,46}, we find that the strong interaction between molecule and the silver substrate leads to more than 100 nm red shift of the Q and B bands in the absorption spectra in Fig. B.4. Hence it is questionable to assume the free H₂TBPP excitation in resonant TERS simulations. In our simulations we took the polarization interactions between the molecule and the metal substrate into account, and found that the B_x(0,0) and B_y(0,0) transitions of H₂TBPP is excited at around 560 nm, while Q_y(0,0) band is excited at 760 nm (Table B.1). So the 532 nm laser used in the experiment is more likely to excite the B-band transition of H₂TBPP. Therefore, we revisit the resonant TERS imaging of H₂TBPP, and interpret the invariant patterns across different normal modes based on the LIRPD mechanism.



Figure 4.4. The resonant TERS images of H_2 TBPP molecule absorbed on a Ag(111) surface. The excitation energy corresponds to the B_y transition. (a, b) TERS images of individual degenerate modes of the bands centered around 810 cm⁻¹ and 1185 cm⁻¹. The schematic representations of molecular vibrations lay on the individual TERS images and the corresponding frequencies (in cm⁻¹) are given in the top left corners. (c, d) The experimental TERS images (left panel) and simulated TERS images by integrating band width of 20 cm⁻¹ (right panel).

In order to well describe the near-field distributions in plasmonic junction, the correlation between gap size and near-field confinement was investigated. The details are provided in Table B.2. A reasonable approximation to the plasmonic near field is that FWHMs are 12 Å for the x and y components and 6.0 Å for the z component. The narrower distribution along z-axis is due to the fact that the near field is squeezed by the short-range dipole-dipole interaction in the nanocavity^{14,94}. The center of this field distribution is placed 2.7 Å above the molecule. The TERS spectrum obtained by LIRPD with the field center on top of a lobe agrees well with experimental spectrum (Fig. B.8). Based on the simulated TERS spectrum, the TERS mapping at the critical spectral peaks were elaborately explored. We find that there exists multiple degenerate modes within the integration window in Ref. 10, and each of these modes has a distinct TERS image. The modes with the largest TERS intensities are featured by prominent butyl vibrations. For example, the region around 810 cm^{-1} is associated with the modes at 807.8, 808.4, 810.0, and 811.5 $\rm cm^{-1}$, which are characterized by the vibrations of different butyl groups (Fig. 4.4 a). The simulated TERS images with $B_{\mu}(0,0)$ excitation are shown in Fig. 4.4. Combining the TERS images of the dominant modes around 810 cm^{-1} within a 20 cm⁻¹ band width, we find the total TERS image matches the experimental mapping (Fig. 4.4 c), also exhibiting the four-lobe symmetric pattern covering the butyl groups. Since the integration volume is above the entire molecule, the pyrrole vibrations are not captured in the TERS image (see Fig. B.7). The combined TERS image at around 1185 cm^{-1} is similar to 810 cm⁻¹. The simulated four-lobe pattern matches the experimental mapping (Fig. 4.4 d), and the multiple modes featured by butyl vibrations dominantly contribute to the TERS image (Fig. 4.4 b). The TERS images at frequencies at 900, 990, and 1520 $\rm cm^{-1}$ are simulated as well (Supplementary Information Fig. B.9), and all are consistent with the experimental results. Particularly, the contrast and central dark area becomes smaller towards the high wavenumbers in our simulations.

The four-fold symmetry in H_2 TBPP TERS images was previously attributed to hydrogen tautomerization^{15,85}. However, in this work we clearly see that the four-fold symmetry is obtained by combining the TERS images of degenerate modes, without tautomer contributions. The degenerate vibrations comes from the symmetry of the molecular structure. In the experiment reported in Ref. 10, it is very likely that all the four degenerate modes are included in the integration window, which leads to the same four-fold symmetry across different frequency regions. By enforcing tautomerization, the TERS images remain the same except being slightly more smooth and symmetric (Fig. B.10). Thus, we believe that TERS images of H_2 TBPP are not sensitive to hydrogen tautomerization. We will further discuss the tautomerization effect on TERS images using a porphycene molecule whose tautomers have been clearly identified in STM experiments.

Moreover, we find the TERS images calculated at $Q_y(0,0)$ and $B_y(0,0)$ transitions are almost identical, as shown in Fig. B.11. This suggests that the Raman scattering properties of the side groups, which dominates the TERS images, are insensitive to these excited states. This is expected because both of these electronic excitations are localized in the base porphyrin ring. The TERS tip won't be able to probe the base ring unless is forced down to the bottom of the molecule.

It is generally difficult to differentiate H_2 TBPP normal modes based on TERS images, as was seen in experiment. Our simulation results suggest that the prevailing four-fold symmetry in H_2 TBPP TERS images is largely due to the combination of multiple degenerate modes with butyl vibrations, rather than tautomerization or electronic resonance effects. One would expect the TERS images of H_2 TBPP to be more differentiable if higher spatial resolution is achieved in experiments, and if more precise Raman measurements are performed so that the integration window becomes narrower to eliminate multiple mode contributions. Nevertheless, the LIRPD method offers a consistent and flexible approach to the interpretation of experimental measurements on large molecules.

4.2.5 TERS Imaging for Microscopic Structure Characterization

We further explore the effect of hydrogen tautomerization on TERS images, and at the same time demonstrate how TERS imaging can be applied as a structural characterization tool. We take porphycene as an example, of which the tautomers have been identified in experiment with the help of low-temperature STM⁹⁵. The optimized geometries of three porphycene tautomers, one *trans* and two *cis* configurations (denoted as *cis* and *cis'*), are shown in Fig. B.12. The *trans* and *cis* porphycene are planar, while the hydrogen atoms in the cavity of *cis'* porphycene are out of the macrocycle plane due to a strong steric repulsion. In the TERS simulation using the LIRPD methods, we examine the normal mode around 1250 cm⁻¹, as it was previously reported to be a prominent peak in resonant SERS⁹⁶. The near field is represented in 3D Lorentzian distribution with the FWHM of 5 Å for all three Cartesian components and is centered at 2 Å above the molecule.

The resonant TERS images generated by the LIRPD method at the excitation energy of 2.21 eV are shown in Fig. 4.5. The simulations suggest that two modes contribute to the total TERS image at 1250 cm⁻¹ with the band width of 20 cm⁻¹. The dominant mode for each tautomer is characterized by central hydrogen atoms vibrations coupled with pyrrole moieties (Figures 4.5 a and b). The Raman polarizability density distributions of the individual modes within the scanning volumes are illustrated in Fig. B.13. We again see the resonant TERS image is largely determined by the real densities. The *para*-hydrogen atoms vibrating oppositely in the cavity lead to the large density distributions on the *para*-pyrrole moieties in the *trans* configuration. In the *cis* configuration the prominent density distributions are related to the *ortho*-hydrogen vibrations. The modes with the large displacement of the central hydrogen atoms provide the major contributions to the total TERS images. Generally, the overall hotspots symmetry follows the configuration of the two central hydrogens. There are four hotspots with one brighter pair on *para*-pyrrole moieties for the *trans* configuration. For the *cis* configuration, there are two connected hotspots on the adjacent pyrrole and separate lobes on the other two pyrrole moieties. The TERS image of the *cis'* configuration was simulated as well (Fig. B.14).

The simulations indicate that different tautomers can be identified and differentiated through distinct TERS images, and the patterns are either *trans* or *cis* following the configuration of the central hydrogens. TERS imaging carries both structural and chemical information of mode vibrations, and TERS images can be even more distinguishable among tautomers. Thus, by combining the LIRPD interpretation with high-resolution measurements, we envision TERS to be complementary to STM for microscopic characterization.



Figure 4.5. Normal modes and TERS images of porphycene tautomers. Normal modes (a) at 1256 cm⁻¹ and (b) at 1252 cm⁻¹ make the dominant contributions to the TERS images at \sim 1250 cm⁻¹ of (c) trans and (d) cis tautomers adsorbed on a Cu(110) surface, respectively.

4.3 Conclusion

In this work we illustrated that high-resolution TERS probes the molecule's local polarizability density changes. The Raman polarizability densities are locally enhanced by the confined near field and then integrated over space giving rise to the molecule's near-field response. The density distribution is unique for specific normal mode, and leads to the also unique TERS image. The local symmetry breaking in the integrated density distribution is the root of the spatial variation of TERS intensities, and explains the gradient-based selection rules in TERS. The locally integrated Raman polarizability density provides theoretical insights into experimental TERS images and origin of the hotspots from a point of view of the molecule's locally probed property. The LIRPD mechanism is a simple and intuitive approach to the interpretation of high-resolution TERS imaging can be applied to resolve subtle changes in molecular structure with atomic precision.

The key to achieve the atomistic resolution is to confine the near field down to a few Ångstroms in experiment. Previous simulations indicate that such confinement requires the tip to be atomically sharp^{17,55,56,94,97}. To maintain a stable sharp tip during the scanning, cryogenic and high-vacuum environment is preferred in experiments^{14,98}. Moreover, this work and previous simulations⁸⁵ suggest that the TERS images are also very sensitive to the height of the focal plane relative to the molecule and the field confinement in the vertical axis, and thus flat molecules are generally favored. All these conditions to obtain high-resolution TERS images are difficult to fulfill. However, we still expect TERS imaging has the potential to rival with state-of-the-art scanning tunneling microscopy for microscopic characterization, and thus holds great promise for monitoring chemical structure and transformation with sub-molecular resolution.

Methods

DIM/QM calculations. A locally modified version of the Amsterdam Density Functional (ADF) program package^{73,74,99} was employed to perform all the simulations. The geometry optimizations, frequency, and linear-response calculations were carried out using the Becke-Perdew (BP86) exchange-correlation functional with the triple- ζ polarized (TZP) Slater-type basis, except for the H₂TBPP molecule, which was calculated at the BP86/DZP theoretical level in order to reduce the computational cost. The geometries of benzene and porphyrin molecules were optimized with small frozen core in the absence of metal substrate to be consistent with conditions of the previous work⁸⁵. The adsorbed structures of H₂TBPP and the porphycene molecules are strongly influenced by the molecule-substrate interactions. The metal substrate was included in the geometry optimizations accordingly.

Polarizability density calculations. The excited state lifetime is set to 0.1 eV⁸⁰ and the metal substrates which are large enough to support a sample molecule were treated with the discrete interaction model (DIM)⁶⁰. The frequency-dependent complex dielectric functions of metal surface were obtained from Johnson and Christy⁸³. The cubic grids used for representing the density are determined by the sample molecule structure and orientation on the surface. The boundary of the box is 4 Å away from a H₂TBPP molecule and 3 Å for the other molecules. The step size is 0.4 Å for generating grids parallel to the metal surface and 0.2 Å for H₂TBPP and 0.1 Å for others in the vertical direction. The Raman polarizability densities are obtained by the three-point numerical differentiation method. The Raman polarizability densities are locally enhanced by near fields and are locally integrated. From the locally integrated Raman polarizability density, differential cross section ($d\sigma/d\Omega$) of Raman scattering is written as

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\omega} = \frac{\pi^2}{\epsilon_0^2} (\tilde{\nu}_{\rm in} - \tilde{\nu}_k)^4 \frac{h}{8\pi^2 c \tilde{\nu}_k} \frac{|\alpha'|^2}{1 - \exp(-hc \tilde{\nu}_k/k_{\rm B}T)} \quad , \tag{4.8}$$

where $\tilde{\nu}_{in}$ is the incident frequency and $\tilde{\nu}_k$ is the frequency of k^{th} normal mode. α'_k is the locally integrated Raman polarizability density related to polarizability density of k^{th} normal mode. Here we considered only zz component contributes to TERS cross sections, and the temperature was set to 298 K.

Chapter 5 Resolving Molecular Structures with High-Resolution TERS Images

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Abstract

Vibrational modes of a single molecule can be visualized uniquely by tip-enhanced Raman spectroscopy with atomic resolution. However, the exact vibrations associated with these Raman scattering images are still in debate due to the lack of theoretical interpretation. In this work, we systematically study the Raman scattering images of a single Co(II)-tetraphenylporphyrin molecule. The stable structure whose Raman scattering images consistently match experimental results is discovered. Furthermore, we elucidate the effects of near-field localizations and field gradient on the resolution in Raman scattering images. The approach of locally integrated Raman polarizability density employed in this work provides an intuitive pictorial explanation of the origin of the experimental Raman scattering images.

[†]Contributed equally.

^{*}L.J. conceived the basic idea. P.L.and X.C. carried out the simulations. P.L., X.C., and L.J. analyzed the results. P.L. and L.J wrote the manuscript.

5.1 Introduction

Mapping the Raman scattering intensity variations with the corresponding tip positions for each individual mode, one can visualize the vibrational mode by its brightspot pattern in the TERS image. 10,43,45,100,101 . Atomic-resolution TERS images of single molecules were predicted by theoretical models 16,85,102 , where molecular polarizabilities in the presence of Å-scale near field were calculated within the framework of time-dependent density functional theory (TDDFT). The predicted TERS images of small molecules like benzene are mode-specific, and the brightspots are often off the vibrating atoms. 85,102 Recently, TERS images with these characteristics were realized in experiments with a single Co(II)-tetraphenylporphyrin (CoTPP) molecule anchored on a Cu(100) substrate. 13 . The atomic resolution in the CoTPP Raman scattering images sets the stage for a different way of understanding molecular vibrations and unveils the potential of TERS to be used for microscopic structural characterization.

Interpretation of the mode-specific TERS images relies on theoretical simulations to associate molecular vibrations with the brightspot patterns, which requires the understanding of the origin of the spatially varying brightspots.¹⁰³ In Ref. 13, the vibrational modes of the CoTPP molecule are calculated from its gas-phase structure, and the TERS brightspots are obtained using the free-molecule atomic polarizabilities scaled by a narrow distribution of near-field intensities. The phenyl rings are artificially flattened so that the simulated TERS images conform with the planar geometry of the molecule indicated by the experimental images. Although the overall symmetry patterns and the assigned vibrational modes of the simulated images seem plausible, the interpretation of the TERS images requires further investigation, mainly because of two reasons. Firstly, the artificially flattened structure is not stable due to the strong steric hindrance between the adjacent phenyl- and pyrrole-hydrogens. Secondly, the use of atomic polarizabilities localizes the TERS brightspots onto atoms, which contradicts the feature of off-atom brightspots that are commonly seen in the experiment images.

This work aims to address the above two concerns in the simulations, and attempts to shed light on the mechanisms underlying the spatial resolution of TERS. Specifically, a stable planar structure of CoTPP that reproduces all experimental TERS images is identified. We will illustrate that similar molecular structures can be differentiated by contrasting their TERS images and the associated vibrational modes. The recently developed approach, termed "locally integrated Raman polarizability density" (LIRPD)¹⁰², is employed in this work. It effectively reproduces the spatial variation of TERS intensities and provides an intuitive explanation. Meanwhile, its computational efficiency allows for a systematic search for TERS images of various structures of a large molecule like CoTPP. Furthermore, we will elucidate the importance of near-field localization and field-gradient effects to the resolution of TERS imaging.

5.2 Results and Discussion

5.2.1 Conformers of CoTPP and their TERS images

Conformers of CoTPP on Cu(100) surface. The gas-phase CoTPP molecule has a phenyl-pyrrole torsion angle $\phi = 80.2^{\circ}$ (Fig. 5.1a). Geometries of CoTPP adsorbed on a copper substrate are optimized using the hybrid discrete interaction model/quantum mechanics (DIM/QM) approach¹⁰⁴, where the Cu substrate is treated in atomistic electrodynamics and the embedded molecule is described by time-dependent density functional theory (TDDFT). The Cu(100) surface is in xy plane and the molecule is placed on top (+z direction). Two stable conformers are found, namely, pyrrole-up (Fig. 5.1b) and phenyl-up (Fig. 5.1c). In the pyrrole-up conformer, the phenyl groups are almost completely flat. The averaged phenyl-pyrrole torsion angle is $\phi = 5.0^{\circ}$. The four pyrrole groups in this structure are "pushed" upwards by the steric force from the phenyl groups. The averaged dihedral angle is $\theta = 21.4^{\circ}$, and hydrogens are at about 1.5 Å above the central Co atom. For the phenyl-up conformer, the averaged torsion angle of the phenyl groups is $\phi = 51.2^{\circ}$ (the top hydrogens at 2.8 Å above Co), and the base porphyrin ring is flat. The phenyl-up conformer is the most stable in terms of the total energy, but the pyrrole-up conformer is a local minimal (see Fig. S1 for details). We also consider the dehydrogenated CoTPP molecule (Fig. 5.1d), which is known for its flat geometry on metal surfaces 105,106 . For all three structures, the central Co atom is ~ 3.6 Å above the substrate (center to center).

After the normal modes and frequencies of each stable structure are obtained, the Raman polarizability densities are calculated using numerical differentiation of electronic polarizability densities without the presence of the confined near field. The incident wavelength is set to 634 nm, which is the same as in the experiment 13 . Neither the substrate or the molecule is on resonance under this incident wavelength. The substrate remains same in the following simulations. The TERS images are then simulated using the LIRPD method described in detail by Ref. 102. In short, the Raman polarizability densities are locally scaled by a confined plasmonic near field, so that the densities near the center of the field distribution are greatly enhanced, whereas the contributions from the densities away from the field center are rapidly reduced by the decay of the field magnitude. The TERS intensity is then obtained by a spatial integration of these locally enhanced Raman polarizability densities. The near field is represented by a unimodal 3-dimensional distribution function (Lorentzian in this case) with given magnitudes, full-widths at half maxima (FWHMs) in each Cartesian direction, and the position of center (field maximum). The near field is considered to be polarized in the z direction (perpendicular to the substrate surface). The xy plane cutting through the near-field maximum is considered as its focal plane⁸⁵. Only the zz component of the molecular polarizability tensor is considered in the calculation of Raman scattering intensities. All normal modes of all the three structures are scrutinized. The pyrrole-up structure's TERS images are found to consistently match the experimental images. We now closely examine some representative modes, each of which entails different chemical and structural information.



Figure 5.1. CoTPP geometries and TERS images. Optimized geometries: (a) free molecule with $\phi = 80.2^{\circ}$, (b) pyrroles pointing up with $\theta = 21.4^{\circ}$ and flat phenyls, (c) phenyls pointing up with $\phi = 51.2^{\circ}$, and (d) dehydrogenated molecule. TERS images and the underlying modes: (e) experimental image adapted from Ref. 13; (f) 1531 cm⁻¹ mode of pyrrole-up structure; (g) 1556 cm⁻¹ mode of phenyl-up structure; and (h) 1539 cm⁻¹ mode of dehydrogenated structure. Simulated TERS images (f-g) are obtained with a field confinement of 10 Å and focal plane at +0.5 Å relative to the base porphyrin.

Competition between pyrrole and phenyl vibrations. Among the TERS images of all three structures, we find that the most differentiating mode is in the 1500 cm⁻¹ region. In Fig. 5.1(e-h), we present a typical TERS image for each structure in this region and compare them with the experimental image adapted from Ref. 13. The experimental image at 1555 cm⁻¹ (Fig. 5.1e) features relatively delocalized brightspots in between the phenyl groups, each of which has two vaguely separable lobes. The 1531 cm⁻¹ mode of the pyrrole-up structure gives rise to the best matching TERS image (Fig. 5.1f). In this mode, the pyrrole and the phenyl groups (*para*and *ortho*-hydrogens) both vibrate, with the hydrogens and the attached carbons vibrating in opposite directions. The near-field distribution used to obtain this TERS image has (*xy*) FWHMs of 10 Å (noted as w = 10 Å hereinafter) and the focal plane is at 0.5 Å above the center Co atom (noted as h = +0.5 Å hereinafter). Generally, using a more confined field makes the brightspots more discrete. Moving the focal plane higher or lower may lead to different TERS images. The effects of field localization (confinement and focal-plane position) will be discussed in detail later.

Similar TERS images are not found for the phenyl-up and the dehydrogenated structures, even though they share similar vibrational modes in the same frequency range as the pyrroleup structure. This appears to be a result of the competition between the pyrrole and phenyl vibrations. For the pyrrole-up structure, the magnitudes of the atomic displacements of the pyrrole and the phenyl hydrogens are about the same. Also, the displacement vectors of the

pyrrole hydrogens have small out-of-plane (perpendicular to the molecular plane) components that are more enhanced due to the z polarization of the near field. This balance leads to the brightspot being delocalized in the areas outside the adjacent pyrroles and phenyls. For the phenyl-up structure, the vibrations are largely on the pyrrole groups in the 1555 $\rm cm^{-1}$ mode, and the brightspots in the corresponding TERS images are thus localized around the pyrrole groups as well (Fig. 5.1g). Even though there exists strong phenyl modes in the 1500 cm⁻¹ region for the phenyl-up structure, the TERS images of those modes have brightspots mostly around the phenyls (same positions as the weaker spots around the phenyl para-hydrogens in Fig. 5.1g). This is due to the lack of competitive contributions from pyrrole vibrations, since the phenyl vibrations are out-of-plane and are favored by the z-polarized near field. The importance of the competitive pyrrole vibrations is also evident in the dehydrogenated structure. In its 1539 $\rm cm^{-1}$ mode, both phenyls and pyrroles are vibrating. But due to the removal of hydrogens on each pyrrole and the adjacent phenyl ortho-hydrogen, the contributions from the pyrrole vibrations are much weaker, and the associated TERS image has prominent brightspots only near the phenyl groups (Fig. 5.1h). The dehydrogenation makes the TERS images generally lack the pyrrole characteristics and have "spiral" patterns, so it is ruled out as a possible structure probed in the experiment despite its flat geometry.

5.2.2 Matching experiment and simulation with flat phenyl groups

Flat phenyl groups. It was argued in Ref. 13 that the CoTPP molecule has a planar geometry based on the scanning tunneling microscopy (STM) images. The TERS images in the 3000 $\rm cm^{-1}$ region (vibrations of the artificially flattened phenyls) seemed to also support the claim. We find in our simulations that the flat phenyl groups are indeed necessary to reproduce the experimental TERS images in the 3000 cm^{-1} region. In Fig. 5.2, we present the TERS images of the two 3000 $\rm cm^{-1}$ modes obtained from the two different conformers in comparison with the experimental images. In the first mode (2982 cm^{-1} in experiment), the TERS image features discrete brightspots around the phenyl hydrogens. The TERS image of the pyrrole-up structure reproduces such feature. As shown in Fig. 5.2b, the brightspots closely follow the vibrating meta-hydrogens of the phenyl groups in the 3097 cm^{-1} mode. One notable discrepancy between the experiment and the simulation is that there are three brightspots around each phenyl in the experimental image, whereas in the simulated image there are only two brightspots next to the *meta*-hydrogens. Actually, in a different vibrational mode at 3090 cm⁻¹, the *para*-hydrogens vibrates as strongly as the *meta*-hydrogens, and the resulting TERS image does have three brightspots around each phenyl (Fig. S3). However, we believe the brightspots around the two meta-hydrogens better represents the symmetry seen in the experimental TERS image. The missing brightspots at the C–C bonds may be due to the repulsive forces experienced by the molecule in the presence of the STM tip pressing down on the molecule. Nevertheless, the feature of discrete brightspots cannot be reproduced without the flat phenyl groups, as is illustrated in Fig. 5.2c. The standing-up phenyls lead to the brightspots being grouped into one lobe around each phenyl group, regardless of the number of vibrating hydrogens. The loss of resolution for a vertical geometry is in agreement with the benchmark results obtained from the DIM/QM

approach⁸⁵. In the second 3000 cm⁻¹ mode, the brightspots are delocalized over each phenyl group (Fig. 5.2d). Again, the pyrrole-up conformer has a mode (3185 cm⁻¹) of which the TERS image well reproduces the experimental image (Fig. 5.2e). The brightspots come from the strong vibrations of the pyrrole hydrogens. Similar mode is also found for the phenyl-up conformer, but the brightspots in the resulting TERS image are more localized than desired (Fig. 5.2f).



Figure 5.2. TERS images of modes in the 3000-3200 cm⁻¹ region. Row (a-c): phenyl vibrations at around 3000 cm⁻¹; (d-f): pyrrole vibrations of higher frequencies. Column (a,d): adapted experimental images; (b,e) simulated images of pyrrole-up CoTPP; (c,f) simulated images of phenyl-up CoTPP. The field confinement used in this figure is 6 Å and focal plane at -0.5 Å relative to the base porphyrin. Each image consists of the vibrations of the four phenyl vibrational modes, which are degenerate in energy (within 1 cm⁻¹ difference).

It is worth mentioning that the focal plane is placed below the molecular plane (h = -0.5 Å) to reproduce the phenyl TERS images, especially for the 3185 cm⁻¹ mode. The lowered focal plane implies a narrower tip-substrate separation in reality. Thus the near field is expected to be more confined⁹⁴, and FWHM decreased to 6 Å in this simulation. The lowered focal plane is plausible: in experiment the actual STM tip is pressed extremely close to the molecule, and may move the focal plane below the molecule as a result. Also, the smaller-sized brightspots around the phenyl hydrogens in the 2982 cm⁻¹ mode suggest the near field probing the phenyl groups is more confined than for other parts of the molecule. We will now discuss in detail the effects of the near-field widths and focal-plane positions, which can be jointly called the near-field "localization".

Effects of near-field localization. We take the 3097 cm^{-1} mode of the pyrrole-up conformer

as an example to illustrate how the field width affects the TERS image, as it is the image of the highest resolution. The width of the near field (w) refers to the FWHMs in the xy plane. The field distribution is circularly symmetric by construction, resembling the near field induced by a cone-like plasmonic tip. The near field is found to be more confined vertically than parallel¹⁰², so the FWHM in the z direction is set to be half of that in the xy plane.



Figure 5.3. TERS images under various field distributions. (a-c) 3097 cm^{-1} mode images with field confinements of 2.0 Å, 6.0 Å, and 15.0 Å, and the focal plane is -0.5 Å relative to the porphyrin ring. (d-f) 3185 cm^{-1} mode images with field confinement of 10 Å, and the focal-plane heights are -0.2 Å, 0.0 Å, and 0.5 Å relative to the porphyrin ring.

As shown in Fig. 5.3 (a-c), when the near-field width is increased from 2 Å to 15 Å with the focal-plane height fixed at -0.5 Å (same as in Fig. 5.2), the size of individual brightspots becomes larger and they eventually blur out. By comparing the size of the brightspots with the experimental image, we find the field width is roughly 6 Å (as in Fig. 5.2). It should be noted that the "width" in this work is defined with respect to the field magnitude ($|\mathbf{E}|$) rather than the intensity ($|\mathbf{E}|^2$). For a width of w = 6.0 Å in terms of field magnitude, the width of the intensity distribution is $w' = 6.0/\sqrt{2} \approx 4.24$ Å. This value is in good agreement with previous simulations using self-consistent polarizabilities under localized near fields:^{17,85} an atomically sharp tip localizes the field to a sub-nanometer volume, of which the field distribution (in terms of $|\mathbf{E}|^2$) in the *xy* plane have FWHMs of about 4-5 Å. This confinement is close to the size of the apex atom itself, and, in our opinion, approaches limit of the field confinement of atomically sharp tips. The atomic resolution in TERS images doesn't necessarily require the field distribution to be significantly narrower than the half-nanometer limit. Forcing the field to be confined to 2 Å in magnitude leads to much smaller brightspots than what the experiment can measure (Fig. 5.3a).

The focal-plane height that reproduces the images of the 3000 $\rm cm^{-1}$ modes is below the molecular plane (h = -0.5 Å). Given the $\sim 2.5 \text{ Å}$ separation between the focal plane and the tip atom^{85,94}, the focal plane at h = -0.5 Å corresponds to a tip atom about 2 Å above the phenyl groups, which is already a very small distance considering the size of the metallic tip atom. Therefore, here we only present the simulated TERS images of the 3185 cm^{-1} mode as the focal plane gradually moves higher. When the focal plane moves from h = -0.5 to -0.2 Å, we find that the brightspots on the base porphyrin ring emerges (Fig. 5.3d). As the focal plane continues to rise, these brightspots disappear and the brightspots around the vibrating pyrrole hydrogens stand out. This observation can be explained by the 1.5 Å height difference between the pyrrole and the phenyl hydrogens of this conformer. When the focal plane is underneath the phenyl rings, the vibrations on the phenyl rings are favored due to the narrower confinement in the z axis, even though the strongest vibrations are on the pyrrole hydrogens. The corresponding TERS image shows smeared brightspots around both the phenyls and pyrroles. When the focal plane is moved to higher positions, the pyrrole hydrogen vibrations start to dominate the intensities. Even without a widened field distribution, the simulated TERS images with the raised focal plane appear to have better resolution (smaller brightspot size).

The above analysis suggests that it is the convoluted effect of both near-field size and focalplane position that determines the resolution in TERS images. The effect varies from mode to mode, especially for the modes where atoms with different heights vibrate simultaneously. In general, vibrating atoms closer to the focal plane of a sub-nanometer near field are more enhanced. For flat geometries, the width of the field confinement largely determines the size of the brightspots, and a half-nanometer confinement suffices to achieve the atomic resolution in TERS images. The best matches to the experimental images are found with two sets of field localizations: w = 10.0 Å, h = +0.5 Å for brightspots around pyrrole groups; and w = 6.0 Å, h = -0.5 Å for brightspots around phenyl groups. Using two sets of field localizations is an approximation to the "constant-current" scanning scheme adopted in Ref. 13. To keep a constant current in the STM junction, the tip moves slightly up and down while scanning over the molecule. The near field becomes more confined in smaller junctions (shorter tip-substrate distance), and vice versa⁹⁴. Considering the fact that the height profile of CoTPP is mostly determined by the arrangement of the pyrroles and the phenyls, it is reasonable to represent the change in tip height by two focal planes of the near field: lower (more confined) around the flat phenyls and slightly higher (less confined) around the tilt-up pyrroles. A comprehensive comparison between the TERS images generated from both field localizations are provided in Supporting Information (Fig. S4 and S5).

Field-gradient effects. One of the important features of high-resolution TERS images is that the brightspots can be away from the vibrating atoms, which is ascribed to the field-gradient effect.⁸⁵ The field-gradient effect in TERS has two aspects. The first aspect comes from the confinement of the near field. The molecule's Raman polarizability densities tend to be distributed symmetrically with opposite signs along the atomic displacement vectors. Integrating these densities over all space recovers the molecule's far-field property, and the densities with opposite signs cancel each other in the integration. For a Raman-inactive mode, these densities sum up to

zero. Such symmetry can be broken by the confined near field. When the field distribution is close to but not at the symmetric center of the polarizability density distribution (the equilibrium position of the vibrating atom), part of the densities around it are included into the effective integration volume defined by the widths of the field distribution, and the rest rapidly smeared out.¹⁰² These locally enhanced densities have excessive values that do not sum up to zero anymore and results in a TERS brightspot, which is also why Raman-inactive modes can be activated by an inhomogeneous near field.⁷⁰ If this atom is at the edge of the molecular geometry, the tip position detecting an enhanced Raman scattering signal will be outside the molecule. The gradient of the confined field (rate of magnitude decay in space) is zero at the field center (maximum), but large at positions away from the field center.¹⁴ Thus, the off-atom TERS brightspots can be partially attributed to the large gradient of a highly confined near field.

The field-gradient effect also resides in the molecule's oscillating quadrupoles.⁹³ Using only the density of dipole-dipole polarizability (α -tensor), the TERS images of small molecules like benzene and porphine are well reproduced by the LIRPD approach ¹⁰², and the quadrupole-dipole polarizability (\mathcal{A} -tensor)⁹¹ has merely no effect other than moving the brightspots slightly further away from the molecule. However, in this work we find that it is critical to include the \mathcal{A} -tensor densities in the calculations for the reproduction of CoTPP TERS images. The magnitude of its \mathcal{A} -tensor densities are generally comparable to α -tensor densities, and are about an order of magnitude larger for many modes. But their distributions are different for different types of modes, and thus exert different effects on TERS images. In Supporting Information (Section 3), the Raman polarizability density distributions of both tensors for all the discussed modes are provided, and each tensor element's effect on the TERS image is analyzed in detail. Here, we present two exemplar modes of the pyrrole-up CoTPP conformer to highlight the different ways in which the \mathcal{A} -tensor densities can affect TERS images.

The effect of \mathcal{A} -tensor densities on TERS images is the most prominent for in-plane scissoring modes that have inner-molecule vibrations, for example, the 1176 cm⁻¹ mode (top row of Fig. 5.4). The experimental TERS image (measured at 1156 cm⁻¹) features four strong brightspots outside the phenyl groups and weak intensities in the base porphyrin ring. This image is well reproduced in our simulation using both α -tensor and \mathcal{A} -tensor densities of the 1176 cm⁻¹ mode. However, without the \mathcal{A} -tensor densities, the simulated TERS image loses the resolution and has blurry brightspots scattered over the phenyl rings. In this mode, the strongest vibrations are on the *ortho*-hydrogens of the phenyls, and the adjacent *meta*-hydrogens vibrates weakly (scissoring). On the other hand, we find that for a stretching mode like the 3097 cm⁻¹ mode, \mathcal{A} -tensor densities only very slightly changes the positions of the brightspot. This is because for a mode with the vibrations on the edge atoms, the distributions of the α -tensor and \mathcal{A} -tensor densities are similar in terms of the overall symmetry (see Fig. S6 for details).



Figure 5.4. Contribution of \mathcal{A} -tensor densities to TERS images. Top row (a-c): TERS images of the 1176 cm⁻¹ mode; the near field used for simulating this mode has w = 6.0 Å and h = -0.5 Å. Bottom row (d-f): TERS images of the 760 cm⁻¹ mode; the near field used for simulating this mode has w = 10.0 Å h = +0.5 Å. Column: (a,d) Experimental images; (b, e) simulated image with both α -tensor and \mathcal{A} -tensor densities included; (c, f) simulated image with only α -tensor densities.

The visual effect of \mathcal{A} -tensor densities on TERS images are less obvious for out-of-plane vibrational modes. One typical example is the image of the mode at around 730 $\rm cm^{-1}$ (Fig. 5.4 d-f). The brightspots are mostly distributed outside the pyrrole hydrogens in this mode, forming a cross pattern. From our simulations we find that the 760 $\rm cm^{-1}$ mode matches the experimental images, where the eight pyrrole hydrogens vibrate asymmetrically out of plane. The same cross pattern exists in the simulated TERS images either with or without the \mathcal{A} -tensor contributions. The only difference is that the brightspots with \mathcal{A} -tensor included are slightly further away from the molecule and have large sizes. The reason why the TERS image of an out-of-plane mode is not sensitive to A-tensor contributions lies in the distribution of Raman polarizability densities. Both α -tensor and \mathcal{A} -tensor densities are symmetrically distributed around the vibrating atoms, with opposite signs across the molecular plane (Fig. S7). Hence, the yielded excessive densities by localized field are at similar positions for the two tensors. Furthermore, even though each tensor element's distribution follows the direction of atomic displacements, the phase difference in the atomic vibrations is not distinguished in the TERS image. This is because the sum of the excessive densities are squared in the calculation of Raman scattering intensities. Another example is that the simulated TERS image of the 787 $\rm cm^{-1}$ mode (symmetric pyrrole wagging) is very similar to the 760 cm^{-1} mode (Fig. S2).

In the case of small molecules as in previous work¹⁰², the TERS images of the out-of-plane modes of benzene and porphine do not change significantly with \mathcal{A} -tensor included. And the in-plane mode of porphine at 1539 cm⁻¹ is dominated by the edge atom vibrations, so it does not benefit from the \mathcal{A} -tensor densities either. As for the H₂TBPP, the effect of \mathcal{A} tensor is not obvious because the analyzed modes are dominated by out-of-plane vibrations on the standing-up butyl groups, and the near field is very broad. Our simulations suggest that it is generally more accurate for analyzing TERS images to include the \mathcal{A} -tensor contributions, especially for large planar molecules like CoTPP that have many intricate in-plane vibrations.



Figure 5.5. Overview of the comparisons between experimental and simulated TERS images. Row A: experimental TERS images adapted from Ref. 13. Row B: the simulated TERS images with corresponding vibrational modes. In (B1, B2, B4), the field confinement is w = 10.0 Å and focal plane is at h = +0.5 Å; in (B3, B5, B6), w = 6.0 Å and h = -0.5 Å.

5.2.3 Molecule-substrate coupling and beyond.

We have discussed the effects of near-field confinement, focal-plane position, and field-gradient effects on TERS images, and demonstrated how experimental images are reproduced under the consideration of all these effects using the LIRPD method. In Fig. 5.5, an overview of simulated and experimental images is provided, and an overall good agreement across all the modes is found. Thus, we conclude that the pyrrole-up conformer is the most probable structure probed in the experiment. However, it should be noted that the assignments of modes to experimental TERS images are not deterministic. The experimental images in Ref. 13 were obtained using some integration window of the spectra. For the six main experimental images, the size of the integration window ranges from about 50 $\rm cm^{-1}$ to as narrow as a few wavenumbers. Thus, some experimental TERS images can be a combination of several modes with closed frequencies. However, we find that different modes have similar TERS images more often than not for the TERS images obtained in wide integration windows (Fig. S2). On the other hand, the modes at 1555 cm^{-1} and 3000 cm^{-1} are more likely to be different despite their similar frequencies (Fig. S3). However, the experimental TERS images associated with these frequencies were generated from very narrow integration windows, *i.e.*, single modes. Therefore, in this manuscript we stick to analyzing the TERS images of single modes such that no additional arbitrariness is introduced by linear combinations of multiple modes.

Since the extreme sensitivity of TERS requires delicate experimental techniques, current theoretical treatments are not able to decisively capture all the complex TERS processes, and many open questions still need to addressed. For example, the flattening of the CoTPP molecule may have altered the dynamics of Raman scattering, which can lead to discrepancies between the simulated normal modes and actual molecular vibrations. More importantly, the choice of substrate that anchors the molecule during the tip scan is critical for the sub-molecular resolution; however, the chemical interactions between the molecule and the substrate are only partially accounted for through van der Waals interaction and mutual polarization.¹⁰⁷ The importance of the molecule-substrate coupling is twofold. In the experiment of Ref. 13, the background signals produce a cross-pattern TERS image and extend relatively far away from the molecule. The background TERS signals are considered as an electronic Raman scattering (ERS) process, which arises from the inelastic light scattering by the substrate due to changes in the local dielectric environment.¹⁰⁸ In the ERS image, the outer fringe of brightspot is attributed to the substrate polarization, which is also visible in other TERS images. In Fig. S9, we show that the current method does not take the substrate scattering into account, and thus cannot capture the outer fringe of brightspots. Therefore, our simulated TERS images are focused in a smaller area covering the molecule. On the other hand, the vibrational modes that involve the substrate atoms are not considered in our simulations, which may also make substantial contributions to the brightspot patterns in TERS images, especially around the core part of the molecule.

To fully understand the mechanism of high-resolution TERS, further efforts have to be made for a better description of the roles that the near field plays. Even though the spatial variation of TERS signals seen in experiments can be qualitatively reproduced by the LIRPD approach, the accurate reproduction of TERS spectra remains challenging. In the LIRPD model, the Raman polarizability densities are obtained without being solved self-consistently in the presence of a confined near field. The "tip-independent" polarizability densities significantly reduce the computational cost, and thus allow for studies of large molecules. However, as a compromise, out-of-plane modes are favored over in-plane modes in terms of relative intensities, as the near field is assumed to be perpendicularly polarized. On the contrary, both experiments^{13,109} and the selfconsistent calculations⁸⁵ in the literature have suggested that Raman scattering signals of in-plane vibrational modes can also be enhanced to a similar order of magnitude as the out-of-plane modes. In Fig. S10, we provide the simulated spectrum obtained from the polarizabilities self-consistently solved by the DIM/QM method, in comparison with the LIRPD result. At the given tip position, the DIM/QM spectrum qualitatively agrees with the experiment, whereas the LIRPD spectrum is dominated by out-of-plane modes. The specific tip position used for the DIM/QM calculation is an estimation, which is not expected to fully reproduce the experimental spectrum. But still, the enhancement of in-plane modes is observed. Considering the complexity and sensitivity of TERS spectra to the near-field localization, an exhaustive search for the correct junction geometry is infeasible due to the high computational cost of DIM/QM. The LIRPD method used in this manuscript is advantageous in its flexibility of adjusting the near field confinement and focal plane. Additionally, we provide the localized Raman polarizability densities calculated by both methods (Fig. S10, c-d). The similarity between the normalized distribution obtained from the

two method further justifies the treatment of LIRPD on TERS images. It is important for future work to unravel how the near field and the sub-molecular density influence each other in the self-consistent cycles.

5.3 Conclusion

In this work, we systematically studied the TERS images of a single CoTPP molecule on a Cu(100) substrate. A planar conformer whose TERS images consistently match the experimental results was discovered. We found that the resolution in TERS images is determined by both the field confinement and the focal-plane position. A half-nanometer near field placed close to an vibrating atom suffices to reach the atomic resolution. The field-gradient effects were found to play a vital role in calculating the spatially variant TERS intensities, especially for large planar molecules with intricate vibrational modes. We demonstrated the significant contributions from the \mathcal{A} -tensor and its effects on TERS images of different modes. While having larger magnitudes than α -tensor densities in general, the A-tensor densities are critical for the simulation of TERS images of in-plane modes, especially for those with inner-molecule vibrations. The LIRPD model adopted in this work proves to be an effective and flexible approach to the simulation of high-resolution TERS images, and provides an intuitive pictorial explanation. However, the accurate description of TERS spectra remains very challenging. Fully self-consistent TDDFT solutions to the molecular polarizability in the presence of a confined near field are computationally expensive, and thus hinders the systematic search of molecular geometries and near-field localizations to reproduce experimental spectra. Moreover, the effect of the substrate on TERS measurement requires further investigations.

Methods

A locally modified version of the Amsterdam Density Functional (ADF) program package^{73,74,99} was employed to perform all the DFT simulations. The geometry optimizations, frequency, and linear-response calculations were carried out in the presence of the copper substrate using the Becke-Perdew (BP86) exchange-correlation functional with the double- ζ polarized (DZP) Slater-type basis. The molecule is charged with one electron to make it closed shell. The metal-molecule interactions are accounted for in the discrete interaction model/quantum mechanics method.^{104,107,110} All metal atoms were treated with the discrete interaction model (DIM). The frequent-dependent complex dielectric functions of copper atoms were obtained from Johnson and Christy⁸³. The substrates were constructed as a large block of copper unit cells and molecules were placed on the Cu(100) surface.

TERS intensities are represented by differential cross section $(d\sigma/d\Omega)$ of Raman scattering, which is given by

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\omega} = \frac{\pi^2}{\epsilon_0^2} (\tilde{\nu}_{\mathrm{in}} - \tilde{\nu}_k)^4 \frac{\mathrm{h}}{8\pi^2 \mathrm{c}\tilde{\nu}_k} \frac{|\alpha'_k|^2}{1 - \exp(-\mathrm{hc}\tilde{\nu}_k/\mathrm{k_B}T)} \quad , \tag{5.1}$$

where $\tilde{\nu}_{in}$ is the incident frequency and $\tilde{\nu}_k$ is the frequency of k^{th} normal mode. α'_k is the molecular

polarizability derivative of the normal mode, obtained by locally integrated Raman polarizability densities. The local integration of Raman polarizability densities (zz component) in the finite space is written as:

$$\alpha'_{zz}(\mathbf{R}) = \int \left[1 + F_z^{\text{loc},z}(\mathbf{r} - \mathbf{R})\right] \cdot \delta\rho_{zz}^{(\boldsymbol{\alpha})}(\mathbf{r}) \cdot \left[1 + F_z^{\text{loc},z}(\mathbf{r} - \mathbf{R})\right] d\mathbf{r} + \int \frac{1}{3} F_{z\epsilon}^{\text{loc},z}(\mathbf{r} - \mathbf{R}) \cdot \delta\rho_{z\epsilon,z}^{(\boldsymbol{\mathcal{A}})}(\mathbf{r}) \cdot \left[1 + F_z^{\text{loc},z}(\mathbf{r} - \mathbf{R})\right] d\mathbf{r} .$$
(5.2)

with r being a position vector (dr being volume of a unit grid cell). The Raman polarizability densities ($\delta \rho^{(\alpha)}$) are the derivatives of polarizability densities with respect to the mass-weighted normal modes, which were calculated using the three-point numerical differentiation approach,

$$\delta\rho^{(\alpha)}(\mathbf{r}) = \frac{\partial\rho^{(\alpha)}(\mathbf{r})}{\partial Q_k} = \frac{\rho^{(\alpha)}(Q_k + \Delta Q_k) - \rho^{(\alpha)}(Q_k - \Delta Q_k)}{2s_Q \Delta Q_k} , \qquad (5.3)$$

where s_Q is the mass-weighted step size. The polarizability densities were calculated at the equilibrium geometry distorted in $+\Delta Q_k$ and $-\Delta Q_k$ directions. The same procedure was done for $\rho^{(\mathcal{A})}$ as well. In the linear-response calculations of the perturbed densities, the incident wavelength is set to 634 nm and the excited-state lifetime is set to 0.1 eV⁸⁰. The cubic grids used for representing the density are determined by the sample molecule structure and orientation on the surface. The boundary of the box is 3 Å away from the molecule. The step size is 0.4 Å for generating grids parallel to the metal surface and 0.2 Å in the vertical direction.

 $F_z^{\text{loc},z}(\mathbf{r} - \mathbf{R})$ is the z-polarized plasmonic local field induced by an uniform external field also polarized in z direction, of which the center is at \mathbf{R} . $F_{z\epsilon}^{\text{loc},z}$ is the ϵ component of its gradient, obtained as $\partial F_z^{\text{loc},z}(\mathbf{r} - \mathbf{R})/\partial \epsilon$. In this work, the induced local field is modeled as a 3D Lorentzian distribution:

$$F_{z}^{\text{loc},z} = M \left[\left(\frac{x-a}{\frac{1}{2}\tau_{x}} \right)^{2} + \left(\frac{y-b}{\frac{1}{2}\tau_{y}} \right)^{2} + \left(\frac{z-c}{\frac{1}{2}\tau_{z}} \right)^{2} + 1 \right]^{-1} + N \left[\left(\frac{x-a}{\frac{1}{2}\tau_{xi}} \right)^{2} + \left(\frac{y-b}{\frac{1}{2}\tau_{yi}} \right)^{2} + \left(\frac{z-c}{\frac{1}{2}\tau_{zi}} \right)^{2} + 1 \right]^{-1} \cdot i , \qquad (5.4)$$

Here, τ represents FWHM of Lorentzian distribution for the x, y, and z components, and a, b, and c denote the Cartesian coordinates of the field center. The FWHMs for x and y components are considered to be equal and twice as large as for the z component. The widths for both the real and imaginary fields along the same axis are identical. M, N represents the maximal magnitudes of the real and the imaginary parts of the near field, which are both set to 25 in this work. Since the molecule is not on resonance, the contribution of the molecule's imaginary polarizabilities is orders of magnitudes smaller than the real part.

Part III

Plasmonics in a Subnanometer Gap

Chapter 6 Atomistic Electrodynamics Simulations of Plasmonic Nanoparticles

Chen, X.; Liu, P.; Jensen, L. Atomistic Electrodynamics Simulations of Plasmonic Nanoparticles. J. Phys. D: Appl. Phys. **2019**, 52, 363002. (Adapted)*

Abstract

Plasmonic properties of metal nanoparticles can be precisely controlled by tuning their size, shape, and surrounding environment. Nanoparticles in the quantum size regime with dimensions of a few nanometers exhibit unique plasmonic properties that are different than their bulk counterparts. In this regime, the plasmonic response becomes sensitive to microscopic details of the nanoparticle due to prominent quantum effects such as electron tunneling. Classical electrodynamic model fails to describe the plasmonic behavior in this region and fully quantum mechanical approaches are often needed although limited by their high computational demand. Alternatively, atomistic electrodynamics provides a promising approach as they benefit from both the efficiency of classical electrodynamics and the accuracy of atomistic representations like in quantum mechanics. Taking advantage of the atomistic description, the effects of subtle changes in nanoparticle structure and its influence on the plasmonic response and the near-field distribution in a cavity created by the strongly interacting nanoparticles can be captured. The atomistic electrodynamics model naturally fills the gap between quantum mechanical models and classical electrodynamics and holds great promise for studies of optoelectronics and near-field spectroscopies with dimensions such that the atomic structure of nanoparticles plays a central role in determining the optical response.

^{*}X.C., P.L. and L.J wrote manuscript. X.C. focused on single nanoparticles, and P.L. focused on coupled plasmons.

6.1 Introduction

Noble metal nanoparticles have unique plasmon resonance frequencies commonly in the visible/near infrared range.^{111,112} Their optical properties of nanoparticles are determined by their size, shape, and surrounding environment.¹¹³ Thanks to the advances in sophisticated fabrication and synthesis techniques, these key attributes of nanoparticles can be precisely controlled and thus the optical properties can be rationally adapted for many applications, including optical sensing¹¹⁴, optoelectronic devices^{115–117}, medical thermotherapies¹¹⁸, light harvesting^{115,119–121}, and photocatalysis^{122,123}. Moreover, the plasmon resonances give rise to significantly enhanced electromagnetic fields near the surface of the nanoparticle, which is particularly important for near-field spectroscopies^{10,12,46,124}.

The plasmonic properties of large-size nanoparticles (diameter > 10 nm) are typically described in classical electrodynamics by solving Maxwell's equations. Mie theory 125 , as a simple and computationally low-cost model, is widely used for spherical, ellipsoidal, and core-shell particles.¹²⁶ More general classical electrodynamics methods, such as the discrete dipole approximation $(DDA)^{127}$ and electromagnetic finite difference time domain $(FDTD)^{128}$, can be applied to nanosystems with more complicated structures $^{129-131}$. As the control of nanoparticle' size reaches sub-nanometer scales, the nanoparticles fall into the regime where quantum effects become non-trivial or even dominant, termed as "quantum size regime" (diameter < 5 nm). In this regime classical electrodynamics fails since these approaches use local dielectric functions without considering the spatial nonlocality and quantum tunneling which are prominent in the quantum size regime.^{132–136} The nonlocal effect can be taken into account by introducing correction terms to the dielectric function. Improved models, such as the hydrodynamic models¹³⁷ and spatiallydependent dielectric function based models,¹³⁸ can predict the characteristic that is size-dependent absorption shift in the quantum size regime.^{139,140} However, the electron spill-out effect is missing in these nonlocal corrected models, which may cause an incorrect description for the near field in strongly interacting plasmonic systems especially for the subnanometer dimensions of relevance to near-field spectroscopies.¹⁴¹

On the other hand, the electronic states of large-size nanoparticles are typically regarded as a continuum which described by the band structure. When the size shrinks to a dimension comparable to the Fermi wavelength of an electron (~0.5 nm for Ag and Au), the electronic states become discrete. The interband transitions coupled with the collective excitations in the noble metal clusters play a key role in the optical response. The detailed information about the relations between electronic transitions and optical properties are addressed elsewhere. ^{142–144} The microscopic structures of nanoparticles is essential to the electronic configuration of metal cluster. Thus, additional complexities in the theoretical models are required to account for the atomistic details of nanoparticles. Fully quantum mechanical approaches, such as time-dependent density functional theory (TDDFT), naturally describe the nanoparticles in terms of electronic state at the atomic level and capture the behavior of electron excitations. ¹⁴⁵ Moreover, the quantum mechanical methods can accurately describe the strong coupling between adjacent nanoparticles, especially the so-called charge transfer plasmon arising from electron tunneling.⁵⁵ However, fully quantum mechanical approaches are hindered by their high computational demand. Although many acceleration strategies were recently developed, such as the Liouville-Lanczos approach, ¹⁴⁶ real-time propagation method, ^{147–149} and the complex polarizability algorithm, ^{150,151} the quantum mechanical simulations are still typically limited to small metal clusters at sub-nanometer scales (diameter < 2 nm) as the realistically sized systems remain computationally intractable.

Atomistic electrodynamics models have been developed to integrate the explicit representation of the atomic structures and the efficiency of classical approaches.^{58,152} It thus naturally bridges the quantum mechanical methods and the macroscopic electrodynamic description. Recent advances in atomistic electrodynamics models include representing metal atoms by spherical Gaussian charge distributions with the assigned atomic polarizabilities depending on the local dielectric environment.^{59,60} The unified description at atomic level is able to deal with various nanoparticle shapes and with or without ligands covering.

In this review, we will highlight the atomistic treatment in simulating plasmonic responses with an emphasis on the improved atomistic electrodynamics approach. In particular, we will discuss the recent systematic studies of the size, shape, and environment effects on the plasmonic properties. We will also discuss the simulations of the near-field spectroscopies where the atomistic features in the nanostructures are necessary to achieve the sub-molecular resolution.

6.2 Size effect on the plasmonic response of nanoparticles

In the quantum size regime, nanoparticles are featured by high surface-to-volume ratios. Accordingly, the optical response shows behaviors differing from large nanoparticles. For small-size metal clusters, typically less than 2 nm, the decreasing number of atoms leads to spatial confinement of the electrons resulting in molecular-like electronic structure and discrete electronic transitions due to the quantum effect. In this regime, the atomistic structure plays a key role in determining the optical properties and quantum effects become crucial and need to be accounted for in theoretical simulations.¹⁵³

Significant efforts have been devoted to understanding the birth of plasmons in noble metal cluster and in general understand the size-dependent optical properties $^{113,154,154-160,160-164}$ A TDDFT investigation of the absorption spectra of tetrahedral silver clusters consisting of 10 to 120 atoms found a correlation between size and plasmon energy that enabled them to extrapolated the plasmon energy to larger size nanoparticles and found excellent agreement with continuum electrodynamics results.¹⁵⁵ To understand the size-dependence of the plasmonic response, the absorption spectra of Ag₁₃ to Ag₁₄₀ was characterized using TDDFT.¹⁶⁵ As shown in Fig. 6.1, a main peak in the absorption spectrum of small cluster companied by secondary structures appears instead of a well-defined prominent surface plasmon in the large clusters, particularly for Ag₁₃. The multiple absorptions beyond 3.5 eV arise from interband transitions involving the *d* electrons. With the cluster size increasing up to Ag₁₄₀, a broadened peak appears at 3.1 eV. The transition from molecule-like excitations to collective excitations occurring at the large cluster was found in the spectra of tetrahedral Ag_n cluster (n=10, 20, 35, 56, 84, 120) as well.¹⁵⁵

example, the main peak is blue-shifted by 0.3 eV from Ag_{38} to Ag_{140} in the TOh symmetry. It is due to the fact that the increased surface-to-volume ratio reduces the *d* electron screening and increases the plasmon frequency with the compensation of the spill-out of 4s electrons.^{166,167} The broadening and damping of resonance mainly stem from the coupling of the interband transitions whose threshold energy lies slightly below the plasmon resonances.¹⁶⁸ Besides the size effect, it is found that the shape, solvent environment, and binding ligand also play a key role in optical response.^{160,169,170}



Figure 6.1. Size dependence of the absorption spectra for the pure fcc Ag clusters. Ag₁₃ and Ag₅₅ in cuboctahedral symmetry. Ag₃₈ and Ag₁₄₀ in TOh symmetry. The spectra are normalized by the number of atoms for comparability. The spectra are averaged over the three Cartesian axes for the clusters which do not have an isotropic response. Reprinted with permission from Ref. 165 Copyright 2011 American Physical Society.

TDDFT based on a *jellium* model is widely used to treat large clusters consisting hundreds of metal atoms. In the *jellium* model, ions are treated as a homogeneous background and the conduction electrons are allowed to freely move in a confined field.^{133,171–174} The *jellium* model performs well for free-electron metals such alkali-metallic nanoparticles. However, it is questionable for noble metal nanoparticles due to the contribution from bound *d*-electrons, which causes the charge centroid to be pushed towards to the nanoparticle center.¹⁴¹ Another problem of the *jellium* model is the lack of microscopic structure details at the atomic level, which affects the optical response in turn. The time-dependent self-consistent charge density functional tight-binding (TD-SCC-DFTB) method was another efficient tool to simulate the surface plasmon excitations of large-size metallic nanocluster. The electronic structure of ground state is treated by the DFTB method¹⁷⁵ and electronic dynamics is treated by the real-time propagation of the single-particle reduced density matrix in an external time-dependent potential.¹⁷⁶ The advantage of the DFTB methods is the lower computational cost as compared to TDDFT while still retaining the atomistic description of the nanoparticles.

TDDFT is often used as a benchmark for describing quantum effects on the plasmon excitations in nanoclusters. Although TDDFT has been demonstrated to be accurate for many systems, it is well known that local and semi-local exchange-correlation (XC) functionals have certain failures, such as describing charge-transfer excitations between weakly interacting systems and in condensed-phase systems.^{177–180} Correct description of these charge-transfer excitations is important for understanding strongly coupled noble nanoparticles due to the onset of charge transfer plasmon¹⁴¹ and the chemical enhancement mechanism in surface-enhanced Raman scattering (SERS).¹⁸¹ One approach to overcome some of these challenges is to use semiempirical models. In particular, the recently developed INDO/CI approach allows for double excitations.¹⁸² This method has also been successfully used in identifying the quadrupolar plasmonic excited states in Ag nanoparticles, describing the charge transfer between molecule and electrodes, and evaluating the magnitudes of electromagnetic and chemical effects in SERS.^{182–184}

Medium (2-10 nm in diameter) and large (>10 nm in diameter) nanoparticles have broader absorption band arising from the high density of states and thus continuous excitation energies. While fully quantum mechanical models are limited for these system sizes due to high computational demand, atomistic electrodynamic models⁶⁰ require significantly lower computational cost due to the simplified representation of atoms as fluctuating atomic dipoles, and at the same time retain the atomistic description of the nanoparticle structure and its plasmonic properties. Therefore, atomistic electrodynamic models are attractive alternatives for simulating mediumsized nanoparticles.



Figure 6.2. Optical absorption cross-section of bare Ag nanoparticles. Comparison between theoretical predictions and experimental EELS measurements, (a) the cd-DIM and (b) the DDA model. The experimental data is taken from Ref. 185, where the horizontal error bars indicate 95% confidence intervals.

Recently, an atomistic electrodynamics model named coordination-dependent discrete interaction model (cd-DIM) was developed.⁶⁰ In this model, the atoms are explicitly represented with dielectric properties depending on their local environment and thus differentiates between bulk-like atoms and surface-like atoms. It has been demonstrated that cd-DIM performs well in predicting the optical properties of the medium-size nanoparticles. Specifically, the characteristic blue-shifting of the plasmon resonances with decreasing sizes was reproduced using cd-DIM (Fig. 6.2 a). The cd-DIM results were found to be consistent with the experimental measurements using electronic energy-loss spectroscopy (EELS), which measures plasmons and interband transitions,^{186–188} especially for the nanoparticles of diameters less than 6 nm.¹⁸⁵ The observed blue shift was attributed to spill-out effects and quantum size effects incorporated into the coordination-dependent atomic polarizabilities. Atoms at the surface are assigned a larger radius than atoms in the bulk to account for spill-out effects at the surface and the screened dipole-dipole interactions between the atoms at short distances. Treating the atoms as point-like objects described by a local bulk dielectric constant (DDA) leads to the expected size-independent plasmon excitation (Fig. 6.2 b).

6.3 Shape effect on the plasmonic response of nanoparticles

The spectral character of metal clusters is also determined by the cluster's symmetry. ¹⁸⁹ Fig. 6.3 illustrates the shape effect on the optical properties of small-size Ag clusters. In Fig. 6.3 a, the differences are related to the absorption intensity and the energy shift in the high energy region. The intensity of main absorption peak increases 3 times and the peaks in the low energy region are redshifted by 0.2 eV from the icosahedron to the cuboctahedron of Ag₁₃. The big difference between the icosahedron and the cuboctahedron of Ag₅₅ is the main peak shift. The small-size Ag clusters (up to 85 Ag atoms) in various shapes including octahedra, truncated octahedra, and icosahedra show a blue shift of the maximal absorption as the shape becomes more symmetric (from octahedra to icosahedra). ¹⁶² For the monoatomically thick Ag nanocages in various polyhedral shapes, the absorption peaks of icosahedral cluster is generally blue-shifted by 0.2 eV compared to their counterpart of cuboctahedral cluster in Fig. 6.3 b and c. It indicates an inverse correlation between size and excitation energy of maximal absorption. ¹⁷⁰ The origin of the plasmon shift lies in the fact that the fcc(111) facet (icosahedron) has a large electronic gap compared to fcc(100) facet (cuboctahedron).



Figure 6.3. (a) Absorption spectra of Ag nanoculsters in the shape of icosahedron (Ih) and cuboctahedron (cubo) at equal size; (b) Absorption spectra of Ag Ih nanocages; (c) Absorption spectra of Ag cubo nanocages. Reprinted with permission from Ref. 165 Copyright 2011 American Physical Society and Ref. 170 Copyright 2014 American Chemical Society.

The shape effect on the plasmonic response of medium-size nanoparticles were explored using the atomistic electrodynamics approaches.¹⁵⁷ In Ref. 64, the shapes alter from the low symmetry morphologies (cube and octahedron) with less vertices and facets to the high symmetry


Figure 6.4. The optical absorption of bare Ag polyhedral nanoparticles. The absorption spectra are simulated by (a) DDA, (b) DIM, and (c) cd-DIM. The surrounding medium described by a refractive index of n=1.379.

morphologies (truncated-octahedron, cuboctahedron, and icosahedron) with a identical diameter (5.8 nm). The absorption spectra were obtained by the different methods referring to DDA (local dielectric constant and without screening), DIM (without coordination-dependent dielectric function), and cd-DIM to show the importance of screening and nonlocal effects. The simulated absorption spectra are shown in Fig. 6.4. DDA predicts a dipolar plasmon accompanied by multipolar plasmons that blue-shifts with the increasing symmetry of nanoparticles. Particularly for the cubic and the octahedral nanoparticles, the multipolar modes are well separated from the main dipolar modes. This feature is attributed to the low symmetry of nanostructures, which leads to rather complex charge distributions¹⁵⁷. However, both DIM and cd-DIM suggest the higher-order plasmon modes are less important due to the dipole-dipole interaction screening at short distances between two atoms. In cd-DIM, single narrow absorption band is observed for each polyhedral nanoparticle. The vanishing multipolar modes are due to the coordination-dependent atomic polarizability. The atoms sitting on edges and vertexes are assigned relatively larger radii (thus higher polarizability) than those on face and in bulk giving rise to the smooth edges. The theoretical prediction regarding the behavior of multipolar modes is consistent with the recent experimental work where the EELS of icosahedral Ag nanoparticles was measured.¹⁹⁰ Naturally, it is not expected that such shape independence holds for highly anisotropic nanoparticles such as nanorods, of which optical response depends on the different axes of the particle.

6.4 Plasmonic Response of Strongly Coupled Nanoparticles

When individual plasmonic nanoparticles are placed close to each other, the original plasmons interact strongly and create new plasmonic modes. The strongly interacting plasmonic systems have important applications in various fields, including high-sensitivity spectroscopies^{93,191–196}, molecular sensing and imaging^{10,197–201}, and optoelectronics.^{202–207} Thus, great efforts have been made to rationalize the novel plasmonic responses of such systems and unravel the underlying mechanism^{208–216}.

The conceptual picture of plasmon interactions can be described by considering two identical metal nanoparticles approaching each other and forming a dimer⁵³ (see Fig. 6.5 a). As the distance of the two plasmonic monomers reaches the regime of a few nanometers, the two plasmons start to interact strongly and the dimer absorption peak gradually shifts to a lower energy. This red-shifted plasmonic mode is commonly referred to as the "bonding dipolar plasmon" (BDP). This plasmonic mode can be described by the plasmonic hybridization model²¹⁷, which is an classical electrodynamics analogy to the chemical bonding model⁴⁹. In this model the monomer plasmons are considered as electric dipoles, and can be coupled either symmetrically (bonding) or anti-symmetrically (anti-bonding). The symmetrically bonded plasmon is an overall dipolar mode and has a lower energy than the anti-bonding mode. If the gap distance of the dimer system becomes smaller than one nanometer, quantum tunneling becomes prominent and generates a new charge-transfer plasmonic mode (CTP) at a much lower energy than the BDP (usually around a half of the BDP energy). The BDP and CTP are the two dominant plasmon modes in the plasmonic dimer picture and have been experimentally observed ^{50,51,218,219}, although there are also higher-order, e.g., quadrupolar, plasmonic modes for both bonding plasmons and CTPs. The near fields induced within the gap of dimers also exhibit unique features. The near-field distribution and enhancement are determined by the gap distance and the incident frequency. For a strongly interacting plasmonic dimer, the strongest and most confined near field can be obtained at the BDP frequency (Fig. 6.5 b), which has important applications in plasmon-enhanced spectroscopies. 55,85

To correctly model these strongly interacting plasmons, quantum mechanical effects need to be accounted for. A quantum-corrected model (QCM)⁵² was pioneered to incorporate the quantum tunneling effect into classical electrodynamics by describing the dimer gap with a fictitious dielectric material. TDDFT was also used for a quantum mechanical description of the plasmonic dimers²²⁰, where a *jellium* model for the metal atoms was employed to significantly simplify the calculations and thus were able to simulate large nanoparticles²²¹. Both QCM and the *jellium* TDDFT approaches, though lacking the microscopic details for the metal nanostructure, can roughly capture the overall plasmonic responses of dimer systems. Atomistic TDDFT simulations have shown that representing metal nanostructures with atomistic details is necessary to accurately model the localization and enhancement of the near field.^{55,148}

The atomistic electrodynamics model (cd-DIM) has been employed to simulate the confinement and enhancement of the plasmonic near field in sub-nanometer junctions, where the atomistic features of the junction structure determine the local field distribution and the overall plasmonic response. This model not only reproduces the near-field distributions of tip-to-tip, tip-to-face, and face-to-face conformations^{14,85,94,196} when compared with the full quantum mechanics results reported in Ref. 55, but also allows for modeling the near-field distributions perturbed by single small molecules¹⁴. As illustrated in Fig. 6.6, atomically sharp tips of a tip-to-surface junction



Figure 6.5. Typical plasmonic response of a strongly interacting dimer system calculated by an atomistic quantum mechanical approach: (a) Absorption spectra as a function a dimer gap distance; (b) Local field distribution induced by the BDT at gap distance 10 Å, corresponding to the green dot in (a). Reprinted with permission from Ref. 55 Copyright 2015 American Chemical Society.



Figure 6.6. Cross-sectional views of the near field distributions of a plasmonic junction consisting of a Au_{2057} icosahedron and a Au(111) surface, calculated by the atomistic electrodynamics model: (a) facet-to-surface conformation; (b) single atom protrusion tip; (c) single CO molecule tip. Published in Ref. 14.

can significantly enhance and localize the near field down to a sub-molecular length scale. The near field confinement produced by the CO terminated tip is less pronounced than the Au atom terminated tip, which is attributed to the polarizability of the chemical species, which is already sufficient to activate TERS signals upon the introduction of CO into the vacuum STM chamber.¹⁴ Furthermore, the recent research shows that the highly confined field gives rise to large field-gradient volume particularly in a tip-to-surface junction. The field-gradient ratio distributions are sensitive to the local morphology of junctions and drastically modified by the tip curvature. These findings are critical for understanding the origin of high-resolution near-field spectroscopy and for manipulating optical cavities through atomic structures in the strongly coupled plasmonic

systems. The atomistic electrodynamics model was recently extended to simulate periodic 2D nanostructures of silver nanoparticles²²².

6.5 Summary

In this review, we have presented an overview of recent theoretical approaches and results focusing on describing the plasmonic response of metal nanoparticles that retain the atomistic description of the nanoparticles. This growing field of atomistic plasmonics illustrates the importance of accurately describing the nanoparticle structure and interacting molecules for understanding the size, shape, and environment effects on the plasmonic properties. This becomes increasingly important for understanding plasmonic response in the quantum-size regime, strongly coupled plasmonic systems and near-field spectroscopy. Although fully quantum mechanical methods such as TDDFT provide accurate descriptions, they are sometimes excessively computational demanding. The atomistic electrodynamics approach is a promising alternative. By representing each metal atom with a frequency-dependent dielectric function, atomistic electrodynamics models bridge the efficiency of classical methods and the accuracy of quantum mechanical methods. At the same time, the atomistic representation of the nanoparticles allows for capturing the changes in the plasmonic properties due to subtle modifications of the nanoparticles in their microscopic structure, size. The near-field distributions of the nanoparticles can also be accurately described using these models, especially for the strongly interacting systems. Atomistic electrodynamics approaches have important applications in studies of near-field spectroscopies, such as TERS where recent experimental studies are reaching sub-molecular resolution and require atomistic representations of the plasmonic junctions to generate the confined near field.

Chapter 7 Atomistic Characterization of Plasmonic Dimers in the Quantum Size Regime

Liu, P.; Chulhai, D. V.; Jensen, L. Atomistic Characterization of Plasmonic Dimers in the Quantum Size Regime. J. Phys. Chem. C 2019, 123, 13900–13907.*

Abstract

Plasmonic dimer systems show great promise in a wide range of applications due to their unique optical and electronic properties that arise from the coupling of monomer plasmons. To determine the origin of each plasmonic mode and understand the plasmon coupling, atomistic quantum mechanical simulations are required. Here we adopt a Hirshfeld partitioning scheme of atomic charges and polarizabilities within the time-dependent density functional theory framework to study the plasmonic properties of plasmonic dimers. We are able to separate the charge-transfer plasmons due to electron tunneling from local-resonance plasmons by the partitioned polarizabilities and induced charges. We find the strength of charge-transfer plasmons is limited by the charge-flow pathways and dependent on the chemical species. New plasmonic modes for a series of tetrahedral dimers are identified by mapping the induced charges. This approach allows for intuitive and consistent characterizations of strongly coupled plasmonic systems.

L.J. conceived the basic idea. P.L. and D.V.C. implemented the method. P.L. carried out the simulations. P.L. and L.J. analyzed the results and wrote the manuscript.

7.1 Introduction

Strong plasmonic coupling is a key mechanism to many important applications, such as plasmon-enhanced vibrational spectroscopies 193,195,196 , molecular imaging/sensing $^{197-201}$, and optoelectronics $^{202-206,223}$, and the like. Particularly, recent developments of tip-enhanced Raman spectroscopy and nanocavity chemistry $^{10,17,18,85,224-226}$ pose new challenges in understanding plasmonic couplings within a gap of sub-nanometer size.

As two plasmonic nanoparticles approach each other, a "dimer" is formed and the two plasmons are coupled into new bonding modes. When the gap size reaches a sub-nanometer scale, the monomer plasmonic mode red shifts slightly, and a new plasmonic mode emerges at a lower energy. This region of transition is referred to as the quantum regime.⁵⁰ The red shift of the monomer plasmon is attributed to capacitive coupling between the two identical plasmons, which is considered as bonding of the two dipolar plasmon (BDP)⁴⁹. The low-lying dimer plasmon arises from the conductive coupling between the two monomers, named as charge-transfer plasmon (CTP).^{217,227} Theoretical simulations of BDPs and the induced near field can be handled well and consistently using either classical eletrodynamics or quantum mechanical models^{52,55,94,97,209,228}.

In experiments, the transition from BDP to CTP in the quantum region is initially observed before the two nanoparticles makes physical contact ^{50,218,229}, and the CTP becomes stronger and blue shifts when the two nanoparticles are conductively connected ^{51,219}. Classical methods are able to reproduce the conductive CTPs with two overlapping nanoparticles.^{97,228,230,231} But the CTPs with non-overlapping nanoparticles can only be created by introducing artificial conductive medium to bridge the junction. The dimer absorption spectrum measured in experiment is then fully reproduced under the assumption of electron tunneling. To better understand the physical mechanism of the CTPs, quantum mechanical methods are needed. The *jellium* model provides a valid description of CTPs in the quantum tunneling regime, but is limited to large spherical nanoparticles. Due to the increased interests in nanocavities, where the plasmonic response is sensitive to the microscopic structure, atomistic quantum mechanical calculations are needed. Previous work in time-dependent density functional theory (TDDFT) was able to obtain the emergence of CTPs before the nanoparticles overlap.²³² The prominent CTP, as well as other plasmonic modes in the quantum regime, was visualized by mapping the induced surface charge distribution (imaginary part). In Ref. 232, the charge-transfer process for the low-lying CTP is clearly shown to have an overall dipolar charge distribution, while the BDP mode entails two dipolar charge distributions for both nanoparticles aligned along the long axis.

In this work, we use a Hirshfeld partitioning scheme to describe dimer plasmonics in the quantum regime. The Hirshfeld partitioning scheme was originally proposed in 1977²³³, and has become a popular method to study atoms-in-molecule response properties.^{234–236} Based on the partitioning of induced charge densities, intrinsic and charge-fluctuation atomic polarizabilities can be obtained.^{237,238} The charge-fluctuation polarizability describes the polarization of the atom due to delocalized charges upon molecule formulation. It is conceptually intuitive to describe the electron oscillations in plasmonic nanoparticles if extended to frequency-dependent polarizabilities. However, a clear distinction has to be made between the electron oscillation

within a nanoparticle and the charge transfer across the dimer, which we will discuss in detail. The charge transfer across various fragment can be described also by a polarizability. For example, Stone *et al.* proposed the distributed multipole analysis that separates the atoms and the bonds in a molecule.^{239,240} The calculation of bond (interatomic) polarizability was further developed into the computational efficient LoProp method.²⁴¹ It is also noted that various Hirshfeld-based partitioning schemes have been developed in recent years to improve the original Hirshfeld method in terms of neutral pro-atom selection, open-shell systems, efficiency, etc.^{242–246} In principle, other schemes of real-space partitioning of charge densities should work as well.²⁴⁷ In this paper we will adapt the original Hirshfeld method for the sake of simplicity, since the metal nanoparticles are charge-neutral closed-shell species.

In this paper, we demonstrate a clear separation between the CTPs and BDPs in the absorption spectra by partitioning the charge-transfer and local polarizabilities. We also illustrate how the partitioned induced charges are mapped to visualize different plasmonic modes and compare the strengths of CTPs for different metal species.

7.2 Hirshfeld partitioning of molecular polarizability

In this section we briefly review the Hirshfeld partitioning scheme and the modified treatment to a dimer system. Consider a pro-molecule with non-interacting atoms of charge density $\rho_i^{\text{free}}(\mathbf{r})$. The Hirshfeld weight function is constructed as:

$$W_i(\mathbf{r}) = \frac{\rho_i^{\text{free}}(\mathbf{r})}{\sum_j \rho_j^{\text{free}}(\mathbf{r})} \quad , \tag{7.1}$$

where the subscript i(j) is the index of each atom, and **r** is a spatial vector. Then the induced atomic charges are given by partitioning the induced molecular charge density with the weight function:

$$q_{i,\beta} = \int W_i(\mathbf{r})\delta\rho_\beta(\mathbf{r})d\mathbf{r},\tag{7.2}$$

where β denotes the Cartesian direction of the external perturbation, and $\delta \rho_{\beta}(\mathbf{r})$ is the induced molecular charge density obtained from linear-response TDDFT. Subsequently, elements of the atomic polarizability tensor are given by:

$$\alpha_{i,\alpha\beta} = -\int r_{\alpha} W_i(\mathbf{r}) \delta \rho_{\beta}(\mathbf{r}) d\mathbf{r} \quad . \tag{7.3}$$

Here r_{α} is the component of the vector **r** in the α direction. The atomic polarizability can be partitioned into a sum of two contributions as:

$$\begin{aligned} \alpha_{i,\alpha\beta} &= -\left[\int (r_{\alpha} - r_{i,\alpha})W_{i}(\mathbf{r})\delta\rho_{\beta}(\mathbf{r})d\mathbf{r} + \int r_{i,\alpha}W_{i}(\mathbf{r})\delta\rho_{\beta}(\mathbf{r})d\mathbf{r}\right] \\ &= -\int (r_{\alpha} - r_{i,\alpha})W_{i}(\mathbf{r})\delta\rho_{\beta}(\mathbf{r}) \cdot d\mathbf{r} - r_{i,\alpha}q_{i,\beta} \\ &= \alpha_{i,\alpha\beta}^{\text{intrinsic}} + \alpha_{i,\alpha\beta}^{\text{cf}} \quad , \end{aligned}$$
(7.4)

where $r_{i,\alpha}$ denotes the coordinate of the *i*-th atom in *a* direction. Here the total polarizability is partitioned into the sum of an intrinsic term($\alpha_{i,\alpha\beta}^{\text{intrinsic}}$) and a charge-fluctuation term ($\alpha_{i,\alpha\beta}^{\text{cf}}$). The intrinsic term is translation-invariant due to the subtraction of the atomic coordinate, and thus accounts for the induced dipoles localized on each individual atom. The charge-fluctuation polarizability describes the polarization of the atom due to the delocalization of electrons. By summing up all the atomic polarizabilities, we can also partition the total molecular polarizability into intrinsic and charge-fluctuation terms:

$$\alpha_{\alpha\beta} = \alpha_{\alpha\beta}^{\text{intrinsic}} + \alpha_{\alpha\beta}^{\text{cf}} = \sum_{i} \alpha_{i,\alpha\beta}^{\text{intrinsic}} + \sum_{i} \alpha_{i,\alpha\beta}^{\text{cf}}, \qquad (7.5)$$

The molecular charge-fluctuation polarizability describes the polarization of the system due to the collective electron oscillation of the whole system, which closely resembles the concept of plasmonic resonance.

However, in a plasmonic dimer system, it is necessary to distinguish between the electron oscillation within a nanoparticle and the charge transfer across the junction. Therefore, the charge-fluctuation polarizability requires another step of partitioning. In analogy to the intrinsic polarizability, we partition α^{cf} into a translation-invariant term by subtracting the center of mass of the monomers, and then add a charge-transfer term to recover the total polarizability:

$$\alpha_{\alpha\beta}^{\rm cf} = \sum_{i} r_{i,\alpha} q_{i,\beta} = \sum_{M,i\in M} \{ (r_{i,\alpha} - R_{M,\alpha}) \cdot q_{i,\beta} + R_{M,\alpha} \cdot q_{i,\beta} \} = \sum_{i} (\alpha_{i,\alpha\beta}^{\rm intra} + \alpha_{i,\alpha\beta}^{\rm CT}), \quad (7.6)$$

with $R_{M\alpha}$ being the *a* Cartesian component of the mass center of the monomer *M*. Similar polarizability partitioning method was previously used to study water clusters.²³⁸ Here the term α^{intra} is defined as the intra-molecular polarizability, and is translation-invariant. It accounts for the charge fluctuations within the monomer *M*. The second term, α^{CT} , is called the chargetransfer polarizability. It entails the inter-molecular charge transfer between the two monomers in the system.²³⁸. The intrinsic and the intra-molecular polarizabilities are combined into one term describing the "localized" plasmon of the monomer (α^{Local}), and subsequently the dimer polarizability is partitioned into sum of two contributions:

$$\alpha_{\alpha\beta}^{\text{Dimer}} = \left(\alpha_{\alpha\beta}^{\text{intrinsic}} + \alpha_{A,\alpha\beta}^{\text{intra}} + \alpha_{B,\alpha\beta}^{\text{intra}}\right) + \alpha_{\alpha\beta}^{\text{CT}}$$

$$= \alpha_{\alpha\beta}^{\text{Local}} + \alpha_{\alpha\beta}^{\text{CT}}$$
(7.7)

We will demonstrate in the following section that $\alpha_{\alpha\beta}^{CT}$ accounts for CTPs, and the $\alpha_{\alpha\beta}^{Local}$ describes the bonding plasmons.

7.3 Results and Discussion

7.3.1 Absorption spectra of a Na₂₀ dimer

We apply this partitioning scheme to a Na₂₀ tetrahedron dimer. The two Na₂₀ clusters are symmetrically aligned along Z axis in a tip-to-tip configuration (Fig. 7.1a). As the gap distance of the dimer is gradually decreased from ~10 Å to 2.7 Å (1 Å shorter than the Na-Na bonding length), we calculated the absorption spectrum of each distance with the linear-response TDDFT framework. Only the *zz* component of the polarizability tensor (imaginary part) is considered here as it is the dominant element of the polarizability tensors (see Appendix D). The total absorption spectrum (Fig. 7.1b) features three plasmon peaks. The first peak is 2.0 eV at distances longer than 7.5 Å. The second one is 1.63 eV ~ 1.77 eV at shorter distances, which can also be regarded as a transition region from the 2.0 eV peak as the distance decreases. The third one is at ~ 0.9 eV, which appears at distances shorter than 6 Å. The total absorption spectrum agrees well with the literature 50,52,53,55,60,218 , and the three plasmonic peaks can be assigned to a bonding mode and two charge-transfer modes based on their positions in the spectrum.



Figure 7.1. (a) Na_{20} tetrahedron dimer in a tip-to-tip conformation; the distance in the long axis (Z) is defined as the distance between the centers of the two tip atoms; (b) the total absorption spectra of the Na_{20} dimer at various gap sizes; (c) the absorption spectra due to only the charge-transfer plasmons; (d) the absorption spectra due to only the bonding plasmons. The white dash lines denote the length of a Na-Na bond.

We then plot the absorption spectra generated separately from the local and charge-transfer terms partitioned out of the total polarizability (Eq. 7.7). As is shown in Fig. 7.1 c & d, the 0.9 eV peak appears only in the charge-transfer absorption spectrum. It emerges before the tip atoms establish physical contact, which aligns with the concept of CTPs due to electron tunneling. The 2.0 eV mode only exists in the local absorption spectrum. The band of 1.63 eV ~ 1.77 eV appears in both of the spectra in the region between 5 Å and 7.5 Å, which suggests the transition from BDP to CTP. The red-shift of the 2.0 eV mode with respect to the single-monomer peak (see Appendix D) at short gap distances indicates it is a bonding plasmon.

7.3.2 Distribution of induced charges of Na₂₀ dimer

In order to visualize the plasmonic modes and to further confirm the mechanism of each plasmonic mode, we plot the induced atomic charge distribution of each mode (Fig. 7.2). Here we consider only the induced charge (imaginary part) in the Z direction as it is where the charge transfer takes place. The four exemplary cases are marked with blue dots in the absorption spectra (Fig. 7.1b).



Figure 7.2. Imaginary atomic induced charge (Z component) distribution of the Na₂₀ dimer for different plasmonic modes: (a) 0.95 eV at distance 3.7 Å; (b) 1.63 eV at distance 3.7 Å; (c) 1.77 eV at distance 5.2 Å; (d) 2.04 eV at distance 8.7 Å. The net charge for each cluster is noted above it (a.u.). The colorbars contain the ranges of induced atomic charges. The partitioned absorption cross sections, σ^{CT} and σ^{Local} , are provided under each plot.

As is illustrated in Fig. 7.2 a ~ c, the modes at around 0.9 eV and 1.7 eV give rise to large net charges for the metal clusters (provided above each cluster in atomic unit) and have relatively large charge-transfer absorption cross sections (σ^{CT}). The opposing signs of the net charges for

the two clusters indicate that the electrons flow from one cluster to the other. This observation is again in alignment with the intuition of CTPs. At the same distance of 3.7 Å, the two CTPs are shown to have different charge distributions. The 0.95 eV mode (Fig. 7.2 a) exhibits an overall dipolar pattern of induced charges, although the two tip atoms in the gap have charges opposite to their respective cluster bodies. In the 1.63 eV mode (Fig. 7.2 b) the opposing charges in the gap are delocalized, rather than localized only on the two tip atoms, which can be considered as a high-order CTP (CTP'). For the plasmon of 2.0 eV at longer gap distances (Fig. 7.2 d), the charge distribution is dipolar within each cluster, and the net charges are negligible compared with the charge-transfer modes. This confirms the assignment of BDP. The induced charge distributions of these two modes are in good agreement of the results in Ref. 232. Furthermore, local absorption cross sections decrease with decreasing gap sizes, while the charge-transfer absorption becomes stronger. In all four cases, the tip atoms in the junction have the largest induced charges (noted as the maxima in the colorscale bars). The 1.63 eV, 1.77 eV (Fig. 2 c), and the 2.04 eV modes can be regarded as one absorption band, and their charge distributions exhibit the transition from CTPs to local resonances. From Fig. 7.2 b to Fig. 7.2 d, the net induced charges decrease, and the maximal atomic charges becomes larger and more localized on the tip atoms. The bonding plasmon eventually decouples and recovers the monomer modes (see Appendix D).

7.3.3 The facet-to-facet configuration of a tetrahedral dimer

Ideally, one would expect that in a CTP, especially the low-lying dipolar CTP, the charges flow consistently from one cluster to the other. However, all four modes selected above have induced charges in the gap with signs opposite to their respective cluster bodies. We believe this observation results from the atomically narrow pathway limiting the charge flow in the tip-to-tip conformation. To test this hypothesis, we re-arrange the sodium clusters into a facet-to-facet configuration (Fig. 7.3), which effectively broadens the charge-flow pathway. In this case the onset of the CTPs is at a even longer distance and they are much stronger. For the primary CTP that spans 1.3 eV \sim 1.7 eV (Fig. 7.3d), the charges of the gap atoms are of the same sign as their cluster bodies, and the whole dimer is a consistent dipole. In the high-order charge-transfer mode of ~ 2.0 eV at short distances, the local term also contributes strongly to the absorption. This is captured in Fig. 7.3e, where we see high cross sections of the local term, and dipolar charge distribution within a certain cluster. At long distances (Fig. 7.3f), the plasmonic resonance again converges with the monomer mode with vanishing net charges of both monomers. Interestingly, the CTP in the this facet-to-facet configuration blue-shifts, which agrees with experimental observations 50,218. However, for the tip-to-tip configurations, CTP red-shifts for decreased distances. We believe this can be attributed to the finite size effect (large spherical nanoparticles are used in experiments) and the limit charge-transfer pathway.



Figure 7.3. Absorption spectra of the Na₂₀ dimer in a facet-to-facet conformation: (a) total absorption; (b) charge-transfer absorption; (c) local absorption. Imaginary atomic induced charge (Z component) distribution: (d) 1.64 eV at distance 4.7 Å; (e) 2.0 eV at distance 4.7 Å; (f) 2.0 eV at distance 9.2 Å.

7.3.4 Ag₂₀ dimer and Ag₂₀ dimer

We expand the Hirshfeld partitioning analysis to silver and gold, the two most common plasmonic materials. Adopting the similar but re-optimized tetrahedral structures, we calculate the absorption spectra of Ag₂₀ dimer (Fig. 7.4) and Au₂₀ dimer (Fig. 7.5), and map the atomic induced charges for the exact descriptions of plasmonic modes. The Ag₂₀ dimer also has three main plasmonic modes: ~1.6 eV and ~3.2 eV at short gap distances, and ~3.6 eV for large gaps. The presence of these three peaks agrees with previous reports²¹⁸. The partitioned spectra (Fig. 7.4 b & c) show that the 1.6 eV and 3.2 eV modes are CTPs and the 3.6 eV plasmon is a bonding mode. Comparing the two CTPs (Fig. 7.4 d & e), one can find the 1.6 eV mode (primary CTP) has more charge-transfer contribution than the 3.2 eV mode (high-order CTP), as is indicated by the net charges and the partitioned absorption cross sections. The 3.2 eV mode also benefits largely from the local resonance, and the induced charges are more localized in the junction than the primary CTP (Fig. 7.4e). And the 3.6 eV mode is a pure local bonding plasmon as the monomers have negligible net charges and nearly zero charge-transfer cross section.



Figure 7.4. Partitioned absorption spectra of the Ag₂₀ dimer in the tip-to-tip conformation: (a) \sim (c). Induced atomic charge distributions: (d) 1.90 eV at distance 3.8 Å; (e) 3.26 eV at distance 3.8 Å; (f) 3.67 eV at distance 8.3 Å.

The Au₂₀ tetrahedron dimer has more complicated absorption spectra than the sodium and silver dimers, especially for the charge-transfer term (Fig. 7.5 b). In the case of gap distance ~ 3.7 Å (Fig. 7.5 d \sim f), there are three charge-transfer peaks: 1.90 eV, 2.31 eV and 2.85 eV. The 1.90 eV mode is the primary CTP, similar to the lowest-lying peaks of the sodium and silver systems. The 2.31 eV mode at gap distance 3.7 Å is a high-order CTP of the gold dimer, and it has a similar charge distribution pattern to the high-order CTPs of sodium and silver. The slight difference is that for the 2.31 eV mode of the gold dimer, the atomic charges are more evenly distributed among the four tetrahedral vertices, instead of being strongly localized only in the junction. Interestingly, the induced charges of the 2.85 eV mode are found to be localized on the second layer of the junction atoms for each cluster (Fig. 7.5 f), instead of on the two tip atoms. It can be considered as an even higher-order CTP. The long-distance bonding mode (3.13 eV in Fig. 7.5 g) exhibit features similar to the sodium and silver dimers, which is evidenced by the zero charge-transfer cross section and nearly zero net charges of the monomers.



Figure 7.5. Partitioned absorption spectra of the Au₂₀ dimer in the tip-to-tip conformation: (a) \sim (c). Imaginary atomic induced charge (Z component) distribution: (d) 1.90 eV at distance 3.7 Å; (e) 2.31 eV at distance 3.7 Å; (f) 2.85 eV at distance 3.7 Å; (g) 3.13 eV at distance 8.2 Å.

Comparing the tip-to-tip tetrahedron dimers of Na_{20} , Ag_{20} , and Au_{20} , we find some common features of the charge-transfer plasmons. Generally there are two prominent CTPs found in the three cases. The primary CTP is the lowest in energy, and gives rise to the largest cluster net charges. The secondary CTP has a higher energy, which is usually slightly lower than the bonding plasmon energy and can be regarded as a transition from the bonding mode. Due to the tetrahedron shape, it is hard to define this mode as quadrupolar, but the difference in the induced charge distributions reveals that it is a high-order CTP. However, in this high-order CT mode, the local plasmon also contributes strongly to the absorption. This is also implied by the smaller cluster net charges compared to the primary CTP. As a matter of fact, the local term has consistently larger absorption cross sections than the CTP cross section throughout the absorption spectrum, which suggests that the local resonance is pervasively the dominant factor of a plasmonic dimer system. Additionally, more high-order CTPs are observed in the gold dimer system. Strictly speaking, similar high-order CTPs also exist in the other two systems, but their cross sections are approximately zero. Overall the sodium dimer has the strongest absorption for both the charge-transfer and local terms, and the gold dimer has the weakest. This can be explained by the availability of d-orbital electrons. Noble metal clusters like Ag and Au have strong s-d hybridization, and thus it's harder to excite the electrons to the conduction band to be transferred across the the two monomers than simple metals like Na.¹⁶⁷

7.4 Conclusion

In summary, we have studied the plasmonic properties of a series of small tetrahedron dimers using the Hirshfeld partitioned atomistic polarizabilities within the TDDFT framework. By separately plotting the absorption spectra based on the two different terms of the polarizabilities, we have clearly partitioned the dimer absorption into the charge-transfer absorption and the local absorption. Generally there are two prominent CTPs in the dimer systems that emerge at short gap distances. We have also mapped the induced charges distribution atomistically, which presents an intuitive and consistent description of the plasmonic modes. Based on the induced charge distributions and the net charges for each cluster in a specific mode, we are able to identify the CTPs between each other and from the local-resonance modes, which complements the characterization by absorption spectra. The Hirshfeld partitioning scheme we adopted in this work distinguishes the intra- and inter-molecular charge fluctuations. The partitioning of the total polarizability and induced atomic charges provides a well-defined analysis methods of dimer plasmonics in the quantum tunneling regime. Such analysis can be generalized for studies of two-fragment systems.

Methods

A locally modified version of the Amsterdam Density Functional (ADF) program package^{73–75} was used to carry out the calculations. The Becke-Perdew (BP86)^{76,77} exchange-correlation functional and the triple- ζ polarized (TZP) Slater-type basis set from the ADF library were used for the geometry optimizations of the monomer clusters.

A dimer was constructed by the optimized monomer and its mirror geometry with respect to the Cartesian origin in the Z direction. Then the gap distance of the dimer was gradually increased by translating the coordinates along the Z axis with a step size of 0.5 Å. For each gap distance, the frequency-dependent polarizabilities of the system were calculated with the incident light frequencies. The scanned frequencies, with a step size of 0.005 atomic unit (a.u.), ranged from 0.020 a.u. to 0.105 a.u. for the Na₂₀ dimer, 0.040 a.u. to 0.170 a.u. for the Ag₂₀ dimer, and from 0.020 a.u. to 0.140 a.u. for the au₂₀ dimer. All polarizabilities were calculated using the AOResponse module implemented in ADF with a finite excited-state lifetime of $\Gamma =$ 0.1 eV⁷⁸⁻⁸², and the Adiabatic Local Density Approximation (ALDA). The statistical average of orbital model exchange-correlation potentials²⁴⁸ was employed together with the triple- ζ polarized (TZP) Slater-type basis set from the ADF library. The scalar relativistic effects were accounted for by the zeroth-order regular approximation²⁴⁹. The partitioned atomic polarizabilities and atomic charges were obtained in ADF with a local implementation of the Hirshfeld partitioning scheme described in the main text. The absorption cross section at a frequency ω was calculated as:

$$\sigma_{abs}(\omega) = \frac{4\pi\omega n}{c} \cdot Im\{\alpha_{zz}(\omega)\},\tag{7.8}$$

where n is the refractive index of the environment (in this work, vacuum), and c is the speed

of light. The zz element of the polarizability tensor , α_{zz} , can be from either the total or the partitioned polarizabilities as derived in the main text.

All molecular geometries and induced atomic charge distributions were rendered using the Visual Molecular Dynamics (VDM) 1.9.3 software⁸⁴.

Part IV

Frozen Density Embedding

Chapter 8 Exact Frozen Density Embedding for the Time-Dependent Density Functional Theory

Abstract

This chapter describes an exact frozen density embedding (FDE) method within the framework of time-dependent density functional theory (TDDFT). In the first section, a brief introduction to the FDE method for the molecular ground states is provided to describe the general idea of FDE. The chapter derives the exact FDE method for molecular response properties with an emphasis on the polarizabilities. It approaches the polarizability from both the sum-over-states (SOS) method, which involves calculating the excitation energies and transition dipole moments, and the linear response theory that directly yields the polarizabilities. We will demonstrate that both methods provides exact results when compared with those obtained by conventional TDDFT ("supermolecular") calculations.

8.1 Introduction

For plasmon-enhanced spectroscopies including SERS and TERS, both EMM and CM contribute to the signal enhancement¹⁴². EMM accounts for the molecular responses to the local field induced by plasmons, while CM encodes the modifications of the geometry and electronic structure of the molecule adsorbed on a metallic surface. EMM is usually considered as the dominating mechanism to the signal enhancement of vibrational spectroscopies; however, CM can be just as important in that it is responsible for changes of spectral shapes due to changes in the molecule's electronic structure.⁹³

In the DIM/QM model, the metal-molecule interaction is treated by an additional DIM operator incorporated into the molecular time-dependent Hamiltonian. Although previous work suggests that DIM/QM captures most of the EMM enhancement in TERS, the description of CM is limited to the mutual polarization and classical dispersion/repulsion. The dispersion/repulsion potential at the metal-molecule interface is represented by a Lennard-Jones (LJ)-type force field. The LJ potentials are chemical species specific, of which the parameters are obtained by fitting against full QM calculations or experimental data. While the LJ force field approximately reproduced the molecule-metal bonding energies, it is not able to include charge transfer effects. Full QM calculations such as TDDFT can describe the metal-molecule interactions accurately, but is limited by its expensive computational cost when treating high density-of-states systems such as metal nanoparticles. Moreover, full QM treatment of a metal-molecule system can introduce more complications when the properties of interests are mostly localized on the molecule. For example, to simulate TERS, one would need to separate the molecular polarizabilities from the metal fragment whereas conventional TDDFT procedures provide only the polarizability of the total system.

One alternative to full QM calculations is subsystem DFT, or specifically, frozen density embedding (FDE)^{179,250}. In FDE, the electron density of one subsystem is kept "frozen", and the energy of the whole system is minimized with respect to the other subsystem (noted as "active"). The FDE theory allows for the partitioning of the system into fragments of reasonable chemical intuition²⁵¹, which in the case of TERS can be the active molecule and the frozen metal junction. FDE is exact in the limit of exact energy functionals²⁵². The inter-fragment interactions are described quantum mechanically, which eliminates the requirement of force field parameterization. Thus, one would expect a more accurately described molecule-metal interface than the classical force field in DIM/QM.

In the partitioning of the whole system into fragments, the total energy can be expressed as the sum of subsystem energies. However, in the presence of inter-fragment molecular orbital (MO) overlaps, there exists non-additive kinetic energy and XC energy that make the sum of energies of the two fragments not exact. While the non-additive XC energy can be well approximated by readily available density functionals, the non-additive kinetic energy requires more careful treatment for FDE to be exact. One popular approach is to eliminate the non-additive energies by making the MOs of the fragments orthogonal to each other (external orthogonality).²⁵³ The external orthogonality (EO) is achieved by the implementation of a level-shifted projection

operator to the Fock matrix of the embedded system so that overlapping MOs are lifted to an infinitely high energy and decoupled²⁵⁴. The FDE-EO approach has proven to be accurate for both ground-state and excited-state calculations, even for strongly coupled systems.^{255–257} In this chapter, I will derive the theory of exact FDE, and provide preliminary results to demonstrate its exactness in calculating molecular polarizabilities from both the sum-over-state and linear-response approaches.

8.2 Exact Frozen Density Embedding for TDDFT

8.2.1 Supermolecular Kohn-Sham DFT

The expression of the system's total energy in Kohn-Sham(KS) DFT²⁵⁸ is written as a sum of various functionals of electron density ρ^{259} :

$$E[\rho] = E_{\rm nn} + E_{\rm nuc}[\rho] + E_{\rm Coul}[\rho] + E_{\rm xc}[\rho] + T_{\rm s}[\rho] , \qquad (8.1)$$

where the different terms from left to right represent the nucleus-nucleus repulsion, electronnucleus interaction, electron-electron Coulomb interaction, exchange-correlation energy, and non-interacting kinetic energy, respectively. These terms are written as

$$E_{\rm nn} = \sum_{I,J}^{N} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \; ; \tag{8.2a}$$

$$E_{\rm nuc}[\rho] = \int \rho(\mathbf{r}) v_{\rm nuc}(\mathbf{r}) d\mathbf{r} , \quad \text{with } v_{\rm nuc}(\mathbf{r}) = \sum_{I} \frac{Z_{I}}{|\mathbf{R}_{I} - \mathbf{r}|} ; \qquad (8.2b)$$

$$E_{\text{Coul}}[\rho] = \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' ; \qquad (8.2c)$$

$$E_{\rm xc}[\rho] = (E_{\rm ee}[\rho] - E_{\rm Coul}[\rho]) + (T[\rho] - T_{\rm s}[\rho]) ; \qquad (8.2d)$$

where N is the total number of nuclei, Z_I, Z_J represent the nucleus charges, $\mathbf{R}_I, \mathbf{R}_J$ are the coordinates of the nuclei, and v_{nuc} is the electrostatic potential from the nuclei. The electron density is obtained with Kohn-Sham orbitals $\phi_i(\mathbf{r})$

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 . \qquad (8.3)$$

Under the constraint of preserving total number of electrons and Kohn-Sham orbitals being orthonormal, the total energy is minimized, which leads to the Kohn-Sham equations (effective single-particle Schödinger Equations):

$$\left(-\frac{\nabla^2}{2} + v_{\text{eff}}[\rho(\mathbf{r})]\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}), \quad i = 1,\dots, N , \qquad (8.4)$$

with the effective potential $v_{\text{eff}}[\rho(\mathbf{r})] = v_{\text{nuc}}(\mathbf{r}) + v_{\text{Coul}}[\rho(\mathbf{r})] + v_{\text{xc}}[\rho(\mathbf{r})].$

8.2.2 Subsystem DFT

The main idea of a subsystem DFT method is to partition the total electron density $\rho_{tot}(\mathbf{r})$ into the electron densities of two (K in general) fragments, I and J:

$$\rho_{\rm tot}(\mathbf{r}) = \rho_{\rm I}(\mathbf{r}) + \rho_{\rm J}(\mathbf{r}) \tag{8.5}$$

The subsystem densities are expressed by the orbitals of the subsystem's corresponding orbitals, similar to (8.3). Besides that each subsystem density should integrate into an integer number of electrons, they are not subject to any other conditions. In general, the subsystem densities are allowed to overlap. In practice, the partitioning is usually intuitively done in line with chemical concepts.

Given this partitioning of the electron density, the DFT total energy can be expressed as a bi-functional of $\rho_{\rm I}$ and $\rho_{\rm J}$, similar to (8.1):

$$E[\rho_{\mathrm{I}}, \rho_{\mathrm{J}}] = E_{\mathrm{nn}} + \int \left(\rho_{\mathrm{I}}(\mathbf{r}) + \rho_{\mathrm{J}}(\mathbf{r})\right) \left(v_{\mathrm{I}}^{\mathrm{nuc}}(\mathbf{r}) + v_{\mathrm{J}}^{\mathrm{nuc}}(\mathbf{r})\right) d\mathbf{r}$$
(8.6)

$$+\frac{1}{2}\int \frac{\left(\rho_{\mathrm{I}}(\mathbf{r})+\rho_{\mathrm{J}}(\mathbf{r})\right)\left(\rho_{\mathrm{I}}'(\mathbf{r})+\rho_{\mathrm{J}}'(\mathbf{r})\right)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'$$
(8.7)

$$+E_{\rm xc}[\rho_{\rm I},\rho_{\rm J}] + T_s[\rho_{\rm I}] + T_s[\rho_{\rm J}] + T_s^{\rm nad}[\rho_{\rm I},\rho_{\rm J}], \qquad (8.8)$$

where the E_{nn} is again the nuclei repulsion energy, v_A^{nuc} and v_B^{nuc} are electrostatic potentials from the nuclei in the two subsystems, E_{xc} is the exchange-correlation energy functional, $T_s[\rho]$ is the kinetic energy of the non-interacting system. T_s^{nad} is the non-additive kinetic energy. It accounts for the error in calculating the kinetic energy due to the splitting of total electron density.

$$T_s^{\text{nad}}[\rho_{\rm I}, \rho_{\rm J}] = T_s[\rho_{\rm I} + \rho_{\rm J}] - T_s[\rho_{\rm I}] - T_s[\rho_{\rm J}].$$
(8.9)

In practical implementations the non-additive kinetic energy is either approximated with a kineticenergy functional, or eliminated in projection-based method that ensures external orthogonality, which will be discussed in detail later in this chapter. Strictly speaking, a similar non-additive term also exist for the exchange-correlation energy; however, it can be obtained in the limit of available exchange-correlation functionals.

For a given density $\rho_{\rm J}$ in one of the subsystems, the electron density $\rho_{\rm I}$ in the other subsystem can be determined by minimizing the total energy bi-functional with respect to $\rho_{\rm I}$ ("active"), which $\rho_{\rm J}$ is kept unchanged ("frozen"). The interaction between the two fragments is treated as an embedding potential on the active fragment due to the presence of the frozen fragment. This method is then termed "frozen density embedding" (FDE)²⁶⁰.

The minimization of the total energy with respect to $\rho_{\rm I}$ under the constraint that the number

of electrons $N_{\rm I}$ in subsystym I is conserved leads to the condition:

$$0 = \frac{\delta}{\delta\rho_{\rm I}} \left[E[\rho_{\rm I}, \rho_{\rm J}] + \lambda_{\rm I} \left(\int \rho_{\rm I}(\mathbf{r}) d\mathbf{r} - N_{\rm I} \right) \right]$$

$$= v_{\rm I}^{\rm nuc}(\mathbf{r}) + v_{\rm J}^{\rm nuc}(\mathbf{r}) + \int \frac{\rho_{\rm I}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \int \frac{\rho_{\rm J}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

$$+ \frac{\delta E[\rho_{\rm I} + \rho_{\rm J}]}{\delta\rho_{\rm I}} + \frac{\delta T_s[\rho_{\rm I}]}{\delta\rho_{\rm I}} + \frac{\delta T_s^{\rm nad}[\rho_{\rm I}, \rho_{\rm J}]}{\delta\rho_{\rm I}} + \lambda_{\rm I} , \qquad (8.10)$$

where $\lambda_{\rm I}$ is the Lagrange multiplier. The electron density $\rho_{\rm I}$ is expressed $\rho_{\rm I}(\mathbf{r}) = \sum_{i}^{N_{\rm I}} |\phi_i|^2$ in terms of the KS orbitals $\{\phi_i^{({\rm I})}(\mathbf{r})\}$ of subsystem I.

In the above equation, one can group all the terms that are related to subsystem J into one effective embedding potential $v_{\text{eff}}^{\text{emb}}[\rho_{\text{I}}, \rho_{\text{J}}](\mathbf{r})$:

$$v_{\text{eff}}^{\text{emb}} = v_{\text{J}}^{\text{nuc}}(\mathbf{r}) + \int \frac{\rho_{\text{J}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}^{\text{nad}}[\rho_{\text{I}}, \rho_{\text{J}}]}{\delta \rho_{\text{I}}} + v_{T}[\rho_{\text{I}}, \rho_{\text{J}}](\mathbf{r}) , \qquad (8.11)$$

where $v_T[\rho_I, \rho_J](\mathbf{r})$ is the non-additive kinetic potential (NAKP). Thus, for a given frozen density ρ_J , the density of the active subsystem can be obtained by solving the following KS-like equations:

$$\left[-\frac{\nabla^2}{2} + v_{\text{eff}}^{\text{KS}}[\rho_{\text{I}}](\mathbf{r}) + v_{\text{eff}}^{\text{emb}}[\rho_{\text{I}}, \rho_{\text{J}}](\mathbf{r})\right]\phi_i^{(\text{I})}(\mathbf{r}) = \epsilon_i \phi_i^{(\text{I})}(\mathbf{r}) ; \quad i = 1, \dots, N_{\text{J}} \quad , \tag{8.12}$$

where the environment (or nanoparticle) is represented by the effective embedding potential.

Minimization of the total system energy is usually achieved through "freeze-and-thaw" cycles, where the role of the two fragments are iteratively interchanged in the FDE calculations until the convergence of both fragment densities. This procedure makes FDE equivalent to supermolecular DFT calculations in the limit of exact NAKP.

8.2.3 Non-additive kinetic energy and external orthogonality

The existence of the NAPK arises from failing to fulfill the condition where the KS orbitals of the two subsystems are orthogonal to each other (external orthogonality, EO). It can be approximated by a functional of electron density. The kinetic energy density functionals (KEDFs) have been widely used in orbital-free(OF) DFT methods. The simplest form of KEDFs is the Thomas-Fermi (TF) functional^{261,262}, a local density approximation to the KEDF. It is defined as:

$$T_s^{\rm TF} = C_{\rm TF} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} = \frac{3}{10} (3\pi^2)^{2/3} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} \quad , \tag{8.13}$$

where $C_{\rm TF}$ is the Thomas-Fermi constant.

In the case where the KS orbitals of the two subsystems are mutually orthogonal, $T^{\text{nad}} = 0$, which is desired since it makes the FDE method exact. One way of enforcing EO is to use a projection operator \hat{P} , which essentially introduces an additional projection potential term on the left-hand side of (8.12). In general, the projection term removes the contributions of the molecular orbitals of the frozen fragment (J) from the occupied orbitals of the active fragment (I) such that the orbitals of the two subsystems are kept orthogonal. Common projection-based embeddings include the level-shift embedding²⁶³), the Huzinaga embedding²⁶⁴, and Hoffman embedding²⁶⁵, among which the level-shifting embedding has recently gained popularity due to its accuracy and scaling efficiency^{254,257}.

The Fock matrix of the embedded system (I) in the atomic orbital (AO) basis with the projection operator is:

$$f_{ij}^{\rm EO} = f_{ij}^{\rm FDE} + \mu P_{\rm ij}^{\rm J}, \qquad (8.14)$$

where i, j are AO indices of subsystem A. The first term on the right hand side is the regular FDE Fock matrix. The projection operator is defined as:

$$P_{ij}^{J} = \langle \chi_{i}^{I} | \left\{ \sum_{k \in J} |\phi_{k}^{J}\rangle \langle \phi_{k}^{J} | \right\} | \chi_{j}^{J}\rangle$$

$$= \sum_{m,n \in J} \langle \chi_{i}^{I} | \chi_{m}^{J}\rangle \gamma_{mn}^{J} \langle \chi_{n}^{J} | \chi_{j}^{I}\rangle$$

$$= \left[\mathbf{S}^{I,J} \gamma^{J} \mathbf{S}^{J,I} \right]_{ij}, \qquad (8.15)$$

where χ^{I} and χ^{J} are sets of AO basis functions describing subsystem I and J. $\{\phi^{J}\}$ are KS orbitals of subsystem J. γ^{J} is the density matrix of subsystem J. $\mathbf{S}^{I,J} = (\mathbf{S}^{J,I})^{T}$ is the overlap matrices between the AOs of the two subsystems. The term $\mu \mathbf{P}^{J}$ raises the the energy of the k-th orbital of subsystem J to $\epsilon_{k}^{J} + \mu$. The orbitals of the two fragments are essentially de-coupled in the limit of $\mu \to \infty$. In practice, μ is usually chosen to be a very large number, e.g., $10^{6} E_{h}$. Previous work in the group²⁵⁴ has implemented the method. The typical workflow includes identifying the fragments of the supermolecular system, determination of the overlap region, KS DFT calculation of each fragment with the overlap region represented by empty AOs, and finally the FDE-EO calculation with freeze-and-thaw cycles. It has been demonstrated that the KS-DFT densities of both weakly and strongly coupled fragments are reproduced exactly. Hereafter, the level-shifting embedding method is used to derive the exact FDE-TDDFT method.

8.3 Exact Frozen Density Embedding in TDDFT

8.3.1 A brief review of the supermolecular TDDFT

The response of the electron density in the frequency domain is

$$\delta\rho(\mathbf{r},\omega) = \int \chi^s(\mathbf{r},\mathbf{r}',\omega)\delta v^{\text{eff}}(\mathbf{r}',\omega)d\mathbf{r}', \qquad (8.16)$$

which describes the relationship between the first-order change in electron density and the effective perturbation potential (δv^{eff}) via the response function, $\chi(\mathbf{r}, \mathbf{r}', \omega)$

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \sum_{i, a, \sigma} \phi_{i\sigma}(\mathbf{r}) \phi_{a\sigma}(\mathbf{r}) \phi_{i\sigma}(\mathbf{r}') \phi_{a\sigma}(\mathbf{r}') \left[\frac{1}{\epsilon_{ia\sigma} + \omega} + \frac{1}{\epsilon_{ia\sigma} - \omega} \right]$$
(8.17)

where $\epsilon_{ia\sigma} = \epsilon_{a\sigma} - \epsilon_{i\sigma}$ is the KS orbital ($\phi(\mathbf{r})$) energy difference, *i*, *a* are indices of the KS orbitals, and σ represents spins. The (changes in) effective potential consists of an external potential and the induced electronic potential due to density response:

$$\delta v^{\text{eff}}(\mathbf{r}') = \delta v^{\text{ext}}(\mathbf{r}') + \delta v^{\text{el}}(\mathbf{r}') = \delta v^{\text{ext}}(\mathbf{r}') + \int f(\mathbf{r}, \mathbf{r}', \omega) \delta \rho(\mathbf{r}', \omega) d\mathbf{r}' \quad .$$
(8.18)

The quantity $f(\mathbf{r}, \mathbf{r}', \omega)$ is called the **response kernel**, which consists of

$$f(\mathbf{r}, \mathbf{r}', \omega) = f_{\text{Coul}} + f_{\text{xc}} = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta v_{\text{xc}}(\mathbf{r}')}{\delta \rho(\mathbf{r}')} = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[\rho](\mathbf{r})}{\delta \rho(\mathbf{r})\delta \rho(\mathbf{r}')} \quad .$$
(8.19)

The density response $\delta \rho$ can also be expressed as²⁶⁶:

$$\delta \rho_{\sigma}(\mathbf{r},\omega) = 2 \sum_{i,j} \delta P_{ij\sigma}(\omega) \phi_{i\sigma}(\mathbf{r}) \phi_{j\sigma}(\mathbf{r}) \quad , \qquad (8.20)$$

where $\delta P_{ia\sigma}$ is the coefficient for the orbital product in the expansion of density change. The subscripts i, j represent the orbital indices and the the letter σ, τ represent the spin. The factor of 2 on the right-hand side is due to the presumption that only closed-shell systems are considered. The response equation defined with the density matrix coefficients is then

$$\delta P_{ij\sigma} = \sum_{k,l,\tau} V_{kl\tau} \chi_{ij\sigma,kl\tau} . \qquad (8.21)$$

The response function for an independent particle system is defined as:

$$\chi_{ij\sigma,kl\tau} = \delta_{\sigma\tau} \delta_{ik} \delta_{jl} \frac{n_{j\sigma} - n_{i\sigma}}{\omega - \epsilon_{ij\sigma}} , \qquad (8.22)$$

where n denotes the occupation number, and $\epsilon_{ij\sigma} = \epsilon_{j\sigma} - \epsilon_{i\sigma}$ represents the energy difference of the KS orbitals.

The electronic perturbation due to density response is given as:

$$\begin{split} \delta v_{ij\sigma}^{el} &= \sum_{kl\tau} \int d\mathbf{r} \int d\mathbf{r}' \bigg[\phi_j^*(\mathbf{r}) \phi_i(\mathbf{r}) f(\mathbf{r}, \mathbf{r}', \omega) \phi_k(\mathbf{r}') \phi_l^*(\mathbf{r}') \bigg] \delta P_{kl\tau}(\omega) \\ &= \sum_{kl\tau} K_{ij\sigma, kl\tau}(\omega) \delta P_{kl\tau}(\omega). \end{split}$$

 $f(\mathbf{r}, \mathbf{r}', \omega)$ is the response kernel. $K_{ij\sigma,kl\tau}$, an element of the coupling matrix **K**, which determines

the response of the electronic potential $\delta \mathbf{v}^{\text{ind}}$ due to the electron density perturbation $\delta \mathbf{P}$:

$$K_{ij\sigma,kl\tau} = \frac{\delta v_{ij\sigma}}{\delta P_{kl\tau}}$$
(8.23)

With $\delta P_{ij\sigma} = \sum_{k,l,\tau} \delta_{\sigma\tau} \delta_{ik} \delta_{jl} \cdot \delta P_{kl\tau}$, we arrive at the following expression by combining the above equations:

$$\delta P_{ij\sigma}(\omega) = \frac{n_{i\sigma} - n_{j\sigma}}{\omega - \epsilon_{ij\sigma}} \left[\delta v_{ij\sigma}^{\text{ext}} + \sum_{kl\tau} K_{ij\sigma,kl\tau} \delta P_{kl\tau}(\omega) \right]$$
(8.24a)

$$\sum_{\mathrm{kl}\tau} \left[\delta_{\sigma\tau} \delta_{\mathrm{ik}} \delta_{\mathrm{jl}} \frac{\omega - \epsilon_{\mathrm{ij}\sigma}}{n_{\mathrm{i}\sigma} - n_{\mathrm{j}\tau}} - \sum_{\mathrm{kl}\tau} K_{\mathrm{ij}\sigma,\mathrm{kl}\tau} \right] \delta P_{\mathrm{kl}\tau} = \delta v_{\mathrm{ij}\sigma}^{\mathrm{ext}}$$
(8.24b)

Here we have assumed that all orbitals are real and have Aufbau occupations (0 or 1). From now on, we will also restrict that ALDA approximation is used such that f^{xc} is frequency independent, and that the use of $f^{\text{xc}}(\mathbf{r}, \mathbf{r}')$ further simplifies that $K_{ij\sigma,jk\tau} = K_{ij\sigma,lk\tau} = K_{ji\sigma,lk\tau}$.

The expressions in (8.24) are the same equation in two different forms. We will first use (8.24b) to derive the equation of which the solutions are the excitation energies. Restricting i, j for occupied orbitals and a, b for virtual orbitals (i < a, j < b), we can split the (8.24b) into two parts:

$$\sum_{jb\tau}^{j(8.25a)$$

then another equation for the rest

$$\sum_{jb\tau}^{j(8.25b)$$

Rewriting the above linear system of equations in matrix notation, we arrive at:

$$\begin{bmatrix} \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{bmatrix} - \omega \begin{pmatrix} \mathbf{C} & \mathbf{0} \\ \mathbf{0} & -\mathbf{C} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \begin{pmatrix} \mathbf{V} \\ \mathbf{W} \end{bmatrix}$$
(8.26)

with

$$A_{ia\sigma,jb\tau} = \delta_{\sigma\tau} \delta_{ij} \delta_{ab} \frac{\epsilon_{ia\sigma}}{n_{b\tau} - n_{j\tau}} - K_{ia\sigma,jb\tau}$$
(8.27a)

$$B_{ia\sigma,jb\tau} = -K_{ia\sigma,bj} \tag{8.27b}$$

$$C_{ia\sigma,jb\tau} = -\delta_{\sigma\tau}\delta_{ij}\delta_{ab}\frac{1}{n_{b\tau}}$$
(8.27c)

$$X_{jb\tau} = \delta P_{jb\tau}; \quad Y_{jb\tau} = \delta P_{bj\tau}$$
(8.27d)

$$W_{jb\tau} = V_{bj\tau}$$
 are the matrix elements of the external perturbation. (8.27e)

Inserting the following unitary transformation between $(\mathbf{X}, \mathbf{Y})^T$ and the bracket in (8.26), and

multiplying the whole equation from the left by $\sqrt{2}\mathbf{U}$,

$$\mathbf{U}^{\dagger}\mathbf{U} = \mathbf{1}, \quad \mathbf{U} = \frac{1}{\sqrt{2}} \begin{pmatrix} \mathbf{1} & \mathbf{1} \\ -\mathbf{1} & \mathbf{1} \end{pmatrix}, \tag{8.28}$$

we obtain

$$\begin{bmatrix} \begin{pmatrix} \mathbf{A} + \mathbf{B} & \mathbf{0} \\ \mathbf{0} & \mathbf{A} - \mathbf{B} \end{pmatrix} + \omega \begin{pmatrix} \mathbf{0} & \mathbf{C} \\ \mathbf{C} & \mathbf{0} \end{bmatrix} \begin{pmatrix} \mathbf{X} + \mathbf{Y} \\ \mathbf{Y} - \mathbf{X} \end{pmatrix} = \begin{pmatrix} \mathbf{V} + \mathbf{W} \\ \mathbf{W} - \mathbf{V} \end{pmatrix}$$
(8.29)

(8.29) can be separated into two linear system of equations

$$(\mathbf{A} + \mathbf{B})(\mathbf{X} + \mathbf{Y}) + \omega \mathbf{C}(\mathbf{Y} - \mathbf{X}) = (\mathbf{V} + \mathbf{W})$$
(8.30a)

$$(\mathbf{A} - \mathbf{B})(\mathbf{Y} - \mathbf{X}) + \omega \mathbf{C}(\mathbf{X} + \mathbf{Y}) = (\mathbf{W} - \mathbf{V})$$
(8.30b)

In case of a real external field, $\mathbf{V} = \mathbf{W}$. The symmetric part of $\delta P_{ia\sigma}$, $(\mathbf{X} + \mathbf{Y})$, is then

$$\left[(\mathbf{A} + \mathbf{B}) + \omega^2 \mathbf{S} \right] (\mathbf{X} + \mathbf{Y}) = 2\mathbf{V}.$$
(8.31)

with $\mathbf{S} = -\mathbf{C}(\mathbf{A} - \mathbf{B})^{-1}\mathbf{C}$. We will focus on $(\mathbf{X} + \mathbf{Y})$ first because of its relevance for the polarizability, and this equation is basically the working equation of TDDFT. Starting from this equation, one usually inserts $\mathbf{1} = \mathbf{S}^{-1/2}\mathbf{S}^{1/2}$ in front of $(\mathbf{X} + \mathbf{Y})$ and multiplies the whole equation from the left by $\mathbf{1} = \mathbf{S}^{-1/2}$, and obtain the following equation:

$$\begin{bmatrix} \mathbf{S}^{-1/2} (\mathbf{A} + \mathbf{B}) \mathbf{S}^{-1/2} + \omega^2 \end{bmatrix} \mathbf{S}^{-1/2} (\mathbf{X} + \mathbf{Y}) = \\ \begin{bmatrix} \omega^2 - \mathbf{\Omega} \end{bmatrix} \mathbf{S}^{-1/2} (\mathbf{X} + \mathbf{Y}) = 2 \mathbf{S}^{-1/2} \mathbf{V} \quad .$$
(8.32)

Then we know with $\mathbf{\Omega} = \mathbf{S}^{-1/2} (\mathbf{A} + \mathbf{B}) \mathbf{S}^{-1/2}$:

$$(\mathbf{X} + \mathbf{Y}) = \mathbf{S}^{-1/2} \left[\omega^2 - \mathbf{\Omega} \right]^{-1} 2 \mathbf{S}^{-1/2} \mathbf{V} .$$
(8.33)

It's obvious that the density response $(\mathbf{X} + \mathbf{Y})$ is infinite when the inverse of $[\omega^2 - \mathbf{\Omega}]$ is singular. From that one concludes that the solutions to the following eigenvalue problem corresponds to the singularities:

$$\mathbf{\Omega} \mathbf{F}_{\lambda} = \omega_{\lambda}^2 \mathbf{F}_{\lambda} , \qquad (8.34)$$

where $\omega_{\lambda} = \sqrt{\epsilon_{\lambda}^2}$ are the excitation energies. This equation does not depend on external perturbations, and represents an intrinsic property of the system. In supermolecular TDDFT, **S** is a diagonal matrix (**C** and **A** – **B** are both diagonal), and thus positive definite. Therefore, (8.34) is an Hermitian eigenvalue problem. Explicitly, the matrix elements of **S** and **Ω** are:

$$S_{ia\sigma,jb\tau} = \frac{\delta_{\sigma\tau} \delta_{ab} \delta_{ij}}{\epsilon_{ia\sigma}},$$
(8.35)

$$\Omega_{ia\sigma,jb\tau} = \delta_{\sigma\tau} \delta_{ab} \delta_{ij} \epsilon_{ia\sigma} + 2\sqrt{\epsilon_{ia\sigma}} K_{ia\sigma,jb\tau} \sqrt{\epsilon_{jb\tau}}$$
(8.36)

Then the density response can be find as $(\mathbf{X} + \mathbf{Y})_{\lambda} = (\omega_{\lambda}^{-1/2})\mathbf{S}^{-1/2}\mathbf{F}_{\lambda}$. It is noted that the

same eigenvalue equation can be obtained from (8.25) by assuming $\mathbf{V} = 0$.

Once we solve the eigenvalue problem, we can calculate the transition dipole moments, polarizabilities (sum over states), and oscillator strengths. The transition dipole moments are given as:

$$\mu(\omega_{\lambda}) = \mathbf{D}(\mathbf{X} + \mathbf{Y})_{\lambda} = \frac{1}{\sqrt{\epsilon_{\lambda}}} \mathbf{D} \mathbf{S}^{-1/2} \mathbf{F}_{\lambda}, \qquad (8.37)$$

where $\mathbf{D}_{\mathbf{x},(\mathrm{ia})} = \langle \phi_i | \hat{\mu}_x | \phi_a \rangle$ is element of the electric dipole matrix. The molecular polarizability (static) can be found by the sum-over-states (SOS) method:

$$\begin{aligned} \alpha_{\rm xz} &= \sum_{\lambda} \frac{2\omega_{\lambda} \cdot \langle \Psi_0 | \hat{\mu}_x | \Psi_\lambda \rangle \langle \Psi_\lambda | \hat{\mu}_z | \Psi_0 \rangle}{\omega_{\lambda}^2 - \omega^2} \\ &= 2\mathbf{D}_{\rm x} \, \mathbf{S}^{-1/2} \sum_{\lambda} \frac{\mathbf{F}_{\lambda} \otimes \mathbf{F}_{\lambda}}{\omega_{\lambda}^2 - \omega^2} \, \mathbf{S}^{-1/2} \, \mathbf{D}_{\rm z} \\ &= 2 \sum_{\lambda} \frac{\omega_{\lambda} \cdot \mu_x(\omega_{\lambda}) \otimes \mu_z(\omega_{\lambda})}{\omega_{\lambda}^2 - \omega^2} \,, \end{aligned}$$
(8.38)

where \otimes is the vector/matrix outer product operation. And from the numerator in the polarizability equation, we know the oscillator strengths are:

$$f_{\lambda} = \frac{2}{3} \sum_{i=x,y,z} |\mathbf{D}_{i} \, \mathbf{S}^{-1/2} \, \mathbf{F}_{\lambda}|^{2}$$
(8.39)

8.3.2 Subsystem TDDFT with EO

Excitation Energies

The main idea of subsystem TDDFT, similar to the Kohn-Shan DFT case, is to partition the density response into contributions from individual fragments. The matrix that is most relevant to the TDDFT equations is the coupling matrix \mathbf{K} . Following the same derivation of the supermolecular TDDFT, the two-fragment subsystem TDDFT matrices, for instance, the coupling matrix \mathbf{K} , usually exhibit the following block structure:

$$\mathbf{K} = \begin{bmatrix} \mathbf{K}^{\mathrm{I},\mathrm{I}} & \mathbf{K}^{\mathrm{I},\mathrm{J}} \\ \mathbf{K}^{\mathrm{J},\mathrm{I}} & \mathbf{K}^{\mathrm{J},\mathrm{J}} \end{bmatrix} .$$
(8.40)

For systems with more than two fragments, such structure expands naturally. Explicitly, elements of the coupling matrix are defined as

$$K_{(\mathrm{ia}\sigma)_{\mathrm{I}},(\mathrm{jb}\tau)_{\mathrm{J}}} = \iint \left[\phi_{\mathrm{i}\sigma}^{\mathrm{I}}(\mathbf{r}) \phi_{\mathrm{a}\sigma}^{\mathrm{I}}(\mathbf{r}) f(\mathbf{r},\mathbf{r}',\omega) \phi_{\mathrm{b}\tau}^{\mathrm{J}}(\mathbf{r}') \phi_{\mathrm{j}\tau}^{\mathrm{J}}(\mathbf{r}') \right] d\mathbf{r} d\mathbf{r}'.$$
(8.41)

Similar to (8.25), the response equations are defined as:

$$\sum_{\mathbf{J}} \sum_{(\mathbf{j}\mathbf{b}\tau)_{\mathbf{J}}}^{\mathbf{j}<\mathbf{b}} \left[\delta_{(\mathbf{i}\mathbf{a}\sigma)_{\mathbf{I}},(\mathbf{j}\mathbf{b}\tau)_{\mathbf{J}}} \frac{\omega - \epsilon_{(\mathbf{j}\mathbf{b}\tau)_{\mathbf{J}}}}{n_{\mathbf{j}\tau} - n_{\mathbf{b}\tau}} - K_{(\mathbf{i}\mathbf{a}\sigma)_{\mathbf{I}},(\mathbf{j}\mathbf{b}\tau)_{\mathbf{J}}} \right] \delta P_{(\mathbf{j}\mathbf{b}\tau)_{\mathbf{J}}} - \sum_{\mathbf{J}} \sum_{(\mathbf{j}\mathbf{b}\tau)_{\mathbf{J}}}^{\mathbf{j}<\mathbf{b}} K_{(\mathbf{i}\mathbf{a}\sigma)_{\mathbf{I}},(\mathbf{b}\mathbf{j}\tau)_{\mathbf{J}}} \delta P_{(\mathbf{b}\mathbf{j}\tau)_{\mathbf{J}}} = \delta v_{(\mathbf{i}\mathbf{a}\sigma)_{\mathbf{I}}}^{\text{ext}}$$

$$(8.42a)$$

$$\sum_{\mathbf{J}} \sum_{(\mathbf{j}\mathbf{b}\tau)_{\mathbf{J}}}^{j < b} \left[\delta_{(\mathbf{i}a\sigma)_{\mathbf{I}},(\mathbf{j}\mathbf{b}\tau)_{\mathbf{J}}} \frac{\omega + \epsilon_{(\mathbf{j}\mathbf{b}\tau)_{\mathbf{J}}}}{n_{\mathbf{b}\tau} - n_{\mathbf{j}\tau}} - K_{(\mathbf{a}i\sigma)_{\mathbf{I}},(\mathbf{b}\mathbf{j}\tau)_{\mathbf{J}}} \right] \delta P_{(\mathbf{b}\mathbf{j}\tau)_{\mathbf{J}}} - \sum_{\mathbf{J}} \sum_{(\mathbf{j}\mathbf{b}\tau)_{\mathbf{J}}}^{j < b} K_{(\mathbf{a}i)_{\mathbf{I}},(\mathbf{j}\mathbf{b}\tau)_{\mathbf{J}}} \delta P_{(\mathbf{j}\mathbf{b}\tau)_{\mathbf{J}}} = \delta v_{(\mathbf{a}i\sigma)_{\mathbf{I}}}^{\text{ext}}$$

$$(8.42b)$$

Then, the exact same steps of matrix manipulations as in (4.10) - (4.14) are carried out in the subsystem formulation, and we arrive at (eliminating **C**):

$$(\mathbf{A} + \mathbf{B})(\mathbf{X} + \mathbf{Y}) - \omega(\mathbf{Y} - \mathbf{X}) = (\mathbf{V} + \mathbf{W})$$
(8.43a)

$$(\mathbf{A} - \mathbf{B})(\mathbf{Y} - \mathbf{X}) - \omega(\mathbf{X} + \mathbf{Y}) = (\mathbf{W} - \mathbf{V})$$
(8.43b)

For the EO embedding to be exact in the TDDFT framework, the EO contributions to the coupling matrices \mathbf{A} and \mathbf{B} are different and thus need to be distinguished²⁵⁶:

to **A**:
$$K_{(ia)_{I},(jb)_{J}}^{EO;I\neq J} = \mu S_{ij}^{I,J} S_{ba}^{J,I}$$
 (8.44a)

to **B**:
$$K_{(ia)_{I},(bj)_{J}}^{EO;I \neq J} = \mu S_{ib}^{I,J} S_{ja}^{J,I}$$
 (8.44b)

The EO contribution to the **B** matrix is essentially zero, because the ground-state EO already ensures there is no overlapping between any occupied orbital from either fragment to the shared virtual orbitals, *i.e.*,

$$S_{\rm ib}^{\rm I,J} = S_{\rm ia}^{\rm J,I} = 0$$
 . (8.45)

Consequently, $(\mathbf{A} - \mathbf{B})$ is not diagonal and trivially invertible anymore in the exact subsystem formulation. Thus, the derivation of the eigenvalue equation for excitation energies requires some extra caution. There are two approaches.

The first approach uses the alternative way of formulating the eigenvalue equation mentioned earlier, namely, assuming $v^{\text{ext}} = 0$. In this case, one combines the two subequations in (8.43) and forms the following two equations:

$$(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B})(\mathbf{X} + \mathbf{Y}) = \omega^2(\mathbf{X} + \mathbf{Y})$$
(8.46a)

$$(\mathbf{X} - \mathbf{Y})(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B}) = \omega^2(\mathbf{Y} - \mathbf{X})$$
(8.46b)

Since $(\mathbf{A} - \mathbf{B})$ is not diagonal in the exact embedding regime of subsystem TDDFT, these two equations are now non-Hermitian eigenvalue problems that lead to the same eigenvalues but generally different left $(\mathbf{X} - \mathbf{Y})$ and right $(\mathbf{X} + \mathbf{Y})$ eigenvectors. Solving this non-Hermitian problem directly provides us with the desired $\mathbf{X} + \mathbf{Y}$. And the calculation of other properties follows naturally. However, it has to be noted that the following identities have to be enforced numerically after the solution from the LaPack²⁶⁷ solver is obtained:

$$(\mathbf{A} + \mathbf{B})(\mathbf{X} + \mathbf{Y}) = \omega(\mathbf{X} - \mathbf{Y})$$
(8.47a)

$$(\mathbf{A} - \mathbf{B})(\mathbf{X} - \mathbf{Y}) = \omega(\mathbf{X} + \mathbf{Y})$$
(8.47b)

$$(\mathbf{X} - \mathbf{Y})^{\dagger} \cdot (\mathbf{X} + \mathbf{Y}) = \mathbf{I}$$
(8.47c)

The second approach utilizes the general definition of **S** and $\mathbf{S}^{-1/2}$ that are required to derive the Hermitian eigenvalue equation as in the supermolecular case (8.34):

$$S = -C(A - B)^{-1}C = (A - B)^{-1}$$
(8.48)

$$\mathbf{S}^{-1/2} = (\mathbf{A} - \mathbf{B})^{1/2} \tag{8.49}$$

Because $K_{(ia)_{I},(jb\tau)_{J}}^{EO;I\neq J} = K_{(jb\tau)_{J},(ia)_{I}}^{EO;I\neq J}$, which means $(\mathbf{A} - \mathbf{B})$ is still symmetric positive definite, one can calculate $(\mathbf{A} - \mathbf{B})^{1/2}$ through eigen-decomposition:

$$(\mathbf{A} - \mathbf{B}) = \mathbf{U}^T \lambda \mathbf{U} \quad \Rightarrow \quad (\mathbf{A} - \mathbf{B})^{1/2} = \mathbf{U}^T \sqrt{\lambda} \mathbf{U} .$$
 (8.50)

The one can arrive at an Hermitian eigenvalue equation:

$$(\mathbf{A} - \mathbf{B})^{1/2} (\mathbf{A} + \mathbf{B}) (\mathbf{A} - \mathbf{B})^{1/2} \tilde{\mathbf{F}}_{\lambda} = \omega_{\lambda}^{2} \tilde{\mathbf{F}}_{\lambda}$$
(8.51)

with $(\mathbf{X} + \mathbf{Y})_{\lambda} = \frac{1}{\sqrt{\epsilon_{\lambda}}} (\mathbf{A} - \mathbf{B})^{-1/2} \tilde{\mathbf{F}}_{\lambda}$. The above equation is identical to (8.34) when the coupling matrix is symmetric as in the supermolecular case.

Polarizabilities

For the xz-component of the polarizability, we can derive it in analogy to the supermolecular TDDFT express:

$$\begin{aligned} \alpha_{\rm xz}(\omega) &= \frac{1}{\varepsilon_z} \int \delta \rho(\omega, \mathbf{r}) \hat{\mu}_x d\mathbf{r} \\ &= \frac{2}{\varepsilon_z} \sum_{\rm ia\sigma} \delta P_{\rm ia\sigma} D_{\rm x,ia} \\ &= 2 \sum_{\rm ia\sigma} \sum_{\rm jb\tau} \left\{ \mathbf{S}^{-1/2} \big[\mathbf{\Omega} - \omega^2 \mathbf{1} \big]^{-1} \mathbf{S}^{-1/2} \right\}_{(\rm ia\sigma),(\rm jb\tau)} \cdot D_{\rm z,(\rm jb\tau)} \cdot D_{\rm x,(\rm ia\sigma)}, \end{aligned}$$
(8.52)

where the expression for $\delta \mathbf{P}$ can be obtained from (8.33)

$$\delta \mathbf{P} = \frac{1}{2} (\mathbf{X} + \mathbf{Y}) = \mathbf{S}^{-1/2} [\omega^2 - \mathbf{\Omega}]^{-1} \mathbf{S}^{-1/2} \mathbf{V} . \qquad (8.53)$$

This equation implies that we only need the symmetric part of the perturbed density matrix to obtain the polarizability.

To calculate the polarizability according to (8.52), the occupied-virtual matrix elements of the dipole moment operator and the perturbed density matrix ($\delta \mathbf{P}$) have to be determined. To determine $\delta \mathbf{P}$, one can iteratively solve (8.24a).

$$\delta \mathbf{P} = \chi^s \left[\delta \mathbf{v}^{\text{ext}} + 2\mathbf{K} \ \delta \mathbf{P} \right] \tag{8.54}$$

All matrices in (8.54) exhibit a subsystem structure:

$$\begin{pmatrix} \delta \mathbf{P}^{\mathrm{I}} \\ \delta \mathbf{P}^{\mathrm{J}} \end{pmatrix} = \begin{pmatrix} \delta \chi^{\mathrm{I}} & \mathbf{0} \\ \mathbf{0} & \delta \chi^{\mathrm{J}} \end{pmatrix} \begin{bmatrix} \delta \mathbf{v}^{\mathrm{ext,I}} \\ \delta \mathbf{v}^{\mathrm{ext,J}} \end{pmatrix} + 2 \begin{pmatrix} \mathbf{K}^{\mathrm{I,I}} & \mathbf{K}^{\mathrm{I,J}} \\ \mathbf{K}^{\mathrm{J,I}} & \mathbf{K}^{\mathrm{J,J}} \end{pmatrix} \begin{pmatrix} \delta \mathbf{P}^{\mathrm{I}} \\ \delta \mathbf{P}^{\mathrm{J}} \end{pmatrix} \end{bmatrix}$$
(8.55)

The advantages of this subsystem approach is the reduction of dimension for $\delta \mathbf{P}$ and it allows for studies of individual subsystems, such as charge-transfer behaviors, by decomposing the matrices into fragments.

$$\delta \mathbf{P}^{\mathrm{I}} = \chi^{\mathrm{I}} \left[\delta \mathbf{v}^{\mathrm{ext}} + 2\mathbf{K}^{\mathrm{I},\mathrm{I}} \delta \mathbf{P}^{\mathrm{I}} + 2\mathbf{K}^{\mathrm{I},\mathrm{J}} \ \delta \mathbf{P}^{\mathrm{J}} \right]$$

= $\chi^{\mathrm{I}} \left[\delta \mathbf{v}^{\mathrm{ext}} + \delta \mathbf{v}^{\mathrm{intra}} + \delta \mathbf{v}^{\mathrm{inter}} + \delta \mathbf{v}^{\mathrm{EO}} \right]$ (8.56)

Now the coefficients of the perturbed density matrix of subsystem I are partitioned into three parts: (i) due to external perturbation, (ii) due to change in the potential induced by the density change within the same subsystem, and (iii) due to the change in embedding potential induced by the density change in the other subsystem. The EO potential is given as:

$$\delta \mathbf{v}^{\rm EO}[\delta \rho_{\rm J}] = \mu [\mathbf{S}_{\rm occ}^{\rm I,J} \ \delta \mathbf{P}^{J} \ \mathbf{S}_{\rm virt}^{\rm J,I}]$$

$$\delta v_{\rm ia\sigma}^{\rm EO} = \mu \sum_{j < b}^{j,b \in J} [S_{\rm (ij)}^{\rm I,J} S_{\rm (ab)}^{\rm J,I} \delta P_{\rm jb\sigma}]$$
(8.57)

where $\mathbf{S}^{\mathrm{I},\mathrm{J}}$ is the orbital overlap matrix between subsystem I and J in the MO basis. Note there should not be a factor of two in front of the EO potential. The factor of two in conventional TDDFT comes from the symmetric coupling matrix in $\mathbf{A} + \mathbf{B}$. However, as stated before, the EO coupling only contributes to the \mathbf{A} matrix.²⁵⁶

8.3.3 Implementation in ADF

The FDE-TDDFT calculations are carried out using the ADF program. The original implementation of FDE-TDDFT in the ADF program adopts an approximate version of the method that was first proposed by Neugebauer²⁶⁸, and the EO method was implemented by Chulhai and Jensen.²⁵⁵ The approximate method solves the Hermitian eigenvalue problem similar to (8.34). The exact FDE method is implemented through a modification of the coupling matrix obtained by the approximate model and solving the generalized eigenvalue problem. In this section, I will briefly describe the approximate FDE-TDDFT workflow as a backbone for the method, and then the necessary modifications to make the method exact.

Approximate FDE-TDDFT

The approximate FDE-TDDFT follows the method in the supermolecular case to obtain the eigenvalue problem assuming matrix $(\mathbf{A} - \mathbf{B})$ is symmetric, which leads to the subsystem

formulation:

$$\begin{pmatrix} \Omega^{\mathrm{I},\mathrm{I}} & \Omega^{\mathrm{I},\mathrm{J}} \\ \Omega^{\mathrm{J},\mathrm{I}} & \Omega^{\mathrm{J},\mathrm{J}} \end{pmatrix} \begin{pmatrix} \mathbf{F}^{\mathrm{I}}_{\lambda} \\ \mathbf{F}^{\mathrm{J}}_{\lambda} \end{pmatrix} = \omega_{\lambda}^{2} \begin{pmatrix} \mathbf{F}^{\mathrm{I}}_{\lambda} \\ \mathbf{F}^{\mathrm{J}}_{\lambda} \end{pmatrix} , \qquad (8.58)$$

where each block in the coupling matrix Ω is obtained with the same mathematical transformation as (8.26) - (8.34).

The diagonal block $\Omega^{I,I}$ (or $\Omega^{J,J}$) alone represents the response of the fragment I (or J) without coupling to the other fragment, and can be solved independently through:

$$\begin{bmatrix} \Omega^{\mathrm{I},\mathrm{I}} - \omega_{\lambda}^{2} \end{bmatrix} \mathbf{F}_{\lambda}^{\mathrm{I}} = 0 \quad ,$$

$$\begin{bmatrix} \Omega^{\mathrm{J},\mathrm{J}} - \omega_{\lambda}^{2} \end{bmatrix} \mathbf{F}_{\lambda}^{\mathrm{J}} = 0 \quad .$$
(8.59)

This method is termed "uncoupled FDE-TDDFT" or "FDEu".

Then we can construct the following unitary transformation matrix with a block structure:

$$\mathbf{U} = \begin{pmatrix} U^{\mathrm{I}} & 0^{\mathrm{I},\mathrm{J}} \\ 0^{\mathrm{J},\mathrm{I}} & U^{\mathrm{J}} \end{pmatrix} , \qquad (8.60)$$

where columns of U^{I} are the eigenvectors obtained in (8.59). Multiplying \mathbf{U}^{\dagger} from the left of (8.58) and inserting $\mathbf{U}\mathbf{U}^{\dagger}$, we arrive at:

$$\begin{bmatrix} \mathbf{U}^{\dagger} \mathbf{\Omega} \mathbf{U} - \omega_{\lambda}^{2} \end{bmatrix} \mathbf{U}^{\dagger} \mathbf{F}_{\lambda} = 0$$

or
$$\begin{bmatrix} \widetilde{\Omega} - \omega_{\lambda}^{2} \end{bmatrix} \widetilde{\mathbf{F}}_{\lambda} = 0 \quad , \qquad (8.61)$$

where $\widetilde{\Omega} = \mathbf{U}^{\dagger} \mathbf{\Omega} \mathbf{U}$ and $\widetilde{\mathbf{F}}_{\lambda} = \mathbf{U}^{\dagger} \mathbf{F}_{\lambda}$. This transformation simplifies the working equation of FDE-TDDFT to:

$$\begin{pmatrix} \omega_{\mathrm{I},0}^2 & \widetilde{\Omega}^{\mathrm{I},\mathrm{J}} \\ \widetilde{\Omega}^{\mathrm{J},\mathrm{I}} & \omega_{\mathrm{J},0}^2 \end{pmatrix} \begin{pmatrix} \widetilde{\mathbf{F}}_{\lambda}^{\mathrm{I}} \\ \widetilde{\mathbf{F}}_{\lambda}^{\mathrm{J}} \end{pmatrix} = \omega_{\lambda}^2 \begin{pmatrix} \widetilde{\mathbf{F}}_{\lambda}^{\mathrm{I}} \\ \widetilde{\mathbf{F}}_{\lambda}^{\mathrm{J}} \end{pmatrix} , \qquad (8.62)$$

where $\omega_{I,0}^2$ is a diagonal block matrix with the FDEu excitation energies of fragment I as the diagonal elements. Then for a set of transitions μ_I and ν_J , the off-diagonal block coupling matrix is explicitly written as:

$$\widetilde{\Omega}_{\mu_{I}\nu_{J}} = \sum_{(ia\sigma)_{I}} \sum_{(jb\tau)_{J}} U_{(ia\sigma)_{I}\mu_{I}} \Omega_{(ia\sigma)_{I}(jb\tau)_{J}} U_{(jb\tau)_{J}\nu_{J}}
= \sum_{(ia\sigma)_{I}} \sum_{(jb\tau)_{J}} U_{(ia\sigma)_{I}\mu_{I}} \sqrt{\epsilon_{(ia\sigma)_{I}}} K_{(ia\sigma)_{I},(jb\tau)_{J}} \sqrt{\epsilon_{(jb\tau)_{J}}} U_{(jb\tau)_{J}\nu_{J}}
= \int d\mathbf{r} \sum_{(ia\sigma)_{I}} 2U_{(ia\sigma)_{I}\mu_{I}} \sqrt{\epsilon_{(ia\sigma)_{I}}} \phi_{(i\sigma)_{I}} (\mathbf{r}) \phi_{(a\sigma)_{I}} (\mathbf{r}) \cdot
\int d\mathbf{r}' \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\mathrm{xck}}^{\mathrm{tot}} \right) \times \left[\sum_{(jb\tau)_{J}} \phi_{(j\tau)_{J}} (\mathbf{r}') \phi_{(b\tau)_{J}} (\mathbf{r}') \sqrt{\epsilon_{(jb\tau)_{J}}} U_{(jb)_{J}\nu_{J}} \right] ,$$
(8.63)

where $f_{\text{xck}}^{\text{tot}}$ is the response kernel that includes the exchange-correlation potential, kinetic potential, and the EO potential. Similar to many practical TDDFT implementations, one can choose to express the quantity in the bracket above in terms of a fitted density:

$$\delta\rho_{\mathbf{J}} = \left[\sum_{(jb\tau)_J} \phi_{(j\tau)_J}\left(\mathbf{r}'\right) \phi_{(b\tau)_J}\left(\mathbf{r}'\right) \sqrt{\epsilon_{(jb\tau)_J}} U_{(jb)_J v_J}\right] = \sum_k \alpha_k f_k(\mathbf{r}') \quad , \tag{8.64}$$

where f_k is the fit function and α_k is the corresponding fit coefficient. In such a way, only an induced potential due to the fitted density needs to be calculated:

$$\delta v_{\nu_J}^{\rm el}(\mathbf{r}) = \sum_k \alpha_k \int d\mathbf{r}' \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\rm xck}^{\rm tot} \right) \quad . \tag{8.65}$$

Thus, the matrix element of the transformed coupling matrix can be obtained through numerical integration as:

$$\widetilde{\Omega}_{\mu_{I}\nu_{J}} = \int d\mathbf{r} \sum_{(ia\sigma)_{I}} 2U_{(ia\sigma)_{I}\mu_{I}} \sqrt{\epsilon_{(ia\sigma)_{I}}} \times \phi_{(i\sigma)_{I}}(\mathbf{r}) \ \delta v_{\nu_{J}}^{\text{el}}(\mathbf{r}) \ \phi_{(a\sigma)_{A}}(\mathbf{r}) \quad .$$
(8.66)

After all matrix elements of the system Ω matrix is obtained, the final step is to solve the Hermitian eigenvalue problem of (8.58) to obtain the excited states of the total system. This procedure is often referred to as "FDEc".

The typical workflow of FDE-TDDFT include these steps: (1) calculate and save the KS orbitals of each fragment with ghost (empty) AOs representing the atoms that are not part of the fragment; (2) perform FDEu calculation with freeze-and-thaw cycles to obtain the excited states for fragment I; (3) perform another step of FDEu calculation using the previous freeze-and-thaw results and obtain the excited states for fragment J; (4) perform the FDEc calculation with the eigenvalue and eigenvectors from the previous two FDEu calculations.

Exact FDE-TDDFT

The key to realize the exact FDE-TDDFT is to generate the correct working matrix for the eigenvalue problem. In order to quickly establish proof of principle for the exact method, the above approximate method is modified. Specifically, the same procedure of constructing the Ω matrix is taken but without adding the EO potential, then it is "reverted" to the form of $(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B})$, and finally the correct EO contributions to the coupling matrix \mathbf{K} are added correspondingly. The details are as follows.

Without considering the EO contributions, the matrix manipulations to obtain $\hat{\Omega}$ from $(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B})$ are :

$$\widetilde{\mathbf{\Omega}} = \mathbf{U}^{\dagger} \mathbf{\Omega} \mathbf{U} = \mathbf{U}^{\dagger} \mathbf{S}^{-1/2} (\mathbf{A} + \mathbf{B}) \mathbf{S}^{-1/2} \mathbf{U} .$$
(8.67)

With $S_{(ia\sigma)_{I},(jb\tau)_{J}}^{-1/2} = \delta_{\sigma\tau}\delta_{ab}\delta_{ij}\delta_{IJ}\sqrt{\epsilon_{ia\sigma}}$, we can invert the above transformation to obtain $(\mathbf{A} + \mathbf{B})$:

$$(\mathbf{A} + \mathbf{B}) = \mathbf{S}^{1/2} \mathbf{U} \widetilde{\mathbf{\Omega}} \mathbf{U}^{\dagger} \mathbf{S}^{1/2} .$$
(8.68)

Since EO is not included so far, it is obvious that $(\mathbf{A} - \mathbf{B}) = \mathbf{S}^{-1}$, or $(A - B)_{(ia\sigma)_{I},(jb\tau)_{J}} =$

 $\delta_{\sigma\tau}\delta_{ab}\delta_{ij}\delta_{IJ}\epsilon_{ia\sigma}$. Then we can construct the exact FDE-TDDFT working equation by adding the EO coupling matrix according to (8.44), and solve the generalized eigenvalue problem directly:

$$(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B})(\mathbf{X} + \mathbf{Y}) = \omega^2 (\mathbf{X} + \mathbf{Y}) .$$
(8.69)

8.3.4 Preliminary Results

The proof of principle for the exactness of method derived above is presented in Fig. 8.1. To test the performance of the exact FDE TDDFT method, the two He atoms are moved from a very close distance (1 Å) to long distance (4 Å), where the coupling between the two atoms is tuned from strong to virtually zero. For a simple He–He dimer system, there are four excited states when described by the double- ζ basis set. As shown in Fig. 8.1(a), the FDE results match exactly up to four decimal places with the supermolecular calculations at all distances for all excited states. The FDE method also correctly reproduces the electronic transition dipole moment of each excitation. Averaging the percent error at each distance for the excitation energies, we find the largest percent error is about 0.015%, which is in the case of the strongest coupling (distance 1 Å).

When using a larger basis set such as the double- ζ +polarization (DZP) basis set, the number of excited states increases to 16, and energetically degenerate states start to emerge. The exact FDE method also reproduces the supermolecular results; however, the precision is only up to three decimal places. The largest error occurs at the shortest dimer separation, i.e., the strongest coupling. The increased error is attributed to the numerical instabilities introduced by the discrete integration grid and the legacy density fitting for the calculations of the coupling matrix **K**. However, the the largest percent error is still less than 5%, which is already a much improved accuracy compared with the previous work published in Ref. 255. Also, the error in the FDE-TDDFT method using the larger basis set is more evident for the transition dipole moments and the oscillator strengths. The transition dipole moments calculated by the FDE-TDDFT and the supermolecular KS method have the same structure in terms of direction and lengths. Both methods yield the same bright and dark states (in terms of oscillator strength) and the same orthogonal transition dipole moments for degenerate states. However, the average percent error is around 10%. However, assuming the electric oscillator strengths sum up to the total number of electrons in the system, we find the neither of the method leads to $\sum_i f_i = 4.0$ exactly. Thus, it's reasonable to conclude that the method is exact in the limit of the ADF program's numerical accuracy.

Interestingly, we find the method has better accuracy for practical applications such as calculating the polarizabilities for Raman scattering simulations. As is shown in Fig. 8.1(b), the static polarizabilities obtained by the sum-over-states (SOS) approach using the larger DZP basis set reproduces exactly the supermolecular polarizabilities obtained by the linear-response TDDFT. The largest percent error is less than 0.5%. Two larger systems, $H_2O - H_2O$ dimer and FHF⁻ in Fig. 8.1(c), are used to test the exactness of both the excited states and the linear response in the FDE model. For each system, the static polarizability is obtained in four different ways, namely, the supermolecular linear response (benchmark), the finite difference of molecular dipole moments

in FDE, the linear response in FDE, and the sum-over-states method in FDE. The triple- ζ with polarization basis set is used. It is found that the results from all the four methods agree very well. The small differences (~ 1%) are again ascribed to the numerical errors introduced by the legacy density fitting procedure and the integration grids.



Figure 8.1. Preliminary results of the exact FDE TDDFT method. (a) The comparison of excitation energies of a He–He dimer as a function of distance using the small DZ basis set. (b) The comparison of the static polarizability of the He–He dimer as a function of distance using the larg DZP basis set. (c) The comparison of static polarizabilities of two other model systems: $H_2O - H_2O$ dimer and FHF^- , using an even larger basis set TZP.

The smaller average percent errors between the two methods in terms of static polarizabilities than the excitation energies suggest that the theory of the exact FDE-TDDFT is correct, because when considering the obtained excited states collectively for a system the FDE method is indeed exact. The discrepancies in the excitation energies may also come from the different eigenvalue problem solvers implemented in the ADF program, especially from the different ways of handling degeneracies in the coupling matrix introduced by the larger basis set.

8.3.5 Summary

This chapter derived the exact FDE-TDDFT model. The projection embedding method is used to ensure external orthogonality between the orbitals of the fragments, which eliminates the non-additive kinetic potential. The contributions of the EO potential to different terms of the TDDFT coupling matrix are distinguished, and thus make the method exact. Preliminary results proves the exactness of this method in the limit of numerical accuracy by comparing the excitation energies and the polarizabilities with the results obtained from the supermolecular KS calculations. The FDE method can be applied to the studies of the chemical mechanism of TERS. One can represent the molecule as the active fragment and the metal as the frozen fragment. In this way, the chemical interactions between the two fragments can be described by TDDFT, which is advantageous to the purely classic treatment of the metal fragment. At the same time, the properties of each fragments can be easily separated, and the charge-transfer effects can be extracted by comparing the sum of fragments with the supermolecular results.

Chapter 9 Polarizable Frozen Density Embedding with External Orthogonality

Pal, P. P.; Liu, P.; Jensen, L. Polarizable Frozen Density Embedding with External Orthogonalization. J. Chem. Theory Comput. **2019**, 15, 6588–6596. (Adapted)*

Abstract

We report a polarizable subsystem density functional theory to describe electronic properties of molecules embedded on a metal cluster. Interaction between the molecule and metal cluster is described using the frozen density embedding (FDE). Substituting the non-additive kinetic potential (NAKP) by approximate functionals is circumvented by enforcing external orthogonality (EO) through a projection operator. The computationally expensive freeze/thaw (FT) cycles is bypassed by including a polarization term in the embedding operator. Furthermore, the combination of polarization and EO permits supermolecular basis set calculations, which was not possible for strongly interacting systems with existing kinetic energy functional. To test the method, we described the ground state density of pyridine, water and benzene on a silver cluster. Performing FT on top of EO results in exact density embedding for these category of systems and is thus used for benchmarking the method. We find that the density is reproduced to within 10^{-4} e and the dipole and quadrupole moments are within 18% of the reference points for subsystem separations ranging from bonding to non-interacting distances. Additionally, our formalism allows the flexibility of incorporating different density functionals to the molecular and the metallic subsystems reducing the overall computational cost.

^{*}L.J. conceived the basic idea. P.P.P. and P.L. carried out the simulations. P.P.P, P.L. and L.J. analyzed the results and wrote the manuscript. P.P.P. prepared the initial draft. P.L. and L.J. revised the manuscript into the published version.
9.1 Introduction

Computing the electronic structure of a molecule embedded on a metal cluster or surface is a challenging task owing to non-negligible overlapping electronic densities around the interface. The most popular approach is *via* subsystem DFT^{269–275}, where the entire system is partitioned into subsystems and the electronic structure is determined separately at the Kohn-Sham DFT (KS-DFT) level. Interaction between the fragments can be described through frozen density embedding (FDE)^{251,259} - a method that incorporates the environmental effect through an embedding potential in the fragment Hamiltonian^{276,277}.

Traditional FDE fails for strongly overlapping fragment densities, mainly due to poor approximation of the non-additive kinetic potential (NAKP)^{278,279}. Jacob et al.²⁸⁰ suggested an implementation of three-partition FDE (3-FDE), where the individual fragments are capped with small molecular groups and additional constraints were enforced to satisfy the dangling bonds resulting from splitting a covalent bond. Reconstructing the embedding potential through a 'top-down' or a 'bottom-up' approaches have also been explored extensively using a variety of algorithms^{281–284}. Complete external orthogonalization (EO) of the individual fragment molecular orbitals is another alternative for refraining the use of approximate DFT functionals for the NAKP. Several methods include, the frozen core approximation²⁸⁵, the pseudo-potential approach²⁸⁶, level-shift projection operator²⁸⁷, and orthogonalization as a constraint to the coupled KS Lagrangian^{288–290} or basis set expansion²⁹¹. Recently, a flexible implementation of FDE with EO (FDE-EO) was reported, where starting from subsystem KS-DFT orbitals represented in any basis set, the supermolecular density of small molecules was reproduced^{254,255}. By virtue of freeze/thaw (FT) cycles, FDE-EO expectedly encompasses all the charge transfer and polarization effects the fragments have on each other. However, for molecules embedded on a metal cluster, the computational cost of FDE-EO with FT cycles (FDE-EO-FT) scales up rapidly with enlarging cluster size.

Due to the unfavorable scaling of atomistic first-principles description of the environment hybrid approaches have taken a strong precedence, especially in systems where electrons are fairly localized. A quantum mechanical description of the molecule and continuum polarizability based boundary element method for the metallic portion²⁹² was successfully applied to compute excitation energies²⁹³, Raman²⁹⁴ and fluorescence enhancement of molecules on nanoparticle aggregates²⁹⁵. Later on, a multiconfiguration self-consistent field (SCF) for the quantum mechanical region together with heterogeneous solvation response theory was used to explore the linear and nonlinear response of a metal-molecule system²⁹⁶. In another approach, finite-difference time-domain (FDTD) electrodynamics was combined with a two-state description of the molecule^{129,297}. Other approaches in include the widely popular QM/MM^{298,299}, ONIOM³⁰⁰, and combination of manybody theory and continuum electrodynamics at the level of time dependent (TD)-DFT ^{301,302}. More recently, a polarizable QM/MM method, emerging from a combination of TD-DFT for molecule and discrete interaction model (DIM) for the metal nanoparticle, illustrated the influence of nanoparticles on the excitation energies of two dye molecules (rhodamine-6G and crystal violet)¹¹⁰. The discrete interaction model/quantum mechanics (DIM/QM) treated the molecule as a quantum object and the metal cluster as an assembly of atomic dipoles. DIM/QM results were insightful but the method is insufficient for capturing all the interactions when a molecule is chemisorbed on a metal surface.

This drawback opens up the opportunity of combining FDE-EO and DIM/QM that would automatically allow the electrons to delocalize into the metal system and simultaneously permit polarization of the molecular charge density by the metal. In this article, we implement a combination of FDE-EO and DIM/QM into the Amsterdam density functional (ADF) program package^{73,74,99} and illustrate that this hybrid methodology, termed as FDE-pol, successfully reproduces the molecular density within 10^{-4} e of the reference values obtained from self-consistent FDE-EO-FT calculations. Recently, a similar concept termed as polarizable density embedding. where both electrostatic and non-electrostatic interactions between the active region and the environment is included implicitly in the calculations, showed a systematic improvement with basis set size³⁰³. In contrast, the performance of FDE-pol can be conveniently benchmarked against the exact but expensive self-consistent FDE-EO-FT calculations. We test two configurations of pyridine, water and benzene embedded on the surface of a Ag_{56} cluster. The FDE-pol ground state densities, molecular dipole and quadrupole moments of all the systems are almost identical to the reference FDE-EO-FT values. Additionally, we show the superiority of the projection operator based EO over the use of traditional NAKP functionals such as Thomas-Fermi and PW91 in the binding regime. Finally, we explore the possibility of applying disparate functionals to the embedded molecule and the nanocluster in order to speed up the simulations.

9.2 Theory

The FDE-pol approach adds an extra term, v_{emb}^{I} , to the single particle Kohn-Sham operator corresponding to the molecular fragment

$$\left[-\frac{1}{2}\bigtriangledown^2 + v_{\text{eff,KS}}^{\text{I}}[\rho^{\text{I}}](r) + v_{\text{emb}}^{\text{I}}[\rho^{\text{I}},\rho^{\text{J}}](r)\right]\psi_s^{\text{I}}(r) = \epsilon_s^{\text{I}}\psi_s^{\text{I}}(r).$$
(9.1)

Unless mentioned otherwise, we denote the molecular (metal) subsystem as fragment I (J). The KS orbitals and corresponding canonical energy levels of the molecular fragment are $\psi_s^{\rm I}(r)$ and $\epsilon_s^{\rm I}$, respectively. Environmental effects on the molecule are condensed into the embedding potential $v_{\rm emb}^{\rm I}[\rho^{\rm I}, \rho^{\rm J}](r)$, which has two contributions: (1) electrostatic + non-electrostatic $v_{\rm FDE}^{\rm I}[\rho^{\rm I}, \rho^{\rm J}](r)$ and (2) polarization $v_{\rm DIM}^{\rm I}(r)$. $v_{\rm FDE}^{\rm I}$ takes all quantum mechanical interactions between the subsystems into account. From standard FDE approach²⁶⁰, we can write

$$v_{\rm FDE}^{\rm I}(\mathbf{r})[\rho^{\rm I},\rho^{\rm J}] = v_{\rm nuc}^{\rm J}(\mathbf{r}) + \int \frac{\rho^{\rm J}(r')}{|r-r'|} dr' + v_{\rm xc}^{\rm nad}[\rho^{\rm I},\rho^{\rm J}](\mathbf{r}) + v_{\rm T}^{\rm nad}[\rho^{\rm I},\rho^{\rm J}](\mathbf{r})$$

$$(9.2)$$

where each fragment possess an integer number of electrons. The first two terms of Eq. 9.2 describe the nuclear and electronic potential due to the metal fragment. The last two terms in the same equation arise out of the overlapping subsystem densities and are conventionally

termed as the non-additive (nad) components of the exchange $(v_{\rm xc})$ and kinetic potentials (v_T) . In general, the contribution of $v_{\rm xc}$ is small and is approximated by the same xc functional used for computing the ρ 's. Likewise, an analytical form for $v_{\rm T}^{\rm nad}$ is also indeterminable and moreover, for largely overlapping densities, the contribution of $v_{\rm T}^{\rm nad}$ is quite significant. In this scenario, approximating $v_{\rm T}^{\rm nad}$ by available non-additive kinetic potentials such as, Thomas-Fermi or PW91 doesn't suffice. Alternatively, one can enforce the EO condition to make the KS orbitals of the subsystems mutually orthogonal and reduce the non-additive kinetic energy to zero. We take this route and apply the EO version that was recently developed, tested and implemented in ADF²⁵⁴. Utilizing the projection operator method, the orbital energies of a subsystem were raised by a scaling parameter, μ , which turned out to be a large number $(10^4 > \mu > 10^6 E_h)$ for practical applications²⁵⁴.

After constructing the embedding potential representing the quantum mechanical interaction between the two densities, we proceed to describe the polarization effects of the nanocluster in terms of purely electrostatic interactions. We consider the nanocluster to be the DIM system and the molecule is treated as a QM object at the DFT level. $v_{\text{DIM}}^{\text{I}}(\mathbf{r})$ is the polarization originating from the DIM dipoles¹¹⁰. Here we will be using the polarization interaction model (PIM) variant of DIM/QM, i.e., we consider only atomic dipoles induced in the DIM subsystem by the QM atoms. Following previous prescriptions we expand $v^{\text{DIM}}(\mathbf{r})$ as¹¹⁰,

$$v^{\text{DIM}}(r_k) = -\sum_{m}^{N_J} \frac{\mu_{m,\alpha}^{\text{ind}} r_{mk,\alpha}}{r_{mk}^3} = \sum_{m}^{N_J} \mu_{m,\alpha}^{\text{ind}} T_{mk,\alpha}^{(1)}$$
(9.3)

 $\mu_{m,\alpha}^{\text{ind}}$ is the dipole induced in the m^{th} DIM atom $(m = 1, 2, ..., N_{\text{J}})$ by the QM atoms. $T_{mk,\alpha}^{(1)}$ is a first order interaction tensor and α is a Cartesian coordinate. The Einstein summation convention is followed for the Greek indices. An n^{th} order interaction tensor is generally given by

$$T_{mk,\alpha_1,\dots,\alpha_n}^{(n)} = \nabla_{mk,\alpha_1}\dots\nabla_{mk,\alpha_n}\left(\frac{1}{r_{mk}}\right),\tag{9.4}$$

where r_{mk} is the distance between two atoms m and k. The point dipoles are smeared out by a Gaussian charge distribution to avoid overpolarization. Following the classical response theory, the induced dipoles may be calculated by solving a set of $3N_J$ linear equations via standard linear algebra techniques

$$\mathbf{A}\boldsymbol{\mu}^{\text{ind}} = \mathbf{F}^{\text{SCF}},\tag{9.5}$$

where matrix \mathbf{A} describes the dipole-dipole interactions including self-interactions and the terms are given by

$$A_{mn,\alpha\beta}(\omega) = \begin{cases} \alpha_{m,\alpha\beta}^{-1}(\omega) & m = n, \\ -T_{mn,\alpha\beta}^{(2)} & m \neq n. \end{cases}$$
(9.6)

To proceed, we need to determine $\mathbf{F}^{\mathrm{SCF}}$ - the electric field generated by the QM electrons and

nuclei, whose cartesian components can be expressed as:

$$F_{m,\alpha}^{\rm SCF} = F_{m,\alpha}^{\rm QM,el} + F_{m,\alpha}^{\rm QM,nuc},\tag{9.7}$$

which can be explicitly written as

$$F_{m,\alpha}^{\text{QM,el}} = \int \rho^{\text{I}}(r_k) \frac{r_{km,\alpha}}{r_{km}^3} dr_k = -\int \rho^{\text{I}}(r_k) T_{km,\alpha}^{(1)} dr_k, \qquad (9.8a)$$

$$F_{m,\alpha}^{\text{QM,nuc}} = \sum_{k}^{N_{\text{I}}} \frac{Z_{k} r_{km,\alpha}}{r_{km}^{3}} = -\sum_{k}^{N_{\text{I}}} Z_{k} T_{km,\alpha}^{(1)}.$$
(9.8b)

Initially, μ^{ind} is determined from Eqs. 9.5 and 9.8, and is plugged into v^{DIM} in Eq. 9.3. A new ρ^{I} is then determined using the KS operator and subsequently used to solve Eq. 9.5 via Eq. 9.8. The cycle is continued until self-consistency is achieved.

9.3 Computational Details

We represent the Ag(111) surface by a Ag₅₆ cluster - a model that has been used earlier for benchmarking *ab initio* dispersion corrections for molecules on metal surfaces³⁰⁴. All the calculations were performed using the ADF^{73,74,99} package with triple-zeta (TZP) basis set. The molecular geometries were optimized by applying the revPBE (GGA functional) and dispersion corrections at the level of Grimme3³⁰⁴. However, since this is a proof of principle effort we employ the simplistic LDA functional to compute the SCF ground state densities for both FDE and KS-DFT. All the FDE calculations were performed through the EO projection operator formalism with a level shift parameter of $\mu = 10^6 E_h$. For all FDE-EO calculations, the molecule was considered to be the active fragment. In all hybrid FDE-pol calculations, the densities of the invidual fragments (molecule and nanocluster) were constructed first and then the metal fragment density was frozen and treated as a DIM system. The PIM variation of DIM/QM was used for all the simulations. Normal Becke numerical grid was used and the SCF energy convergence was set to the default value of 10^{-6} au.

9.4 Results and Discussions

We analyze the ground state densities computed from FDE-pol and compare the dipole moments to reference results obtained from the self-consistent FDE-EO-FT calculations, which captures both charge transfer and polarization effects on the molecular density but at the expense of a high computational cost. We perform these benchmark calculations on four supermolecular systems with variable extent of subsystem density overlap. Subsequently, we examine the FDE-pol quadrupole moments and the performance of various NAKPs (if we use them instead of EO) on the system which has significant density overlap, i.e., pyridine oriented perpendicular to the silver surface. We chose this model system because FDE without EO fails in strongly bonded subsystems and FDE with EO requires FT cycles for polarizing the molecular density which is computationally expensive for large systems. On the same system we then explore the feasibility of applying different XC functionals in the molecule and the metal regions.



9.4.1 Molecular Density and FDE Interaction Energies

Figure 9.1. Chemical deformation density computed from (a) FDE-EO-FT, and (b) FDE-pol. Cut off for the isosurfaces is 10^{-3} au. Red (blue) areas denotes loss (gain) of molecular density.

We present illustrative calculations for four test systems, (1) pyridine (perpendicular and parallel), (3) water, and (4) benzene on silver surface represented by a Ag₅₆ cluster. The equilibrium geometries were obtained from supermolecular KS-DFT simulations with a tight convergence of maximum nuclear force $< 10^{-4}$ au. In the first model, pyridine was constrained to remain perpendicular on the surface and equilibrium separation between the nitrogen and cluster turned out to be ~ 2.5 Å.

To compare the densities obtained using the different methods we will calculate the chemical deformation density (CDD) defined as $\rho_{\rm EO} - \rho_{\rm SM}$ and $\rho_{\rm EOD} - \rho_{\rm SM}$, where $\rho_{\rm EO}$ and $\rho_{\rm EOD}$ correspond to the FDE-EO-FT and FDE-pol molecular densities, respectively, and $\rho_{\rm SM}$ is the density obtained from a supermolecular basis set calculation, i.e., using ghost atoms instead of the silver atoms. CDD elucidates the spatial distribution of density exchange between the two fragments and is thus an indicator of the metal-molecule interaction strength. In Fig. 9.1, we plot the CDDs where rearrangement in the molecular charge density of pyridine is specified by the blue and red isosurfaces (isovalue = ± 0.001 au). As expected, most of the molecular density gain or depletion occurs at the interface. The figure illustrates partial drift of π electronic density from pyridine to the metal cluster. However, the most interesting aspect is the strong similarity between the CDD of Fig 9.1(a) and (b) even at such low isovalues. This clearly emphasizes that the FDE-pol pyridine density is very close to that obtained from the expensive FDE-EO-FT calculation. To quantify the error in the FDE-pol method we will calculate the difference density (DD) between FDE-pol and FDE-EO-FT (calculated as $\rho_{\rm EOD} - \rho_{\rm EO}$). In Fig. 9.2(a) we plot the DD for pyridine with an isosurfaces value of 10^{-4} au. DD dominates around N-Ag bond and the red isosurface indicates the tendency of FDE-EO-FT to add density into the interfacial region. The behavior



Figure 9.2. Difference charge density between those obtained from FDE-EO-FT and FDE-pol, i.e., $\rho_{\rm EOD} - \rho_{\rm EO}$. For all the plots, 0.0001 au is the cut-off for the isoplane - blue (red)corresponds to increment (reduction) in density. A contour map (ranging from 10^{-6} to 10^{-4}) is also plotted to detail the spatial variation in the differences. (a) Pyridine oriented perpendicular to Ag₅₆ cluster; (b) water adsorbed on the same cluster; (c) Pyridine oriented parallel to Ag₅₆ cluster. (d) benzene adsorbed on the same cluster.

is attributed to the fact that FDE-EO-FT is designed to capture the interaction between the fragments with a greater accuracy than FDE-pol due the self-consistent FT cycles. Integrating the DD over the entire grid space ($\Delta e = \int |\Delta \rho| dr$) gives a value of 0.126 e, supporting the fact that the densities obtained using FDE-pol are in excellent agreement with the exact density obtained from FDE-EO-FT. For water, the DD between FDE-pol and FDE-EO-FT shown in Fig. 9.2(b) exhibits a similar pattern, i.e., FT favors density around the water-silver interface. Additionally, small lobes for the isosurfaces and Δe of 0.021 e suggest very little deviation of the FDE-pol molecular density from the corresponding reference values. In Fig. 9.2(c) and (d) we plot the DD of pyridine and benzene oriented parallel to the metal surface, respectively. The equilibrium distances between the pyridine and benzene molecule from the silver surface are both $\sim 3\text{\AA}$, which matches previous reports³⁰⁴. The bond lengths along with the DDs indicate both these molecules are physisorbed on the surface with only small density overlap. In these two weakly interacting systems, we see that FDE-pol tends to favor too much density at the interface. However, the Δe for pyridine and benzene are 0.065 e and 0.083 e in, respectively, showing that

the FDE-pol density is in good agreement with the exact density. The contrast between the interfacial isosurfaces in Fig. 9.2(a-b) and (c-d) illustrates the variation in the density overlap across the subsystems. The low DD cut offs in Fig. 9.2 is a clear indication that FDE-pol creates accurate densities for strong to moderately bonded molecule-metal systems and unsurprisingly, exhibits an improved performance for weakly embedded molecules.



Figure 9.3. The FDE interactions energies as a function of molecule-surface separation. (a) Pyridine perpendicular to the silver surface, (b) water, (c) pyridine parallel to the surface, (d) benzene parallel to the surface. Black circles, red diamonds, and blue crosses correspond to μ_z obtained from FDE-EO-FT, FDE-pol and FDE-EOØ (FDE-EO value before starting the freeze/thaw cycles), respectively. The green stars denote the gas phase μ_z for the respective molecules. Inset shows the optimized geometries.

9.4.2 Dipole Moment and Quadrupole Moments

The dipole moment provides a good measure of the accuracy of the embedding method since it reflect the overall quality of the electron density. In the following we will benchmark the performance of FDE-pol in reproducing the dipole moment of the active fragment. In Fig. E.1 we show that FDE-EO-FT accurately reproduces the dipole moment of the supermolecular system i.e., metal + molecule, if FT cycles are done for both the metal and molecule system. Fig. E.1(c) clearly illustrates that the dominant component of the dipole moment (μ_z) obtained from FDE-EO-FT reproduced exactly the supermoleculare DFT results. In Fig. E.1(a) and (b), we also provide the



Figure 9.4. Z component of the molecular dipole moment (μ_z) as a function of molecule-surface separation. (a) pyridine perpendicular to the silver surface, (b) water, (c) pyridine parallel to the silver surface, (d) benzene parallel to the surface. Black circles, red diamonds, and blue crosses correspond to μ_z obtained from FDE-EO-FT, FDE-pol and FDE-EO \emptyset (FDE-EO value before starting the freeze/thaw cycles), respectively. The green stars denote the gas phase μ_z for the respective molecules. Inset shows the optimized geometries.

comparison of $\mu_{x,y}$, which are at least one order smaller than μ_z . Hence, the molecular dipole moment obtained from FDE-EO-FT can be used as the reference to test FDE-pol.

In Fig. 9.4, we plot the major component of the molecular dipole moment - μ_z as a function of molecule-surface separation, where z is the direction normal to the silver surface, for the four test systems studied on this work. In all systems we see that there is a significant increase of the dipole moment of the molecule due to the ability to delocalized the electron density into the metallic fragment. At the minimum energy configuration, FDE-pol μ_z is in good agreement with FDE-EO-FT for pyridine perpendicular to the surface and for water. Interestingly, these two systems have larger metal-molecule density overlap among the four model systems studied. Larger deviations are found for benzene and pyridine perpendicular to the surface. To quantify the error in FDE-pol, we calculate the relative difference in the magnitudes ($\delta\mu$) of molecular $\vec{\mu}$ by defining: $\delta\mu_{\rm rel} = (|\vec{\mu}_0| - |\vec{\mu}_1|)/|\vec{\mu}_0|$, where $\vec{\mu}_0$ is the molecular dipole moment of FDE-EO-FT and $\vec{\mu}_1$ is the FDE-pol molecular dipole moment. The largest error found is $\delta\mu_{\rm rel} \sim 10\%$ for benzene parallel to the surface whereas for pyridine perpendicular to the surface and for water the error is $\delta \mu_{\rm rel} \sim 1\%$ at the equilibrium distance. This shows that the polarization is described accurately by DIM/QM and is a low-cost alternative for FT cycles. Comparison of the other two minor components (x and y) as a function of distance are given in Fig. E.2.



Figure 9.5. Quadrupole moments of the active fragment (pyridine). Pyridine is perpendicular to the silver surface. Green stars mark the corresponding molecular gas phase quadrupole for each component.

A more stringent measure of the quality of the computed electronic densities is to compare the quadupole moments as it reflects asymmetric changes in the density. This is particular true for highly symmetry molecular like benzene. In Fig. 9.5, we plot two components (xy and zz) of pyridine quadrupole moment when the molecule is oriented perpendicular to the silver surface. Barring Q_{xx} , both diagonal and off-diagonal components of the FDE-pol quadrupole moments are within 18% of the reference values (FDE-EO-FT) at the equilibrium configuration. Here the axes are such that "z" and "x" are perpendicular to the silver surface and the pyridine ring, respectively. At equilibrium separation, the charge exchange and polarization effects on the molecular region distorts the density more along the "y" and "z" axes, which is reflected from the high values of Q_{yy} and Q_{zz} . At an optimal distance between the subsystems the FDE-pol Q_{yy} and Q_{zz} are off by 8 and 18% respectively. Beyond 4 Å separation the FDE-pol quadrupole moments are in near perfect agreemeent with FDE-EO-FT values due to the limited polarization.

9.4.3 Non-additive Kinetic Potentials

The FDE-pol method can also be used with NAKPs instead of EO. This is illustrated in Fig. 9.6 where we plot μ_z of pyridine oriented perpendicular to the metal surface as a function of pyridinesurface distance using various NAKPs. The results obtained using the different NAKPs are obtained using a monomer basis set instead of the full supermolecular basis set used in the FDE-pol and FDE-EO-FT simulations. It was not possible to run the FDE-pol method using NAKPs and the full supermolecular basis set due to an overpolarization of the density in the bonding region. The inclusion of the polarization embedding operator leads to an increased density in the bonding region and thus a larger density overlap that the NAKPs could not compensate for which resulted in an unphysical electron density. The main consequence of using a monomer basis



Figure 9.6. Dipole moments of the active fragment with various NAKPs.

is that the density cannot delocalized into the silver fragment which results in a much smaller dipole moment as shown in Fig. 9.6.

In Fig. 9.6 we compare FDE-pol and FDE-FT for the Thomas-Fermi (TF) NAKPs. We see that the FDE-pol is able to describe the increased dipole moment at shorter distances but tends to overestimate the dipole moment as compared with TF-FDE-FT. A possible explanation for this is that TF-NAKPs is not able to describe strongly overlapping densities and thus tends to move density away from the bonding region during the FT-cycles limited the polarization due to the metal cluster. The dipole moment calculated using FDE-pol and the PW91K and NDSD NAKPs are also shown in Fig. 9.6. Both of these NAKPs gives slightly larger dipole moments that TF likely due to their better description of the density in the bonding region.

9.4.4 Mixed Functionals

One of the main advantages of the FDE method is the flexibility to use different functionals for various fragments. In the following we will explore using LDA for the metal nanocluster and LDA, PBE and SAOP functional for the molecule using the FDE-pol method. The dipole moment of the active fragment is expected to be sensitive to how a given functional allows for the polarization of the density. For this reason we choose the SAOP functional due to its correct Coulombic decay of the potential at long distances which is important for the description of response properties.^{248,305} In Fig. 9.7, we plot the components of the dipole moment of pyridine oriented perpendicularly to the Ag₅₆ surface. We see that although all three functionals gives very similar dipole moments of free molecule they differ significantly as short distances from the surface. The results from SAOP is almost 1 debye less than that obtained using LDA with PBE somewhere in between. This



Figure 9.7. Comparison of the components of the dipole moments calculated using a combination of different functionals (pyridine) and LDA (metal). Same XC functionals as the pyridine are used for the calculations of non-additive XC potentials, except for the SAOP case where the default GGA potential of the ADF program (BP86) is used for the non-additive XC potential. Pyridine is oriented perpendicular to the metal surface. Green star marks the corresponding value for molecule in the gas phase.

is likely a reflection of how these functionals describe the polarizability of the active fragment. Since LDA tends to overestimate the polarizability it also leads to the largest dipole moment in the FDE-pol method. Therefore, we expect that it will be important to use functionals that accurately describes the polarizability of molecules such as SAOP or hybrids functionals when using the FDE-pol method.

9.5 Conclusion

In this work we have presented a polarizable frozen density embedding method for computing the ground state electronic properties of strongly overlapping systems. The charge transfer effects were described using the subsystem DFT (frozen density embedding) and the polarization through DIM/QM. For FDE, we avoided the use of NAKP by enforcing external orthogonality for mutually orthogonal fragment orbitals. Furthermore, EO also allows supermolecular basis set calculations, which is not feasible with NAKPs. This hybrid method, termed as FDE-pol, produced ground state molecular densities within 10^{-4} e of reference densities obtained from accurate freeze/thaw FDE. The molecular dipole and quadrupole moments are within 18% of the reference values again extracted from FDE-EO-FT calculations. We also illustrated the flexibility of incorporating dissimlar DFT functionals in the molecular and the metallic fragments to reduce the computational cost.

$\mathbf{Part}~\mathbf{V}$

Summary and Outlook

Chapter 10 Summary of Dissertation

This dissertation was focused on the development of theoretical methods to describe and understand the tip-enhanced Raman spectroscopy and its applications in high-resolution imaging of single molecules. As a variant of SERS, TERS shares the same fundamental mechanisms, namely the electromagnetic mechanism and the chemical mechanism. However, the unique setup of molecule in a subnanometer junction leads to significantly different spectral selection rules in TERS. This dissertation addressed the origin of the spatial variance in TERS intensities mostly from a standpoint of the EMM, and developed new theoretical tools that can assist future studies of the CM. As such, this dissertation was presented in four major parts. The first part provided backgrounds of TERS and an overview of the dissertation.

Part II presented a series of efforts in the theoretical interpretation of high-resolution TERS images. Three key features of TERS images were suggested: (1) the pattern in a TERS image is unique to the underlying vibrational mode; (2) many modes that are dark in regular Raman or SERS measurements can be enhanced to the same order of magnitude; (3) a near field distribution with roughly a half nanometer FWHM is sufficient to achieve the atomic resolution in TERS. It was also proposed that it is the local change of the molecule's electronic densities that is the perturbed by the near field in TERS. With this intuitive interpretation, the method of LIRPD was developed and applied to interpret experimental images, of which the sample molecules were too large in size for DIM/QM or other conventional TDDFT methods to handle efficiently. It was demonstrated how high-resolution TERS images can be used for both chemical and structural characterizations as a complimentary tool for state-of-the-art microscopies.

Part III described the properties of strongly coupled plasmonic nanoparticles, which is the fundamental model system for a TERS junction. As two plasmonic nanoparticles approaches each other, their individual plasmons start to couple together through capacitive interactions. An atomically sharp tip on a flat substrate is able to induce and confine the near field down to a sub-molecular volume, and leads to the activation of the unique features of TERS. Also presented in this part was a study of the charge-transfer plasmon across the gap, which usually occurs *via* quantum tunneling at a lower incident frequency. Understanding these gap plasmonic properties is necessary for further studies of TERS considering the central importance of the plasmon-induced near field.

In Part IV, the frozen density embedding method was presented. The FDE method, as a subsystem (TD)DFT approach, was originally developed to treat solvated systems, but it is promising for TERS studies due to its ability to include the quantum mechanical descriptions of the metal-molecule interactions. In this part, the exact FDE method was derived for TDDFT to calculate the molecular polarizabilities in the static limit. The exact FDE relies on the use of a projection operator to de-couple the overlapping molecular orbitals of the two fragments (EO) such that the non-additive kinetic potentials are eliminated. Also, it requires the freezeand-thaw cycles to converge the two fragments, which in practice is time consuming. Therefore, the polarizable frozen density embedding method (FDE-pol) was developed to bypass the freezeand-thaw procedure with tolerable trade-offs in terms of exactness. The mutual polarization is introduced through the DIM operator to the active fragment's Hamiltonian, and thus compensates for the loss of accuracy due to the frozen densities. The FDE-pol method provides a practical alternative to study the CM of TERS/SERS since it can include, at least partially, the quantum mechanical properties of the metal fragment and at the same time the electrostatic properties through DIM.

Chapter 11 Outlook

11.1 Introduction

The theory of TERS stands on the shoulders of the well established SERS theories, which has led to early successes in interpreting experimental results as presented in this dissertation. However, there are still many open questions that needs to be addressed by theorists before robust and efficient theoretical simulations can be applied widely in practice. Taking LIRPD as an example, while the assumptions made in the simulations has reduced the computational cost, some potentially important details in TERS imaging have been overlooked, such as the charge transfer effect. Moreover, the pursuit of matching simulated results with the experiments often requires exhaustive search of tip positions, and similar patterns in TERS images may corresponds to very different tip positions. This is because of the sensitivity of TERS, and will lead to uncertainties in identifying the molecular structure or conformation. This chapter will present a few future directions in the study of TERS theory based on the author's recent findings presented above.

11.2 Future Directions for the Method of Locally Integrated Raman Polarizability Density

The LIRPD method has provided simulated TERS images with qualitatively good agreement with experimental images, and thus is regarded as an intuitive picture of the mechanism of TERS imaging. However, this simplified model is derived based on some assumptions. Although these assumptions seem reasonable, further investigations are necessary, considering the mismatches between the simulated and the experimental images and the failure in reproducing the spectra. Discussions about reproducing spectra have been presented in detail in Appendix C.6.

11.2.1 Tensor Elements of the Molecular Polarizability

In TERS simulations, the common practice is to assume the dominant element of the molecular polarizability is the zz component, where the z axis is perpendicular to the substrate. This assumption is made based on the experimental setup. In the LIRPD model, it is further simplified based on the conjecture that the plasmonic near field is polarized in the z direction. However,

other elements of the molecular polarizability tensor can be important too. The reasons are as follows.

First of all, the difference between the benchmark DIM/QM model and the LIRPD. In the DIM/QM simulations (Chapter 3), the zz component of the solved molecular polarizability is found to be the dominant term, which has led to the use of only the zz component of the free molecule polarizability in LIRPD by zeroing out all but the z component of the near field. However, the DIM/QM model solves for the molecular polarizability and the near field in two self-consistent cycles (α_{zz}^{SCF}), where the incident field is considered to be homogeneous in all three directions. In other words, the effects of the other two directions of the near field on the complete free-molecule polarizability have been implicitly accounted for in the SCF cycles, and the final α_{zz}^{SCF} is only a manifestation or representation of the observable. Moreover, even though in experiments one can ensure the incident laser to be polarized in the z direction, there is no guarantee that the plasmonic near field in the other two directions is trivial. Therefore, from a standpoint of matching the benchmark model, it is worthy of the effort to explore the effect of each component of the near field vector.

Secondly, the enhancement of the in-plane vibrations. The sample molecules in many TERS experiments are generally flat, of which the in-plane vibrations are dominant (represented by large values of α_{xz} and α_{yz} for example). Therefore, it has been seen in both experiments and in DIM/QM simulations (Fig. A.2 and C.10) that the signals of both in-plane and out-of-plane modes can be enhanced to the same order of magnitude, whereas the LIRPD spectra only enhances the out-of-plane modes as pointed out in Appendix C. Therefore, the inclusion of other tensor elements of the molecular polarizability could potentially compensate for some mismatches in the images and correct for the calculation of spectra.

11.2.2 Vibrations of the Substrate

As suggested in Ref. 13 and Appendix C, the strong binding to the substrate is critical for the molecule to be anchored during the scanning. Also, the brightspot pattern detected in the frequency region that has no molecular vibration indicates the inelastic scattering of the substrate atoms. These findings in experiments suggest that the vibrations of the substrate atoms may contribute significantly to TERS during the imaging process. However, both DIM/QM and LIRPD models assume that the metal atoms in the substrate do not vibrate. Moreover, preliminary results from a collaboration with the Apkarian group at UC Irvine have provided more straightforward observations on the substrate vibration in TERS.



Figure 11.1. TERS images of a single CO molecule on a Cu(100) substrate. The substrate is represented by a Cu_{70} cluster (a) Experimental measurements on the FWHMs of TERS images. (b) LIRPD simulated FWHMs of TERS images. (c, d) The Cu-C stretching mode at 361 cm⁻¹ and the LIRPD simulated TERS image. (e, f) The C-O stretching mode at 1947 cm⁻¹ and the LIRPD simulated TERS image. The experimental result is obtained from Apkarian group at UC Irvine. All results are not published at the time of dissertation.

As is shown in Fig. 11.1, a single CO molecule leads to a prominent vibrational mode and corresponding TERS signal when placed on a Copper substrate, which involves the stretching vibration of the Carbon atom and the binding Cu atom. This stretching mode at 361 cm^{-1} is just as strong as the original C-O stretch at around 1947 $\rm cm^{-1}$ in terms of Raman intensity, and also gives rise to a larger sized brightspot in the Raman image. The LIRPD model seems to have successfully captured the correct features of both modes. However, in order to include the Cu-C stretch, the substrate has to be described with full TDDFT. In addition to the undesirable computation cost, the use of a small metal cluster as the substrate in the model requires careful treatment of the edge effect. Specifically, an excessively small cluster as the substrate may lead to drastically different charge distribution compared with its bulk counterpart, and consequently leads to incorrect calculation of TERS images using the LIRPD method. The Raman polarizability densities tend to aggregate around the sharp edges of the small cluster, as shown in Fig. 11.2 (a,b). Moreover, it is found that the two in-plane wagging modes of the CO molecule behave differently on the small Cu₃₄ cluster and the large Cu₇₀ cluster Fig. 11.2 (c,d). It would be a much more expensive calculation if one were to use a quantum mechanical substrate that is large enough to cover a large molecule like CoTPP. Therefore, a careful design of the model system is required.



Figure 11.2. Edge effect of using small Cu cluster as TERS substrate. (a) The Raman density distribution of the Cu–C stretching mode on the small Cu₃₄ cluster. (b) The Raman density distribution of the C–O stretching mode on the small Cu₃₄ cluster. (c) One of the C–O wagging mode on the small Cu₃₄. (d) The same C–O wagging mode on the large Cu₇₀.

11.3 Future Directions for the Frozen Density Embedding Method

11.3.1 Exact FDE for the Damped Response Theory

With the proof of principle for the exact FDE in static linear-response theory, it is natural and important to generalize the method into the damped response theory ⁸⁰ to obtain the frequency-dependent polarizabilities.

The first-order change in the electronic density of fragment I is written as:

$$\delta\rho_{\rm I}(\mathbf{r},\omega) = \sum_{i,a} \delta P_{ia}(\omega)\phi_i(\mathbf{r})\phi_a^*(\mathbf{r}) + \delta P_{ai}(\omega)\phi_i^*(\mathbf{r})\phi_a(\mathbf{r})$$
(11.1)

which is similar to (8.20), but here the orbitals and the densities are assumed to be complex due to the frequency dependence. Following the same steps in Chapter 8 until (8.56), we arrive at the

following expression for the perturbed density matrix element:

$$\delta P_{ia}^{\mathrm{I}} = \chi_{ia}^{\mathrm{I}} \, \delta v_{ia}^{\mathrm{eff}} = \frac{n_a - n_i}{\omega - \epsilon_{ia} + i\Gamma} \cdot \left[\delta v_{ia}^{\mathrm{ext}} + \delta v_{ia}^{\mathrm{intra}} + \delta v_{ia}^{\mathrm{inter}} + \delta v_{ia}^{\mathrm{EO}} \right] , \qquad (11.2)$$

where n_a, n_i are the occupation numbers, and Γ is the phenomenological energy broadening parameter. Γ accounts for the effective lifetime of the electronic excited state, i.e., damping of the excited state. In addition to the external perturbation term δv^{ext} , the three terms constituting the overall effective potential δv^{eff} can be further decomposed into:

$$\delta v_{ia}^{\text{intra}}(\mathbf{r},\omega)[\delta\rho_{\text{I}}] = \delta v_{ia}^{\text{Coul}}(\mathbf{r},\omega)[\delta\rho_{\text{I}}] + \delta v_{ia}^{\text{XC}}(\mathbf{r},\omega)[\delta\rho_{\text{I}}]$$
(11.3a)

$$\delta v_{ia}^{\text{inter}}(\mathbf{r},\omega)[\delta\rho_{\text{J}}] = \delta v_{ia}^{\text{Coul}}(\mathbf{r},\omega)[\delta\rho_{\text{J}}] + \delta v_{ia}^{\text{XC}}(\mathbf{r},\omega)[\delta\rho_{\text{J}}]$$
(11.3b)

$$\delta v_{ia}^{\text{EO}}(\mathbf{r},\omega)[\delta\rho_{\text{J}}] = \mu \sum_{j(11.3c)$$

11.4 Summary

In this chapter, a few future directions for the studies in TERS theory are proposed. Considering all tensor elements of the molecular polarizability beyond the assumed *zz* component will help address the possible effects of in-plane scatterings on TERS images. This could be especially important for resonant TERS of flat molecule where the electronic transition dipole moments are in plane. Also, the substrate vibrations need to be included in the quantum mechanical calculations because the substrate atoms can either incur inelastic light scattering themselves or couple with the adsorbed molecule to alter the vibrational modes of the whole system. The frozen density embedding method implemented in the framework of the damped response theory is crucial for practical applications of the FDE method in simulations of Raman scattering in general. In experiments the system is always excited by a laser rather than a homogeneous electric field, and thus the frequency-dependent polarizabilities are required in simulations. Appendices

Appendix A Supporting Information for Single-Molecule Imaging Using Atomistic Near-Field Tip-Enhanced Raman Spectroscopy





Figure A.1. Absorption spectra of the nanoparticles used as the probing tip calculated by atomistic electrodynamics. The dashed lines in each spectrum denotes the external field energies that are used in the simulations: (a) 3.09 eV, 3.41 eV, and 3.59 eV for Ag₅₆₁; (b) 3.09 eV for Ag₂₀₅₇; (c) 2.30 eV for Au₂₀₅₇

Simulated TERS and regular Raman spectra

TERS and regular Raman spectra are shown in Fig. A.2. TERS spectra are obtained with the tip located at the origin of XY plane and 2.5 Å above the molecule plane. The tip is pointing at the oxygen atom of water, the ring center of benzene, the ring center of porphin (slightly closer to one central H atom), and the central Zn atom of ZnP (slightly off). The tip position drastically changes the TERS intensities. The spetra shown in here is only for one specific tip position, and do not represent the maximal intensities in the scan. As a matter of fact, all of the imaged modes of each molecule have maximal TERS cross subsection*s with the same order of magnitude, $10^{-25} \frac{cm^2}{sr}$. Considering the perfect planar geometries of the molecules optimized without the metallic system, the change in the selection rule from Raman to TERS is not attributed to the symmetry breaking of molecular geometries due to the presence of metal, but to the field-gradient effect.

The enhancement of Raman signals in our simulations still follows the $|E|^4$ enhancement mechanism. Absolute values of TERS intensities for each mode of each molecule are determined by the near-field intensity and the tip position. For similar near-field enhancements (Ag₅₆₁ and Au₂₀₅₇ both give rise to field enhancement of around 300), we calculate the average enhancement factors (EF) of the specific TERS spectra shown in Fig. A.2, using the following equation:

$$EF = \frac{\sum_{i} I_{i}^{\text{TERS}}}{\sum_{i} I_{i}^{\text{Raman}}} \quad , \tag{A.1}$$

where *i* denotes each normal mode of a molecule. This average of EF avoids the infinite values due to some Raman-inactive modes observed in TERS. The average EFs are: 4.56×10^5 for water, 1.14×10^6 for benzene, 1.20×10^5 for porphin, and 5.44×10^5 for Zn-porphin. Due to the small size of NPs modeled in this work, the near-field enhancement may appear weak compared to common experimental measurements. Also, the contrast exhibited in the TERS images is essentially a normalized color map of Raman intensities. Therefore, the absolute enhancement factor or the maximal intensity is not emphasized in this work.



Figure A.2. Simulated full TERS and regular Raman spectra of the four molecules. For (a) water and (b) benzene, the Ag_{561} nanoparticle is used as the tip with the incident energy of 3.09 eV. For (c) porphin and (d) Zn-porphin, the Au_{2057} nanoparticle is used and is excited at 2.30 eV to match the resonance energy of the $Q_v(0,0)$ transition.



Line shape of the electric field along each axis with Ag_{561}

Figure A.3. Line shape of the field along each axis: the first column for X-axis, the second for Y-axis, and the third column for Z-axis. Plots in the same column share the horizontal axis. The FWHMs (Γ) are noted in the first two columns in Ångstroms. The height of near-field focal plane (height of maximum) is noted in the third column. Each row of plots corresponds to an exciting energy: (a ~ c) 3.09 eV; (d ~ f) 3.41 eV; (g ~ i) 3.09 eV. The tip-to-sample height in this figure in 2.5 Å. Each plot of field intensity is generated numerically. The FWHMs are obtained directly from the field data.

Field confinement effect on TERS images of water in the bending and antisymmetric stretching modes



Figure A.4. TERS images of the bending (first column) and anti-symmetric (second column) modes. For reference purposes, the third column shows the field enhancement distribution in the XY-plane. The first row corresponds to 3.09 eV, the second row 3.41 eV, and the third row 3.59 eV. The trend of decreasing resolution as field becomes less confined is very similar to what is described in the main text.

Field maximum location effect on TERS images of water in the bending and anti-symmetric stretching modes



Figure A.5. TERS images of the bending (first column) and anti-symmetric (second column) modes. For reference purposes, the third column shows the field enhancement distribution in the YZ-plane. The first row corresponds to $Z^{Tip} = 2.5$ Å, the second row $Z^{Tip} = 3.0$ Å, and the third row $Z^{Tip} = 3.5$ Å. The trend of decreasing resolution with the focal plane moving higher is very similar to what is described in the main text.

TERS images of water with near-field focal plane below the molecule plane



Figure A.6. TERS images of the water at each normal mode (first row) with $Z^{Tip} = 2.3$ Å and external field energy 3.09 eV. The second row shows the field distribution in this setup. The focal plane is at $Z_{max} = -0.2$ Å, which is below the molecule plane. The simulated TERS images in this case retains the atomic resolution.

TERS images of water using the $Ag_{\rm 2057}$ nanoparticle



Figure A.7. TERS images of the water generated by the large nanoparticle. (a ~ c) $Z^{Tip} = 2.5$ Å. (d ~ f) $Z^{Tip} = 3.0$ Å. (g ~ i) $Z^{Tip} = 2.5$ Å. The large nanoparticle is excited also at 3.09 eV. The larger size only increases the field intensity. The focal plane height remains the same as the smaller NP, and the field confinement is very similar.

Field confinement analyses of the gold SPM junction setup for porphyrins



Figure A.8. The Au₂₀₅₇ icosahedron nanoparticle with Au(100) as substrate. The nanoparticle is 2.5 Å above the molecule plane. The nanoparticle is excited at 2.30 eV.(a) Field distribution on the XY plane; (b) field distribution on the YZ plane; (c) the lineshape of field along each Cartesian axis.

Appendix B Supporting Information for High-Resolution TERS Probes Sub-Molecular Density Changes

B.1 Local approximation and electric multipole expansion

Theory. Within the framework of linear-response time-dependent density functional theory, we are interested in calculating the molecule's polarizability due to an electric field perturbation. The molecule's first-order induced charge density ($\delta \rho$) due to the perturbation and its polarizability (α) are obtained using linear-response time-dependent density functional theory (LR-TDDFT), which is given by

$$\delta \rho_{\alpha}(\mathbf{r},\omega) = \int \chi(\mathbf{r},\mathbf{r}',\omega) \hat{v}_{\alpha}^{\text{pert}}(\mathbf{r}',\omega) d\mathbf{r}' , \qquad (B.1)$$

$$\alpha_{\alpha\beta}(\omega) = \int \hat{\mu}_{\alpha}^{\text{eff}}(\mathbf{r},\omega) \delta\rho_{\beta}(\mathbf{r}) d\mathbf{r} = \iint \hat{\mu}_{\alpha}^{\text{eff}}(\mathbf{r},\omega) \chi(\mathbf{r},\mathbf{r}',\omega) \hat{v}_{\beta}^{\text{pert}}(\mathbf{r}',\omega) d\mathbf{r}' d\mathbf{r} .$$
(B.2)

In these two equations, the subscripts (α, β) , and other Greek indices hereafter) indicate the Cartesian direction, **r** is an arbitrary vector denoting the position in space, and the equation is Fourier transformed into the frequency (ω) domain. The density-density response function, $\chi(\mathbf{r}, \mathbf{r}', \omega)$, is given by ⁹⁰

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \lim_{\eta \to 0} \sum_{m} \frac{\langle 0|\hat{n}(\mathbf{r})|m\rangle \langle m|\hat{n}(\mathbf{r}')|0\rangle}{\omega - \omega_{m0} + \mathrm{i}\eta} - \frac{\langle 0|\hat{n}(\mathbf{r}')|m\rangle \langle m|\hat{n}(\mathbf{r})|0\rangle}{\omega + \omega_{m0} + \mathrm{i}\eta} , \qquad (B.3)$$

where *m* is the sum over all excited states of the system, ω_{m0} is the excitation energy, $\hat{n}(\mathbf{r})$ is the density operator, and η is the damping factor. The perturbation operator, $\hat{v}_{\beta}^{\text{pert}}(\mathbf{r}',\omega)$ accounting for the electric field perturbation polarized in β direction is given by

$$\hat{v}_{\beta}^{\text{pert}}(\mathbf{r}' - \mathbf{R}) = -(\delta_{\beta\delta} + F_{\delta}^{\beta}(\mathbf{r}' - \mathbf{R})) \cdot \hat{\mu}_{\delta}(\mathbf{r}') , \qquad (B.4)$$

where $\hat{\mu}_{\beta}(\mathbf{r}')$ is the dipole moment operator. Here $\delta_{\beta\delta}$ is the Kronecker delta function, and F_{δ}^{β} represents the plasmonic local field in δ direction due to the external field polarized in β direction. For molecules in a TERS junction, \hat{v}^{pert} is dominated by the plasmonic near field that is localized around the tip position **R**. Thus this operator becomes also a function of **R**. The effective dipole operator, $\hat{\mu}_{\alpha}^{\text{eff}}(\mathbf{r},\omega)$, describes the radiation of oscillating dipoles^{54,70}, and can be expanded in the electric multipole format.

$$\hat{\mu}_{\alpha}^{\text{eff}}(\mathbf{r}) \approx -\left[\delta_{\alpha\gamma} + F_{\gamma}^{\alpha}(\mathbf{r} - \mathbf{R})\right]\hat{\mu}_{\gamma} - \frac{1}{3}F_{\gamma\epsilon}^{\alpha}(\mathbf{r} - \mathbf{R})\hat{\theta}_{\gamma\epsilon} .$$
(B.5)

 $F^{\alpha}_{\gamma(\epsilon)}(\mathbf{r} - \mathbf{R})$ is the local field (gradient) distribution in the $\gamma(\epsilon)$ direction that radiates a field polarized in α direction⁷⁰. $\hat{\mu}_{\gamma}$ is the dipole operator and $\hat{\theta}_{\gamma\epsilon}$ is the traceless quadrupole operator. All the molecular properties and near fields are dependent on the frequency (ω) of the external field and generally complex. In the following we drop the ω notation for simplicity. The polarizability in the presence of the tip is then given by

$$\alpha_{\alpha\beta}(\mathbf{R}) = \int \left\{ \left[\delta_{\alpha\gamma} + F^{\alpha}_{\gamma}(\mathbf{r} - \mathbf{R}) \right] \hat{\mu}_{\gamma} - \frac{1}{3} F^{\alpha}_{\gamma\epsilon}(\mathbf{r} - \mathbf{R}) \hat{\theta}_{\gamma\epsilon} \right\} \int \chi(\mathbf{r}, \mathbf{r}') \hat{\mu}_{\delta} \left[\delta_{\beta\delta} + F^{\beta}_{\delta}(\mathbf{r}' - \mathbf{R}) \right] d\mathbf{r}' d\mathbf{r} .$$
(B.6)

Ideally, $\alpha_{\alpha\beta}$ would be obtained self-consistently in the presence of the confined near field ^{15,16,85}. This is what is done in the DIM/QM method. But in doing so, the computational cost scales up with the number of grid points necessary for the tip scanning to cover the whole molecule, which becomes nearly infeasible for large molecules like porphyrin complexes. More importantly, it doesn't allow for decomposing the molecular property into atomic contributions. To simultaneously address these two problems, we make a local approximation to polarizability in Equation B.6. Since both $F^{\alpha}_{\gamma}(\mathbf{r} - \mathbf{R})$ and $F^{\alpha}_{\gamma}(\mathbf{r}' - \mathbf{R})$ are localized around the tip-position \mathbf{R} we expect that the largest contributions to the response comes from $F^{\alpha}_{\gamma}(\mathbf{r} - \mathbf{R}) \sim F^{\alpha}_{\gamma}(\mathbf{r}' - \mathbf{R})$. Making this local approximation for the polarizability we obtain

$$\begin{aligned} \alpha_{\alpha\beta}(\mathbf{R}) & \stackrel{\mathrm{local}}{\approx} \int \left\{ \left[\delta_{\alpha\gamma} + F^{\alpha}_{\gamma}(\mathbf{r} - \mathbf{R}) \right] \hat{\mu}_{\gamma} + \frac{1}{3} F^{\alpha}_{\gamma\epsilon}(\mathbf{r} - \mathbf{R}) \hat{\theta}_{\gamma\epsilon} \right\} \cdot \delta\rho^{\mathrm{free}}_{\delta}(\mathbf{r}) \cdot \left[\delta_{\beta\delta} + F^{\beta}_{\delta}(\mathbf{r} - \mathbf{R}) \right] d\mathbf{r} \\ &= \int \left[\delta_{\alpha\gamma} + F^{\alpha}_{\gamma}(\mathbf{r} - \mathbf{R}) \right] \cdot \hat{\mu}_{\gamma} \delta\rho^{\mathrm{free}}_{\delta}(\mathbf{r}) \cdot \left[\delta_{\beta\delta} + F^{\beta}_{\delta}(\mathbf{r} - \mathbf{R}) \right] d\mathbf{r} \\ &+ \int \frac{1}{3} F^{\alpha}_{\gamma\epsilon}(\mathbf{r} - \mathbf{R}) \cdot \hat{\theta}_{\gamma\epsilon} \delta\rho^{\mathrm{free}}_{\delta}(\mathbf{r}) \cdot \left[\delta_{\beta\delta} + F^{\beta}_{\delta}(\mathbf{r} - \mathbf{R}) \right] d\mathbf{r} \\ &= \int \left[\delta_{\alpha\gamma} + F^{\alpha}_{\gamma}(\mathbf{r} - \mathbf{R}) \right] \cdot \rho^{(\alpha)}_{\gamma\delta}(\mathbf{r}) \cdot \left[\delta_{\beta\delta} + F^{\beta}_{\delta}(\mathbf{r} - \mathbf{R}) \right] d\mathbf{r} \\ &+ \int \frac{1}{3} F^{\alpha}_{\gamma\epsilon}(\mathbf{r} - \mathbf{R}) \cdot \rho^{(\mathcal{A})}_{\gamma\epsilon,\delta}(\mathbf{r}) \cdot \left[\delta_{\beta\delta} + F^{\beta}_{\delta}(\mathbf{r} - \mathbf{R}) \right] d\mathbf{r} \end{aligned}$$
(B.7)

The Einstein summation convention is employed for repeated Greek indices. In Equation B.7 two polarizability densities are defined. $\rho_{\gamma\delta}^{(\alpha)}$ is the density of the free-molecule dipole-dipole polarizability, or alpha density. $\rho_{\alpha\gamma\beta}^{(A)}$ is the density of the free-molecule quadrupole-dipole polarizability, or \mathcal{A} -tensor density. These two terms account for the radiating dipoles and quadrupoles of the molecule. Definitions of the molecular multipole polarizabilies can be found in Ref. 91. As discussed above these molecular densities should have been solved in the presence of the localized near-field around the tip, however, in the local approximation we assume that these are obtained as the response to a uniform electric field. This neglects the nonlocal coupling in the linear response that is present in the full DIM/QM simulations and thus cannot be expected

to describe the full response. In this work the usefulness of this local approximation is carefully benchmarked against the full DIM/QM response as shown in the main text. In this work, we consider only the zz component of the polarizability, which is written as

$$\alpha_{zz}(\mathbf{R}) = \int \left[1 + F_z^z(\mathbf{r} - \mathbf{R})\right] \cdot \rho_{zz}^{(\alpha)}(\mathbf{r}) \cdot \left[1 + F_z^z(\mathbf{r} - \mathbf{R})\right] d\mathbf{r} + \int \frac{1}{3} F_{z\epsilon}^z(\mathbf{r} - \mathbf{R}) \cdot \rho_{z\epsilon,z}^{(\mathcal{A})}(\mathbf{r}) \cdot \left[1 + F_z^z(\mathbf{r} - \mathbf{R})\right] d\mathbf{r} .$$
(B.8)

It is noted that integrating these densities over all space reproduces the corresponding molecular α tensor and \mathcal{A} tensor in the dressed-tensors formalism 92,93 . The difference between LIRPD and the dressed-tensors formalism lies in the multipole expansion of the perturbation operator. For the full dressed-tensors formalism, the dipole-quadrupole (A tensor) and quadrupole-quadrupole(C tensor) are typically used in addition to the α and \mathcal{A} tensors. The A and C tensors describe the molecular dipole and quadrupole induced by the gradient of the near field. This is equivalent to a multipole expansion of the perturbation operator \hat{v}^{pert} in the calculation of induced charge density. The full dressed-tensors method can reproduce the benchmark spectra 70,85,306 , under two assumptions: 1) the field gradient is small; 2) the field distribution has a fixed center. These two assumptions ensure that the leading term in the multipole expansion is the dipole-dipole term, and that the expansion point for A and C tensors is the same as the field gradient. However, these two assumptions break down for the highly confined near field in TERS. Therefore, the use of A and C tensors as was in the dressed-tensors formalism does not correctly describe TERS imaging.

The Raman polarizability densities $(\delta \rho^{(\alpha)})$ are the derivatives of polarizability densities with respect to the mass-weighted normal modes, which were calculated using the three-point numerical differentiation approach.

$$\delta\rho^{(\alpha)}(\mathbf{r}) = \frac{\partial\rho^{(\alpha)}(\mathbf{r})}{\partial Q_k} = \frac{\rho^{(\alpha)}(Q_k + \Delta Q_k) - \rho^{(\alpha)}(Q_k - \Delta Q_k)}{2s_Q \Delta Q_k} , \qquad (B.9)$$

where s_Q is the mass-weighted step size. The polarizability densities were calculated at the equilibrium geometry distorted along the normal mode coordinates in positive and negative directions. The zz components of the locally enhanced Raman polarizability densities $(\delta \rho_{\rm loc}^{(\alpha)}(\mathbf{r}))$, which are plotted for benzene and porphyrin in main text Fig. 3 and 4, are obtained by replacing $\rho^{(\alpha)}$ in Equation B.7 with $\delta \rho^{(\alpha)}$. It is written as,

$$\delta\rho_{\rm loc}^{(\alpha)}(\mathbf{r}) = \left[1 + F_z^z(\mathbf{r} - \mathbf{R})\right] \cdot \delta\rho_{zz}^{(\alpha)}(\mathbf{r}) \cdot \left[1 + F_z^z(\mathbf{r} - \mathbf{R})\right].$$
(B.10)

When the near-field confinement is beyond atomic scale, the alpha density is the dominant term. The use of \mathcal{A} -tensor density improves the imaging for small flat molecules, but its effect becomes insignificant for non-planar large molecules or unconfined field. Higher order terms, *e.g.*, octupole density, should lead to increasingly accurate reproduction of the self-consistent polarizability. We will show in Fig. B.1 that good accuracy is achieved by considering only the first term in Equation B.7.

TERS images involving A-tensor densities. In Fig. B.1, we collectively compare the



Figure B.1. TERS images calculated using both alpha and *A*-tensor densities in the same normal modes of benzene and prophyrin molecules discussed in the main text: (a,b) benzene, FWHM of field is 2.5 Å and 0.8 Å above the molecule plane; (c,d) porphyrin, FWHM of field is 3 Å and 1 Å above the molecule plane. The frequency of each normal mode is given on the left top of individual TERS image.

TERS images simulated by considering both alpha and \mathcal{A} -tensor densities (Equation B.7) with those generated from only alpha densities (in the main text). The most significant change by \mathcal{A} -tensor densities is seen in the benzene TERS images. The molecule itself is known for fieldgradient evoked Raman scattering⁷⁰, and the field band width required to reproduce DIM/QM images is 1.3 Å, below the scale of an atom. With \mathcal{A} -tensor densities included, the hotspots are moved slightly further away from the vibrating atom's positions (Fig. B.1a vs. Fig. 4.2 in the main text). Similar behavior of the \mathcal{A} -tensor densities are also observed for porphyrin (Fig. B.1b), although the hotspots are not moved as much as in the benzene case. It should be noted that for both benzene and porphyrin, the band width of the Lorentzian field is increased to reproduce DIM/QM images when \mathcal{A} -tensor densities are considered. This is expected, especially for atomically confined field, because the representation of the true near field becomes increasingly accurate when the field gradient (or even higher-order terms) is included (Equation B.7). However, the effect of \mathcal{A} -tensor densities becomes trivial when the field confinement is beyond the atomic scale.

In short, we have shown that including the \mathcal{A} -tensor densities does not drastically change the overall hotspot patterns in TERS images. The \mathcal{A} -tensor densities tend to drive the hotspot away from the vibrating atoms, especially for atomically confined near field and field-gradient active modes. But for less confined near field, \mathcal{A} -tensor densities contribute is trivial. Therefore, we



Figure B.2. Locally enhanced Raman polarizability densities of modes (a) at 678 cm⁻¹ and (b) at 1539 cm⁻¹. The confined near fields formulated in 3D Lorentzian distributions with the FWHMs of 2 Å for x, y, and z components are marked by red asterisks. The normalized real and imaginary densities are illustrated on the left and right columns in each panel, respectively. The isovalue is set to 0.2.

conclude using alpha densities alone in the LIRPD approach is sufficient to model TERS imaging for most cases.

B.2 Effects of near field distribution

Lorentzian model of the near field distribution. In our simulations, the plasmonic local field is represented by a 3D Lorentzian function, which is given as

$$F^{\text{loc}} = M \left[\left(\frac{x-a}{\frac{1}{2}\tau_x} \right)^2 + \left(\frac{y-b}{\frac{1}{2}\tau_y} \right)^2 + \left(\frac{z-c}{\frac{1}{2}\tau_z} \right)^2 + 1 \right]^{-1} + N \left[\left(\frac{x-a}{\frac{1}{2}\tau_{xi}} \right)^2 + \left(\frac{y-b}{\frac{1}{2}\tau_{yi}} \right)^2 + \left(\frac{z-c}{\frac{1}{2}\tau_{zi}} \right)^2 + 1 \right]^{-1} \cdot \mathbf{i} ,$$
(B.11)

where M, N are the magnitudes of real and imaginary near fields, respectively. τ is the full width of half maximum (FWHM) of Lorentzian distribution for the x, y, and z components. a, b, and c refer to the displacement of Lorentzian function with respect to the origin, *i.e.*, the center of the near field. The imaginary part is nonzero in resonant Raman, otherwise it is zero. In our simulations, the FWHMs for x and y components are treated equally, and the FWHMs of the real and imaginary fields along the same axis are identical. The total near field distribution in Equation B.7 is obtained by adding the unit-magnitude external field to the diagonal elements to the local field tensor.

It is worth mentioning that the 3D Lorentzian distribution is normalizable in a finite space. In practice, a grid box that is significantly larger than the molecule's size is used for the calculation of the polarizability densities. The modeled near field is bounded within this box, which corresponds to a finite energy of the plasmon. The Raman polarizability densities decay exponentially away from a molecule and near the boundaries the polarizability densities are zero. The local integration of Raman polarizability densities (zz component only) in the finite space is written as:

$$\int_{-r_{\max}}^{r_{\max}} \left[1 + F_z^{\text{loc},z}(\mathbf{r} - \mathbf{R})\right] \cdot \delta\rho_{zz}^{(\alpha)}(\mathbf{r}) \cdot \left[1 + F_z^{\text{loc},z}(\mathbf{r} - \mathbf{R})\right] d\mathbf{r}$$

$$\approx \sum_{i}^{N} \left[1 + F_z^{\text{loc},z}(\mathbf{r}_i - \mathbf{R})\right] \cdot \delta\rho_{zz}^{(\alpha)}(\mathbf{r}_i) \cdot \left[1 + F_z^{\text{loc},z}(\mathbf{r}_i - \mathbf{R})\right] \cdot \Delta V .$$
(B.12)

Here r_{max} represents the boundaries of the box, N is the total number of grid points within the box, and ΔV is volume factor (volume of a unit grid cell). The locally enhanced Raman polarizability at a point (**R**) is obtained by summing over all grids weighted by the volume element.



Figure B.3. Comparison of benzene TERS images at 664 cm⁻¹ obtained from the different near-field distributions. The near fields are in (a) 3D Lorentzianwith the FWHM of 1.3 Å, (b) 3D Gaussian with the FWHM of 1.3 Å, and (c) spherical step-function distributions with the diameter of 1.8 Å, respectively. The near fields are centered 1.0 Å above molecular plane

Field shape independence. It is found that the hotspot pattern in TERS images is not sensitive to the exact shape of the near-field distribution. In Fig. B.3, we show the TERS images of benzene at 664 cm^{-1} obtained from three different local field distributions: 3D Lorentzian, 3D Gaussian, and spherical step function distributions. The three TERS images are overall similar. The Lorentzian field leads to slightly bigger hotspots than the Gaussian, which is expected due to its fatter tail. The subtle roughness in the TERS image obtained by the step function is attributed to the discontinuity of the distribution.

Effects of field width and height. TERS image is strongly dependent on the integration volume in terms of size and position. In simulations, the height from the field center to molecular plane is fixed. Fig. B.4 illustrates the correlation between TERS images and integration volumes. The benzene molecule lies down on a silver surface. With the FWHM increasing from 1.3 to 5.0 Å on xy-plane, the image is blurred (Fig. B.4a). Keeping FWHM at 1.3 Å on the xy-plane and increasing FWHM to 5 Å for the z component do not blur the TERS image (Fig. B.4b), which means the image resolution is more sensitive to the field distributed on scanning plane. It is also



Figure B.4. Comparison of TERS images of 664 cm⁻¹ mode from different local integration volume. The center of integration volume above (a,b) 1 Å and (c) 2 Å away from the benzene plane, respectively. The FWHMs of 3D Lorentzian distributions on the *xy*-plane are (a) 5 Å and (b, c) 1.3 Å. The FWHMs of the z component are (a,c) 1.3 Å and (b) 5 Å.

shown that the drastic changes take place as the integration volume moves slightly up with respect to the molecular plane in Fig. B.4c, which means the scanning height is of importance for TERS imaging as well. These findings suggest that distributing near fields within atomic dimensions over an appropriate imaging plane is the key to the atomic resolution in TERS images.

B.3 Comparison of different methods

To further demonstrate the quality of the approximation made in LIRPD method, we compare it with the method of reported in the original TERS imaging paper ¹⁰ and later adopted in the studies of chemistry in nanocavities ^{17,18}. The gist of that method is to apply the localized near field to the Raman tensor. The idea can also be related to the dressed tensors formalism. The main difference is that the near field tensor dresses the free-molecular polarizability derivatives w.r.t. atomic displacements in the given normal mode, rather than w.r.t. the normal mode coordinate (Q_k). Also, no multipole expansion is used. We refer to that method as dressed Raman tensor.

In Fig. B.5, we show the calculated TERS images of the same three benzene modes as reported in Ref. 85, namely, symmetric bending, anti-symmetric bending, and ring-breathing. The characteristics of these three TERS images are 1) the hotspots are slightly away from the atoms, and 2) normal Raman inactive modes are activated by the strong near field gradient.

Comparing with the DIM/QM method (row a), we find the dressed Raman tensor method (row b) results in the hotspots highly localized on atoms instead of being slightly away. This is expected because the polarizability derivatives and the near field enhancement are evaluated at each atom's position. Moreover, the dressed Raman tensors method does not correctly describe normal Raman inactive modes. The cross-sections of the 664 cm⁻¹ and 835 cm⁻¹ modes in the dressed Raman tensors method (Fig. B.5 b1 and b2) are merely zero compared with the Raman active mode at 988 cm⁻¹ (b3), and the patterns in the TERS images are trivial. In short, the dressed Raman tensors method does not appear to be able to accurately describe the local perturbation of the molecule due to the confined near field in TERS.


Figure B.5. TERS images of benzene generated from three methods. Row a-c: DIM/QM, dressed Raman tensors, and LIRPD. Column 1-3: 664 cm^{-1} (symmetric out-of-plane bending), 835 cm^{-1} (anti-symmetric bending), and 988 cm^{-1} (in-plane ring breathing). The colorscale bars represent the calculated Raman scattering cross-sections.

However, using the same field distribution as in the above dressed Raman tensors method, we find the LIRPD method proposed in this work qualitatively reproduces the key characteristics of the benzene TERS images. The three TERS images all have comparable cross-section maxima. The hotspot positions are already off the atoms with only the alpha densities included. Moreover, include the \mathcal{A} -tensor densities in LIRPD further moves the hotspots away from the atoms, which was discussed in the previous section. Therefore, we conclude that the LIRPD model is a decent approximation to TERS selection rules, and helps explain the mechanism underlying the TERS images.

B.4 Interpreting TERS images of H₂TBPP

According to the previous study¹⁵, H_2 TBPP preferentially adopts concave configuration when adsorbed on the Ag(111) surface under the experimental conditions. We therefore performed the



Figure B.6. Comparison of absorption spectra of H_2 TBPP in free state and adsorbed on Ag surface. The insert illustrates the structure of free H_2 TBPP from the top and the side views (top panel), and the adsorbed structure is inserted as well (bottom panel).

calculations based on the reported concave configuration.

The simulated absorption spectra of H₂TBPP in free state and adsorbed on a Ag(111) surface are plotted in Fig. B.4. The Q-band absorption of free H₂TBPP spans from 500 to 660 nm, and the B-band absorption is centered at 420 nm. In the adsorbed state, both Q and B bands are red shifted by more than 100 nm. It shows the broad Q-band is centered around 770 nm with relatively strong absorbance cross section (Å²/molecule) even though the Herzberg-Teller term is absent. It is because the high symmetry (D_{4h}) in free state is broken due to the strong interaction between molecule and substrate in the adsorbed state. The planar porphyrin fragment is distorted due to the steric hindrance from the phenyl moiety substitutes which parallel orientate on Ag surface. The B-band at 562 nm is close to the incident light at 532 nm in experiment¹⁰. As show in Table B.1, the B_y(0,0) band excitation at 551.4 is more likely to be excited under the experimental conditions than the previously assumed Q_y(0,0) band.

To gain insight into the near-field distributions in the plasmonic junctions, we revisit the correlation between plasmonic gap and near field in the tip-to-substrate junction ⁹⁴. We collected the fitting parameters of near field in terms of the position (d_{center}) where the field magnitude is a maximum and the FWHM of near-field distributions of three components (Γ) at d_{center} correlated with the gap distance (d_{gap}) at the incident field polarized along z-axis in Table B.2. With the increasing gap distance, the field center becomes closer to the tip and the near-field bandwidths become broader. The bandwidths of the x and y components are equivalent and much broader

Table B.1. The lowest five excited states and the properties including vertical transition energy (E), oscillator strength (f), and transition dipole moment (μ) in a.u.

Vertical transition	E (eV)	E (nm)	f	μ_x	μ_y	μ_z
$1 Q_x(0,0)$	1.54	802.3	0.218	-2.39	0.20	-0.44×10^{-3}
$2 Q_y(0,0)$	1.62	763.2	0.455	-0.26	-3.37	-0.42×10^{-2}
3	2.17	571.0	0.059	-1.05	-0.73×10^{-1}	-0.24×10^{-1}
$4 B_x(0,0)$	2.18	569.8	1.351	5.03	0.18	-0.70×10^{-2}
$5 B_y(0,0)$	2.24	551.4	1.056	-0.29	4.37	-0.19×10^{-2}

than that of the z component. The ratio of bandwidths between x (y) and z components is generally smaller than 1/2 for the tips with different curvatures. Additionally, the previous study has shown that the near field is further squeezed and pushed toward tip in the presence of a molecule in the junction due to the screening effects¹⁴. Considering the near-field simulation results and orientation of H₂TBPP adsorbed on Ag substrate (see Fig. B.7), the integration volume in the shape of disk with $\Gamma_{x/y} = 12$ Å and $\Gamma_z = 6$ Å is centered at 9.2 Å above Ag surface.

Table B.2. Fitted parameters of near-field distribution having the maximal magnitude along gap direction. The tips are in the shape of icosahedron and tetrahedron. All the parameters in Å.

	Icosahedron-to-substrate			Tetrahedron-to-substrate			
$d_{\rm gap}$	$\mathrm{d}_{\mathrm{center}}$	$\Gamma_{x/y}$	Γ_z	$\mathrm{d}_{\mathrm{center}}$	$\Gamma_{x/y}$	Γ_z	
4	2.0	8.5	2.5	1.9	6.7	2.8	
5	2.6	10.1	2.9	2.5	7.8	3.0	
6	3.3	12.1	3.3	3.2	8.9	3.4	
7	4.0	13.6	3.9	4.0	9.8	4.0	
8	4.9	14.9	4.6	5.0	10.2	4.6	
9	6.0	15.7	5.5	6.0	10.4	5.3	
10	7.0	16.1	6.4	7.1	10.4	5.9	

To illustrate how the resonant Raman polarizability densities spatially distributed throughout the scanning volume which is the entire space for the integration via scanning, we take one normal mode at 1182.7 cm⁻¹ for example. The center of scanning space is located 2.7 Å above the top of H₂TBPP. A portion of the resonant Raman densities localized on the top of a butyl group are taken into account in the local integration, as shown in Fig. B.7a. As a result, the TERS image arising from the Raman spectral mapping on the midplane of scanning volume is featured by a hotspot on a butyl group (Fig. B.7b).

The simulated SERS and TERS spectra incorporated with experimental TERS spectrum measured on a lobe are demonstrated in Fig. B.8. The SERS spectrum obtained from the zz component of Raman polarizability shows most of important modes. However, the intensity at 1520 cm⁻¹ is quite strong compared with other modes. The TERS simulated by the LIRPD method is in good agreement with the experimental spectrum. All the important peaks and relative intensities are well reproduced. It confirms the LIRPD is a reliable approach for simulating both TERS image and spectrum.

The simulated TERS images at 900, 990, 1520 cm^{-1} are consistent with the experimental TERS mapping results. The characteristic bright four-lobe pattern is hold in low-wavenumber



Figure B.7. Resonant Raman polarizability densities and resonant TERS image of the mode at 1182.7 cm^{-1} (a) The Raman polarizability densities in real part are distributed throughout the scanning volume in green box with the thickness of 6 Å above the porphyrin plane in the perspective view. The distances among the Ag surface, the porphyrin plane, the top of molecule, and the center of integration volume are displayed in red. The densities are normalized and the absolute isovalue is set to 0.05 with the positive sign in blue and the negative sign in yellow. (b) The simulated resonant TERS images.



Figure B.8. Comparison of resonant Raman spectra from the experimental measurements and theoretical simulations. The experimental TERS spectrum measured by the tip on a lobe in red. The simulated SERS spectrum obtained from the zz component of Raman polarizability in blue. The simulated TERS spectrum obtained from the LIRPD by using the integration volume in 3D Lorentzian distribution with $\Gamma_{x/y} = 12$ Å and $\Gamma_z = 6$ Å in green. The experimental spectrum is adapted from Ref. 10.

modes. More importantly, we see the central dark area gets smaller from low to high wavenumbers and eventually collapses to a hotspot in the center, which agrees the experimental results. In addition, it is speculated that the high-wavenumber modes above 1210 cm⁻¹ contain more contributions from the porphyrin core, but the experimental TERS mapping were insufficiently resolved to conclusively make this conclusion.¹⁰ Our simulated TESR image at the frequency of 1520 cm⁻¹ clearly shows the hotspot arising from porphyrin core. It confirms again the LIRPD



Figure B.9. Comparison of resonant TERS image from the experimental measurements (top panel) and the theoretical simulations (bottom panel). The excitation energy at the B_y transition. The resonant TERS images are the combination of the modes at the frequencies around (a) 900, (b)990, and (c) 1520 cm⁻¹, respectively. The experimental images are adapted from Ref. 10.

approach and the assumed near field used for local integration are appropriate.

We now explore the effect of H_2 TBPP tautomers on its TERS images. The TERS images with hydrogen tautomerization are given in Fig. B.10b and B.10d at frequencies at 810 and 1185 cm⁻¹. In comparison, the TERS images of one specific configuration are provided in Fig. B.10a and B.10c. We find that averaging the degenerate modes of only one configuration is already sufficient to match the experimental images, and the enforced tautomerization of the porphyrin leads to nothing more than slightly more symmetric patterns.

We also examined the TERS images under the $Q_y(0,0)$ excitation as was proposed in the experiment (Fig. B.11). However, no significant difference is identified in comparing the TERS images under $B_y(0,0)$ and the $Q_y(0,0)$ excitations. This is expected because the transition dipoles of both these two excited states are associated with the base porphyrin ring, but the TERS tip mainly probes the butyl groups and is not likely to reach the bottom of the molecule. Moreover, the transition dipole moments are mostly in the xy plane with very small z contributions (Table B.1), whereas in TERS the z scattering is the dominant component detected. As a result, the effects of these two resonance states are equally small. Therefore, we conclude that the TERS images of H₂TBPP is insensitive to the resonant Raman effect unless the butyl groups are excited.



Figure B.10. Comparison of resonant TERS image with and without tautomer contribution. The excitation energy at the B_y transition. The resonant TERS images are the combination of the modes at the frequencies around (a,b) 810 and (c,d) 1185 cm⁻¹ (a,c) without and (b,d) with the tautomer contributions. The dashed arrow indicates the hydrogen transfer in tautomerization.

B.5 TERS images of porphycene tautomers.

In Fig. B.13, the left and middle columns illustrate the topview of Raman polarizability densities in scanning volumes. Correlating density distributions with TERS images, we see the hotspot distributions in the images are similar to the real density distribution patterns. Comparing individual TERS images of *cis* with its counterparts in *trans*, we see the subtle differences in the tautomer structures are well identified.

The TERS image of the band at 1250 cm^{-1} and individual mode contributions for the *cis'* configuration are illustrated in Fig. B.14. The total image is a combination of two modes. In the *cis'* configuration, the prominent density distributions are related to the *ortho*-hydrogen vibrations. The mode with the large displacements of the central hydrogen atoms provides the major contribution to the total TERS image, where the hot spots are distributed on the adjacent pyrrole moieties of the *cis'* porphycene. It is evident that the image pattern follows the configuration of the two central hydrogens which bind to the *ortho*-pyrrole in the *cis'* porphycene.



Figure B.11. The resonant TERS images of H₂TBPP molecule with $Q_y(0,0)$ transition excited: (a) 810 cm⁻¹; (b) 1185 cm⁻¹. Each of the TERS images is averaged from the combination of prominent degenerate modes within a 20 cm⁻¹ window, which are the same as in Fig. 4 of the main text.



Figure B.12. The sideview (top row) and topview (bottom row) of the optimized structures of the trans, cis, and cis' configurations on a Cu(111) surface from left to right.



Figure B.13. Raman polarizability densities and resonant TERS images of (a) *trans* and (b) *cis* porphycene molecules. The normalized real and imaginary density distributions with isovalue of 0.2 are on the left and middle columns in each panel, respectively. The vibrational frequencies and the corresponding TERS images are on the right columns.



Figure B.14. The resonant TERS images of the cis' configuration of porphycene. TERS images of the modes at (a) 1246 and (b) 1247 cm⁻¹, and (c) the total image.

Appendix C Supporting Information for Resolving Molecular Structures with High-Resolution TERS Images

C.1 Energetics of CoTPP conformers



Figure C.1. Relative energies of three CoTPP conformers: (a) phenyl-up, (b) pyrrole-up (reference), and (c) pyrrole-down. The Cu substrate included in the geometry optimization is not shown in the figure. (d-h) the simulated TERS images of the pyrrole-down structure that are similar modes to those in Fig. 5 B(2-6).

In light of the CoTPP conformers, we find the phenyl-up structure is the most stable one on Cu(100) surface, and the pyrrole-up structure is a local minimal. The energy difference between these two conformers is -2.280 eV ($E^{phenyl-up} - E^{pyrrole-up}$) in our calculations. Comparing with the previously studied H₂TBPP molecule¹⁵, the relative orientation of the pyrroles is different in the CoTPP conformers. Specifically, the most stable geometry of the H₂TBPP molecule, termed "concave", has pyrrole hydrogens pointing downwards, whereas the pyrrole hydrogens point either flat or upwards in the stable CoTPP geometries. This is because the H₂TBPP molecule is stabilized mostly by the large butyl side groups. The butyl groups are not flat on metal surfaces, and thus give rise to enough room for the pyrrole hydrogens to point downwards. However, the CoTPP molecule has simple phenyl groups, and the steric force pushes the pyrroles to bend upwards when the phenyl groups are forced to lie flat on the metal surface. The terms "concave"

and "convex" used in Ref. 15 refer to the large side groups. In this manuscript, we use "phenyl-up" and "pyrrole-up" to avoid confusions considering the smaller side groups.

We also identified a meta-stable CoTPP conformer that has pyrrole pointing downwards (Fig. C.1 c), which corresponds to the "concave" H_2 TBPP. In this "pyrrole-down" geometry, the phenyl groups are almost flat. This meta-stable geometry can be obtained in either of these two ways: 1) by constraining the phenyl torsion angles to be zero during the geometry optimization on Cu substrate; 2) by flipping the "pyrrole-up" geometry upside down and then optimizing the geometry with a loose convergence criterion. Either lifting the constraint of the first approach or increasing the numerical quality in the second approach leads the optimized geometry back to the most stable "phenyl-up" structure, which explains the meta-stability of this geometry. The energy difference between the "pyrrole-down" and the "pyrrole-up" structures is +0.775 eV.

We simulated the TERS images of the pyrrole-down structure with a 6 Å near field centered at about 0.3 Å above the highest point of the phenyl group. This focal plane is considered to be probing the similar parts of Raman polarizability densities as underneath the molecule in the pyrrole-up geometry. We find that the TERS images more often than not different that those of the stable pyrrole-up geometry (Fig. C.1 d-h). Compared with the pyrrole-up structure, the phenyl groups in the pyrrole-down structure are further away from the substrate, which is the main reason why the TERS images are different. Moreover, we believe that the pyrrole groups are likely to be pressed down to some extent by the scanning tip in the experiment, but not strong enough to permanently flip the pyrrole geometry. This may be result in the discrepancies between the experimental and the simulated Raman scattering images, which cannot be completely captured using one single stable structure.



C.2 TERS images within an integration window

Figure C.2. TERS images obtained in wide integration windows. The images selected as matches to experiment (Fig. 5) are highlighted by the red boxes.

The experimental TERS images reported in Ref. 13 were generated by integrating the recorded spectra within a certain window of frequencies centered, and the size of the integration window is different for different bands. In Fig. C.2 and C.3 we present the simulated TERS images intended to match the experimental images from wide and narrow integration windows, respectively. The experimental TERS images of the bands at 300 cm⁻¹ (Fig. C.2 A) and 700 cm⁻¹ (Fig. C.2 B) have the widest integration windows, approximately 50 $\rm cm^{-1}$, and the integration window for the 1156 cm⁻¹ band (Fig. C.2 C) is about 20 cm⁻¹. As shown in Fig. C.2, different modes that have similar TERS images can be found for each of these three bands, even though some other modes do have different TERS images. For the 300 cm^{-1} mode to have a single round brightspot in the center of the molecule, the associated vibrational mode can either be central Co out-of-plane vibration or symmetric nitrogen vibrations. And these two modes can also be found in the phenyl-up and dehydrogenated CoTPP structures, essentially generating the same TERS images. Therefore, it is the least differentiating TERS image among the three structures. For the 700 $\rm cm^{-1}$ mode, the cross pattern can be found with the modes featuring the eight pyrrole hydrogens' out-of-plane vibrations. However, the TERS image does not clearly differentiate the phase difference in the vibrations. The three in-plane vibrational modes at around 1170 cm^{-1} have nearly identical TERS images. The very subtle difference in the brightspot strengths around the base porphyrin rings may be related to the relative magnitudes of the adjacent pyrrole-hydrogen

and phenyl-hydrogen displacements.



Figure C.3. TERS images obtained in narrow integration windows. The images selected as matches to experiment (Fig. 5) are highlighted by the red boxes.

The three modes presented in Fig. C.3 are obtained from very narrow integration windows, which essentially include only single modes. Comparing to the frequency bands in Fig. C.2, the TERS images change more drastically for different modes around the three frequencies presented in Fig. C.3, which may explain the necessity of using narrow integration windows in the experiments.

To correctly combine nearby modes in the spectrum into one average TERS image requires very accurate descriptions of relative intensities, tip positions, and molecular structures, which is very difficult to achieve. Considering that the experimental images can be well explained by TERS images of single modes, we do not arbitrarily average the TERS images within a window in this manuscript.

C.3 TERS images generated with two configurations of the near field

In our simulations, we find the near field is likely to be more confined and focused below the molecule when the tip is moved to the flat phenyl groups. All the six experimental TERS images can be well reproduced essentially using two near field distributions: 1) w = 10 Å and h = +0.5

Å for pyrrole modes; 2) w = 6 Å, and h = -0.5 Å for phenyl modes. Using two field distributions is an approximation to change in field localizations during the constant-current scanning in experiment. In this section, Fig. C.4 and C.5, we present the TERS images of each mode using each of the field configuration to illustrate the necessity of varying field distributions.



Figure C.4. TERS images generated from two different field distributions. Row A: experimental images. Row B: Lorentzian field distribution has w = 10 Å, and h = +0.5 Å. Row C: Lorentzian field distribution has w = 6 Å, and h = -0.5 Å. Each column represents an experiment-simulation comparison, and is indexed in alignment with main text Fig. 5. The best matching images are in Row B, highlighted by the red box. Experimental images are adapted from Ref. 13.



Figure C.5. TERS images generated from two different field distributions. Row A: experimental images. Row B: Lorentzian field distribution has w = 10 Å, and h = +0.5 Å. Row C: Lorentzian field distribution has w = 6 Å, and h = -0.5 Å.

C.4 Contributions from *A*-tensor densities

In our simulations, we find that the \mathcal{A} tensor (quadrupole-dipole polarizability) contributes significantly to the TERS images of CoTPP. Overall, the \mathcal{A} -tensor densities have much larger value than the α -tensor (dipole-dipole polarizability) densities. Here, "polarizability" generally refers to the Raman polarizability, *i.e.*, the derivative of molecular electronic polarizability with respect to a give normal mode. Interestingly, the \mathcal{A} -tensor densities contribute to the TERS images in roughly three different ways for different vibrational modes. Using the following three figures, we briefly discuss the difference behaviors of \mathcal{A} -tensor densities distributions. Because only the dominant z-polarization of the near field is considered, the elements accounted for in the calculation of TERS intensities are α_{zz} , \mathcal{A}_{zzx} , \mathcal{A}_{zzy} , and \mathcal{A}_{zzz} . The subscripts indicate the Cartesian directions. For example, \mathcal{A}_{zzx} component represents the zx quadrupole induced by a z-polarized field. In each mode, all the density distributions are normalized to the maximum value of the α_{zz} density, such that the relative significance of the α -tensor and \mathcal{A} densities are easily visualized.



Figure C.6. \mathcal{A} -tensor density contributions to inner-molecule in-plane modes. Row A: the mode at 1176 cm⁻¹. Row B: the mode at 3097 cm⁻¹. Each mode presented here is only one of the degenerate modes (two around 1176 cm⁻¹ and four around 3097 cm⁻¹). Each TERS image shown in main text comes from the combinations of all degenerate modes. In the density distribution isosurface plots of each tensor element, the positive values are colored in yellow and the negative in blue, and all values are normalized to the maximum value of α_{zz} . The isovalues in each α_{zz} density distribution plot are ± 0.03 , and ± 0.1 for \mathcal{A} -tensor density distributions. The following two figures share the same color scheme and isovalues.

For the in-plane vibrational modes, the Raman polarizability densities also have in-plane distributions in terms of the locations of the positive and negative values. However, we find two types of in-plane modes to which the \mathcal{A} -tensor densities contribute differently. The 1176 cm⁻¹ mode is a typical mode of which the \mathcal{A} -tensor dictates the TERS image (Fig. C.6A). This mode features inner-molecule scissoring vibrations (the *ortho*-hydrogens on the phenyls being the strongest vibrating atoms). Its α_{zz} densities closely follows the atomic vibrations.

The TERS image with only α_{zz} contributions have brightspots, strictly speaking, away from the vibrating hydrogens, which are coincidentally on top of the phenyl rings. Meanwhile, the distributions of \mathcal{A} -tensor densities are different. The excessive \mathcal{A} -tensor densities around the para- and meta-hydrogens are essentially the origin of the brightspots outside each phenyl groups. When the *ortho*-hydrogens are vibrating strongly in-plane, the associated \mathcal{A} -tensor densities will be distributed in-plane centered around those hydrogens, which leads to their localization outside the phenyl rings. On the contrary, the TERS image of the stretching mode at 3097 cm^{-1} is not altered so much by the \mathcal{A} -tensor contributions (Fig. C.6B). The vibrations are localized on the two meta-hydrogens on each phenyl group, which has plenty of room for the atoms to move and for the densities to be distributed outside the molecule. As a result, both α_{zz} and \mathcal{A} -tensor densities are mostly localized on the vibrating atoms, and the corresponding TERS image is changed only slightly in the positions of the brightspots. It is worth mentioning that while the α -tensor TERS image can be easily understood as a result of the local symmetry breaking in the density distributions and the positive-negative value cancellations, the effect of the \mathcal{A} -tensor densities is not as straightforward. The \mathcal{A} -tensor densities are localized by both the field and the field gradient. The field gradient of a unimodal field distribution has two peaks. Thus, the resulting brightspot is not located perfectly at the excessive densities. Moreover, when the field center is close to the molecular plane, the variation in the A_{zzz} component (also the α_{zz}) along the z direction is more likely to diminish due to positive-negative cancellation, as both the field and the field gradient have symmetric distributions in the z direction.



Figure C.7. A-tensor density contributions to out-of-plane modes. Row A: the mode at 295 cm⁻¹. Row B: the mode at 760 cm⁻¹.

For the out-of-plane vibrations, the \mathcal{A} tensor and α tensor have similar distributions despite the difference in the overall magnitude. The two out-of-plane modes we find that matches experimental TERS images are at 295 cm⁻¹ and 760 cm⁻¹ (Fig. C.7). In the 295 cm⁻¹ mode, the central Co and the eight pyrrole hydrogens vibrates, and its TERS images generated with and without \mathcal{A} -tensor density contributions are very similar except for the size of the brightspot

in the center (Fig. C.7 A). The α_{zz} densities are mostly localized on the central Co atom, which can be explained by its intrinsically larger polarizability than hydrogens. For an out-of-plane mode, the positive and negative values are distributed in the opposite side of plane normal to the atomic displacement vectors. Similar distributions are found for \mathcal{A} -tensor densities as well with positive and negative values distributed above and below the molecular plane. However, the densities around the central Co atom are only found in the A_{zzz} component, whereas for the \mathcal{A}_{zzx} and \mathcal{A}_{zzy} components the densities are mostly localized on the pyrrole hydrogens. \mathcal{A}_{zzx} and \mathcal{A}_{zzy} components also exhibit out-of-phase density distributions, and the localizations of the majority densities aligns with the x or y directions. Specifically, the A_{zzx} component has anti-symmetric distributions localized on the two pyrrole groups in the x directions, and A_{zzy} is in the y directions. The cancellation of opposite signs leads to the zero intensities outside the molecule. The \mathcal{A} -tensor densities of the 760 cm⁻¹ mode behave in the a very similar way (Fig. C.7 B). However, the brightspots outside the pyrrole groups stem from the fact that the positive and the negative densities are not distributed perfectly symmetrically across the molecular plane. Generally speaking, for out-of-plane modes, both α_{zz} and the relevant \mathcal{A} -tensor densities have symmetrical out-of-plane distributions for the positive and negative values, which is the main reason why including *A*-tensor densities does not change the TERS brightspot locations.

The contributions of \mathcal{A} -tensor densities for the 1531 cm⁻¹ and 3185 cm⁻¹ modes are presented in Fig. C.8. These two modes exhibit features of both in-plane and out-of-plane vibrations, and the effects of \mathcal{A} -tensor densities are a mixture of both cases as discussed in the previous two figures.



Figure C.8. \mathcal{A} -tensor density contributions to outer-molecule in-plane modes. Row A: the mode at 1531 cm⁻¹. Row B: the mode at 3185 cm⁻¹. The Raman polarizability density distributions and the mode vector of the 3185 cm⁻¹ mode are associated with only one of the four phenyl degenerate modes. Both modes have in-plane and out-of-plane components of the atomic displacement vectors.

Focusing on any vibrating atom in any mode, both the α and the \mathcal{A} -tensor densities tend to be distribute along its displacement vector in this normal mode, and the positive and negative values

densities are symmetric with respect to the equilibrium coordinate of this atom. For out-of-plane vibrations, the relevant tensor elements $(\alpha_{zz}, \mathcal{A}_{zzx}, \mathcal{A}_{zzx}, \mathcal{A}_{zzy})$ have similar distributions, with positive and negative values on opposite sides of the molecular plane, which makes the TERS images less sensitive to the inclusion of \mathcal{A} -tensor densities in the simulations. For an out-of-plane mode, the vibrating atoms and the nearby Raman polarizability densities seem to be independent of each other. However, this is not the case for atoms that are in the inner part of the molecule in an in-plane mode. The α_{zz} and \mathcal{A}_{zzz} densities still tend to distribute along the displacement vectors. But the \mathcal{A}_{zzx} and \mathcal{A}_{zzy} elements have rather different distributions. The combination of the different distributions make it necessary to include the \mathcal{A} -tensor densities in the calculations. These different distributions can be think of as the in-plane modes that have only outer atoms vibrations, the density distributions of different tensor elements appear to be "independent" again. Therefore, we believe the \mathcal{A} -tensor density should be included in general for the calculation of TERS images. The less obvious effect of \mathcal{A} -tensor densities on some modes is more of a visual artifact than the correct physical mechanism.

C.5 Scattering from the substrate



Figure C.9. TERS images from ERS background. Top row: the background TERS image from (a) experiment and (b) simulations. Bottom row (c-d): TERS images of the 760 cm⁻¹ mode illustrating the range of view for the molecular TERS images. Experiment images are adapted from Ref. 13.

It was proposed in Ref. 13 that the polarization of the substrate atoms is also captured in TERS images, which corresponds to the brightspot fringes that extends outside the molecule. The substrate scattering is the most visible in the electronic Raman scattering (ERS) image. The ERS signals are mapped at the frequency that has no molecular vibrations ($\sim 2000 \text{ cm}^{-1}$ for CoTPP). It is considered as a map of molecule's local electronic polarizabilities.

The ERS image is simulated by the same LIRPD procedure, but using the electronic polarizability (α + \mathcal{A}) densities instead of Raman polarizability densities. As is shown in Fig. C.9(a-b), the LIRPD model reproduces the molecular ERS, with the brightspot localized in the porphyrin central Co atom that is more polarizable intrinsically. However, the electronic densities of the substrate are currently not accessible due to the classical treatment, and as a result the outer ring of brightspots is not captured. Therefore, in this work, the TERS images of the CoTPP are only focused in a smaller area that covers the molecule, highlighted by the grey box in Fig. C.9. For the 700 cm⁻¹, the TERS brightspots also extend outside of the molecule, but it is shown in Fig. C.9(d) that the smaller area of view for the simulated TERS image is sufficient to enclose all the TERS brightspots related to the molecule.



C.6 Spectra with the tip pointing at a pyrrole group

Figure C.10. (a) Spectra of CoTPP with tip around pyrrole. (b) The tip atom in DIM/QM and the field center in LIRPD both point at the same position projected into the xy plane, denoted by the red sphere. The focal-plane at about h = +0.5 Å in DIM/QM with width $w = \sim 7$ Å, and h = +0.5 Å with w = 10 Å in LIRPD. (c) The locally enhanced Raman polarizability density distribution of the 760 cm⁻¹ mode obtained in DIM/QM. (d) The locally enhanced Raman polarizability density distribution of the 760 cm⁻¹ mode obtained in LIRPD.

Here we present the simulated spectra from the DIM/QM method and the LIRPD method

and demonstrate the limitation of current models. The experimental spectrum for benchmarking is published in Ref. 13, corresponding to the tip pointing roughly in between a pair of pyrrole hydrogens. In the DIM/QM simulation, the substrate and the molecule system is the same as used throughout this whole paper, but a Cu icosahedron nanoparticle is used to induce the near field (with parameterized dielectric functions). When the tip is put at a position outside the pyrrole group, the induced near field has a confinement of about 7 Å in diameter and the focal plane is at 0.3 Å above the molecular plane. The DIM/QM spectrum qualitatively reproduces the experiment. The overall characteristics of the experiment spectrum are reproduced in DIM/QM, such as the strong peaks at 1100 cm⁻¹ and 1550 cm⁻¹ and the weak peaks at 300 cm⁻¹ and 3000 cm⁻¹, even though a few other peaks are missing. This indicates that the self-consistently solved molecular polarizabilities should in principle be able to accurately describe the TERS intensities, but it is usually limited by the lengthy and expensive processes of searching for the desired field localization and the repeated self-consistent calculations for tip positions. The LIRPD spectrum currently does not correctly describe the relative intensities of TERS because its local approximation to the molecular response and the simple model of the near field. However, the flexibility in tuning field confinement and positions offered by the local approximation made in the LIRPD model provide an efficient tool in interpreting the spatial distribution of TERS brightspots. In Fig. C.10 (c and d), we present the localized Raman polarizability density distributions obtained from DIM/QM (self-consistent) and LIRPD ($\alpha + A$), using the 760 cm⁻¹ mode as an example. We see that in both subfigures the densities are localized around the vibrating pyrrole hydrogens that are close to the near field center, which further explains why LIRPD is suited for simulating the spatial variance of TERS intensities.

Appendix D Supplementary Information for Atomistic Characterization of Plasmonic Dimers in the Quantum Size Regime



Figure D.1. Normalized total absorption spectra of the Na_{20} monomer and the dimer with different gap sizes (z).



Figure D.2. Normalized total absorption spectra of the Ag_{20} monomer and the dimer with different gap sizes (z).



Figure D.3. Normalized total absorption spectra of the Au_{20} monomer and the dimer with different gap sizes (z).

Appendix E Supplementary Information for Polarizable Frozen Density Embedding with External Orthogonality



Figure E.1. Dipole moment of the metal-molecule supermolecular system build from the individual fragments.



Figure E.2. Minor components (x and y) of the molecular dipole moment as a function of separation between benzene and the silver surface. (a-b) pyridine perpendicular to the silver surface, (c-d) water, (e-f) pyridine parallel to the silver surface, (g-h) benzene parallel to the surface.



Figure E.3. Components of the dipole moment of the active fragment (pyridine oriented perpendicular to Ag_{56}) with various NAKPs.



Figure E.4. Comparison of x, y components of the dipole moments calculated using a combination of LDA, PBE, and SAOP (pyridine) and LDA (metal). Pyridine is oriented perpendicular to the metal surface. Green star marks the corresponding value for molecule in the gas phase.

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Vita

Pengchong Liu

Education

2015 to 2020	Ph.D., Chemistry
	The Pennsylvania State University
	University Park, PA
2013 to 2015	M.S., Materials Science and Engineering
	University of Pennsylvania
	Philadelphia, PA
2009 to 2013	B.Eng., Materials Science and Engineering
	B.A., English Language and Literature
	Zhejiang University
	Hangzhou, China

Awards and Honors

2019Troxell Memorial Scholarship in Chemistry2017-2019Harry and Catherine Dalalian Graduate Student Fellowship

Publications

Pal, P. P.; Liu, P.; Jensen, L. Polarizable Frozen Density Embedding with External Orthogonalization. J. Chem. Theory Comput. 2019, 15, 6588–6596.

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[†]Contributed equally.