

The Pennsylvania State University
The Graduate School

**MEMORY FUNCTION FORMALISM FOR THE ELECTRICAL
CONDUCTIVITY OF PERIODIC SYSTEMS**

A Dissertation in
Physics
by
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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

May 2022

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Abstract

Calculating the conductivity of periodic systems in the presence of scattering is a formidable challenge because scattering couples the many degrees of freedom in the system. The most broadly employed resolution of this dilemma is the semiclassical treatment given by Boltzmann transport theory, which simplifies the coupling to render the problem tractable. In this approximation, all scattering is assumed to be incoherent. While this is usually acceptable in the limit of weak scattering, it is not valid for strong scattering. The conductivity derived within Boltzmann transport theory also only describes intraband motion of electrons, leaving open the question of how the conductivity is affected when multiple bands are present near the Fermi level.

Alternatively to the semiclassical approach of Boltzmann transport theory, the Kubo formula gives the exact conductivity. However, because it requires the system's exact eigenstates and their energies, it may only be applied to microscopic systems which are small enough to be solved numerically. The behavior of such small systems does not mimic that of macroscopic systems, especially in the direct-current (dc) limit of the conductivity. In particular, the dc conductivity of a finite supercell is either zero with open boundary conditions or infinite with periodic boundary conditions. Only with a small numerical broadening does the Kubo formula yield a finite dc conductivity, but strong dependence on the broadening parameter obscures the true dc conductivity. Hence the precision of this approach is limited by the size of a supercell one can diagonalize, making it impractical for the study of realistic macroscopic systems.

In this dissertation, we derive a method to calculate the conductivity of macroscopic multiband systems which is valid for any scattering strength. The conductivity is a dynamical relaxation function, so to calculate it, we must solve the dynamics of operators in the system. We use a Mori projection on the equation of motion for the operators, which separates time evolution of operators into two contributions, one due to the pristine system and a memory term due to scattering. This yields a system of generalized Langevin equations for the relaxation functions, which we solve by approximating the memory term by a single memory function. This memory function describes the relaxation of the slowest collective variables, which dominate long-time dynamics.

With this result, we derive a formula for the conductivity of the full system with scattering in terms of the conductivity of the pristine system without scattering and a complex memory function, $\sigma(\omega) = \sigma^{(0)}(\omega + M(\omega))$. The imaginary part of the memory function describes the broadening of transitions by scattering at low frequencies, and its real part provides a frequency shift. This formula is independent of the nature of the scattering, such as by disorder, the Coulomb interaction, or phonons, is independent

of the method used to evaluate the memory function, and is valid for all scattering strengths.

Our formula for the conductivity includes not only intraband motion, but also the interband contributions which are not described in standard Boltzmann transport theory. Although the interband contributions vanish for zero scattering, they grow with scattering as the bands are broadened, so that this term is important for multiband systems with moderate scattering. Note that multiband systems can refer not only to complex materials, but also simple materials studied through large supercells, where the density of bands is increased through the folded-zone scheme. The importance of the interband contribution is most pronounced when the Fermi level is in a gap, where the intraband contribution vanishes and only interband contributions to the conductivity are present. Surprisingly, we find that at low to moderate scattering strength, scattering increases the dc conductivity by broadening the bands into the gap, an effect that cannot be described by standard Boltzmann transport theory.

By comparing the intraband contribution in our formula for the conductivity to that given by standard Boltzmann transport theory, we show that in the zero-frequency limit the memory function parallels the inverse relaxation time. Hence, this formula can be implemented into existing Boltzmann transport theory codes with the memory function replaced by the inverse relaxation time. This simple extension would make existing Boltzmann transport valid for multiband systems in the weak-scattering limit.

To address the strong-scattering limit, we must calculate the memory function consistently with its formalism. Specifying the case in which scattering is due to disorder, we derive a self-consistent equation for the memory function. In the zero-frequency limit, the self-consistent equation becomes an analytic formula for the memory function. This formula shows that a finite level of disorder, the zero-frequency memory function diverges, which corresponds to vanishing conductivity, i.e., a metal-to-insulator transition. Taking the limit of large $M(0)$, we obtain an analytic formula for the critical disorder.

The only inputs for the formulae described above are the density response function of the pristine system and a potential representing the disorder. The former is readily available in *ab initio* codes and the latter is easily obtained analytically, e.g., a screened Coulomb or a Gaussian potential. Hence, all our equations are suitable for implementation into *ab initio* code, and we have implemented them into the density functional theory code `exciting`. For comparison to previous work, we use a disorder potential which is the continuous analogue of Anderson disorder, and evaluate the zero-frequency memory function and dc conductivity for sodium, chosen as a nearly-free-electron gas. We find that disordered sodium undergoes a metal-to-insulator transition at a finite level of disorder. We compare our results to Boltzmann transport theory and to existing memory function calculations for the free-electron gas. For low disorder, where the approximations of Boltzmann transport theory are valid, the two theories agree, while for strong disorder only the memory function captures the metal-to-insulator transition.

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List of Symbols

$\psi_{n,\mathbf{k}}(\mathbf{r}), u_{n,\mathbf{k}}(\mathbf{r})$	Bloch wavefunction and its periodic part
$c_{\alpha}^{\dagger}, c_{\alpha}$	Creation and annihilation operators for a state ψ_{α}
$\langle \psi_{\alpha} , \psi_{\alpha} \rangle$	Bra and ket for ψ_{α} in the space of states
ε_{α}	Energy indexed by α
H, H_0, H_i	Full, pristine, and scattering Hamiltonians
V, N_e, n_e	System volume, number of electrons, and number density of electrons
\hbar, e, m	Reduced Planck constant, electron mass, and electron charge
k_B, β	Boltzmann constant, and inverse temperature
$f(\varepsilon)$	Fermi-Dirac distribution
$\mathbf{r}, \mathbf{s}, \mathbf{k}, \mathbf{q}$	Vectors in real space (\mathbf{r}, \mathbf{s}) and reciprocal space (\mathbf{k}, \mathbf{q})
$\nabla, \partial_{\mathbf{k}}$	Vector derivative, i.e., gradient, in real and reciprocal space
$\hat{\rho}(\mathbf{r}), \hat{\rho}(\mathbf{q})$	Density operator in real and reciprocal space
$\hat{\mathbf{j}}(\mathbf{r}), \hat{\mathbf{j}}(\mathbf{q})$	Current operator in real and reciprocal space
L, L_0, L_i	Liouvillians for the full, pristine, and scattering Hamiltonians
\underline{X}	Vector or matrix in the space of operators
$A_{\alpha}(\mathbf{q})$	Orthonormal basis operator with index α
$P(\mathbf{q}), Q(\mathbf{q})$	Projectors into and out of the subspace of operators with wavevector \mathbf{q}
$(A, B), (A, B)_0$	Operator inner product between operators A and B evaluated in the full and pristine systems

$\langle A \rangle, \langle A \rangle_0$	Thermal average or ensemble average of the operator A in the full and pristine systems
$\chi(\mathbf{q}, t), X(\mathbf{q}, z)$	Density response functions in time and frequency space
$\phi(\mathbf{q}, t), \Phi(\mathbf{q}, z)$	Density relaxation functions in time and frequency space
$\boldsymbol{\sigma}(\mathbf{q}, t), \boldsymbol{\sigma}(\mathbf{q}, z), \sigma_{\alpha,\beta}(\mathbf{q}, z)$	Conductivity tensor in time and frequency space, and its Cartesian components
$C(\mathbf{q}, z), C^{(0)}(\mathbf{q}, z)$	Correlation functions of full and pristine systems, where $C = \chi, \phi, X, \Phi, \sigma$
$M_{\alpha,\beta}(\mathbf{q}, z), M(z)$	Memory function, exact and approximate

Acknowledgments

To give proper acknowledgment and thanks here to all who have made the completion of my doctorate possible is a monumental task which could double the length of this dissertation. The mentors, colleagues, family, and friends mentioned here are among the most recent and memorable, but there are certainly many more in my heart who have contributed in a large or small way. To all who have encouraged or supported me along my way here, even if they're not written, your names are here too.

First, I would like to thank my adviser, Jorge Sofo, for his seemingly endless patience and support, and for his persistent good cheer. Through our collaboration I learned to go beyond thinking as a student and begin thinking as a researcher. In addition, he has helped me to learn many key scientific lessons, such as effective communication and choosing where best to focus efforts, as well as several personal ones. His mentorship, support, and friendship have been invaluable, and I cannot express my appreciation enough.

My appreciation also goes to my committee members, Jun Zhu, Lasse Jensen, and Chaoxing Liu, for their support, and also my collaborators Santiago Rigamonti, Maria Troppenz, and Claudia Draxl for our beneficial discussions and work together. Through my doctoral studies, I have benefited from many other mentors and colleagues in many capacities, ranging from technical discussions to insights on equity and advice for professional development. I would like to thank Eric Hudson, Kristin Dreyer, Małgorzata Kowalik, Lucas Hackl, Macro Muzio, Pavlo Bulanchuk, and Emmy Albert. I have also been delighted to share in the successes of several mentees, and would like to thank Phoebe McClincy, Jeanpun Antarasen, and Yongcheng Chen for allowing me to be part of their progress.

My officemates Jacob Robbins, Mohamed Mauroof Umar, Garrett DuCharme, and Cristóbal Vallejos made 211 Osmond a much happier place to be. I appreciate our many good conversations and willingness to help one another, as well as their tolerance of my puns and jokes. Special thanks to Jacob for helping to proofread this dissertation and for his uncanny ability to fix my code just by listening, and to Umar for sharing in the delights of gardening and side-hustles.

My time as an undergraduate at Montana State would not have been the same without the support and efforts of Carla Riedel, Warren Esty, John Carlsten, John Neumeier, and Russ Walker, and for this I am most thankful. Likewise, I am indebted to Dan Nicklay, Darren Gabrielsen, Lyn Mugleston, Michael McCormack, Robert Bass,

Virginia Hammond, for their roles in preparing me to reach this far throughout high school. Many of these educators made a way for me to keep moving forward when life seemed determined to stop me, and I will never forget that.

My friends who have been essential to my life up to this point are too many to list. At Penn State I have enjoyed the companionship of Dominic Veconi, Bill Faugno, Parul Maheshwari, Songyang Pu, Yayun Hu, Arnaud Ndayishimiye, Yicheng Zhang, Adam Telatovich, Jackson Henry, Källan Berglund, Hari Padmanabhan, Ya-Wen Chuang, Yaqi Zhang, Ssohrab Borhanian, Yang Ge, Colin Turley, Bill Dusch, friends in the Science Policy Society, and many more. At Montana State, the same is true for Gavin Voeller, Zach Winter, Jake Parker, Jackson Knoll, Slater Kirk, and Jesse Lee.

Outside of my studies postsecondary studies, so many have contributed to my happiness and success that any attempt to list them might eclipse the rest of this dissertation. Therefore, although I am very tempted to fill another several pages with your names, I will trust that you know whom you are. Special thanks to Nathan Voeller for his friendship throughout both my undergraduate and graduate degrees, Maria Barsukova for proofreading this dissertation, and to Hillary Child for her valuable insights from high school through doctoral studies. Thank you also to housemates Dan Bowers, Jordan Batchelor, Keagan Downey, Julia LaFond, Andrew Cwiek, and Phil Chidekel for their company, and to my longtime friends in the Cory family, Jack Johnston, Beth Brubaker, and Jim & Judy Eisses for their ever-present encouragement.

My thanks also go to Lucas Orona, Mary Kaltenberg, and Saumya Shivam for hosting me during conference travel. I would like to thank all the benefactors who have supported my progress financially through scholarships and fellowships. The work presented in this dissertation was completed with support by the National Science Foundation Graduate Research Fellowship Program under Grant No. DGE1255832 and with support and training provided by the Computational Materials Education and Training (CoMET) NSF Research Traineeship under Grant No. DGE-1449785. Any opinions, findings, and conclusions or recommendations expressed in this dissertation are my own and do not necessarily reflect the views of the National Science Foundation.

I am indebted to many for their support during the most difficult times of my life. My greatest thanks go to Maciej, Natalie, Courtney, Karen, T.J., Steve, Dwight, Jordan, Julie, Julie, Linda, and others who helped me to fight on. I will never forget it and will always be grateful.

Most of all, my thanks go to my family, especially my parents Dan & Linda and my brother Ryan. Thank you so much for encouraging me and sharing in both my successes and my trials, being ever-ready with encouragement and having faith in me when my own was running out, supporting me in more ways than I am prepared to count, always being ready to listen and lend your advice, and of course for helping to proofread this dissertation. You are the best I could ask for.

Chapter 1 | Introduction

The electrical conductivity is among the most basic and most technologically important material properties, as the motion of electrons through semiconductor devices and conducting contacts dictates the operation of all modern technology. These devices are inevitably limited by scattering due to impurities or imperfections in the lattice, or disturbances such as phonons or the electron-electron interaction, which cause deviations from their ideal or expected behavior.

Complementing the previous case, in which scattering is a handicap, a change in conductivity with scattering is the working principle of many types of sensors. For example, adsorbed pollutants act as scattering centers when adhered to graphene, metal oxides, and others [2,3]. In such sensors, understanding how various types of disorder affect conductivity enables us to deduce the types and concentrations of adhered molecules.

However, in the presence of scattering, material properties such as the conductivity are not trivial to calculate. These material properties describe macroscopic behavior, yet must be derived from the dynamics of the system's microscopic degrees of freedom. Scattering couples the system's microscopic degrees of freedom, so that for a macroscopic system with astronomically many degrees of freedom, their dynamics are too complicated for us to follow exactly.

In the case of the conductivity, most modern approaches to this problem are based off of one of two theories: Boltzmann transport theory or the Kubo formalism. Both describe macroscopic properties in terms of microscopic physics through statistical mechanics, but they differ in how they make the difficult problem of the microscopic dynamics solvable. Summarily, since we cannot calculate the dynamics of a macroscopic system's many microscopic degrees of freedom exactly, we must approximate either the dynamics by coarse-graining the microscopic couplings into effective macroscopic dynamics, as is the approach of Boltzmann transport theory, or our model for the system by evaluating the

conductivity for a microscopic system, as is done when using the Kubo formalism.

In either approach, the conductivity $\boldsymbol{\sigma}$ is the linear-order coefficient of the current \mathbf{j} generated in the system by an applied electric field \mathbf{E} , as is familiar from Ohm's law,

$$\mathbf{j} = \boldsymbol{\sigma} \cdot \mathbf{E}. \quad (1.1)$$

Our goal is then to calculate the average current to linear order in the electric field, and then we will identify the coupling coefficient as the conductivity. We will consider the system to be described by a Hamiltonian composed of a pristine periodic part H_0 and scattering part H_i ,

$$H = H_0 + H_i. \quad (1.2)$$

1.1 Boltzmann transport theory in the relaxation time approximation

Boltzmann transport theory derives from the Boltzmann equation, originally used to study the dynamics of fluids with interacting particles. Instead of tracking the motion of each particle, one tracks the evolution of a semiclassical one-particle distribution function, which captures all dynamics except that due to interactions. Interactions are then treated approximately. Similarly, in Boltzmann transport theory, we replace the full microscopic dynamics by a semiclassical one-particle distribution function $f(\mathbf{r}, \mathbf{k}, t)$. In a periodic system without scattering, \mathbf{k} is a good quantum number, so in the time evolution of the distribution function, the only part of the dynamics which couples \mathbf{k} to other wavevectors \mathbf{k}' is that due to scattering. To make the problem tractable we need to keep the evolution of the distribution function local in \mathbf{k} , which is accomplished by treating the scattering term approximately.

To derive Boltzmann transport theory and calculate the dc conductivity, we follow the derivation presented by Mahan [4, Sec. 8.1.1]. We begin by considering a homogeneous system at equilibrium with a constant electric field. In equilibrium, the distribution function should be time-independent, so

$$0 = \frac{df}{dt} = \frac{\partial f}{\partial t} + \mathbf{v}_{\mathbf{k}} \cdot \nabla f + \mathbf{F} \cdot \partial_{\mathbf{k}} f + \left(\frac{df}{dt} \right)_{\text{coll}} = -\mathbf{E} \cdot \partial_{\mathbf{k}} f + \left(\frac{df}{dt} \right)_{\text{coll}}. \quad (1.3)$$

Here $\mathbf{v}_{\mathbf{k}}$ is the electron velocity, $\mathbf{F} = -\mathbf{E}$ is the force due to the applied electric field \mathbf{E} , and $\left(\frac{df}{dt} \right)_{\text{coll}}$ is the collision term which accounts for scattering. We have used the facts

that $\frac{\partial f}{\partial t} = 0$ under a constant field and $\nabla f = 0$ by homogeneity, and as a result we can simplify $f(\mathbf{r}, \mathbf{k}, t) \rightarrow f(\mathbf{k})$. We have also taken $\hbar = 1$ and the electron charge $e = 1$.

The collision term is most frequently addressed within the relaxation time approximation,

$$\left(\frac{df}{dt}\right)_{\text{coll}} = -\frac{f(\mathbf{k}) - f_0(\mathbf{k})}{\tau_{\mathbf{k}}}, \quad (1.4)$$

where $f_0(\mathbf{k})$ is the equilibrium distribution that would exist without the perturbing electric field. According to Eq. (1.4), scattering tends to induce an exponential decay toward the current-free zero-electric-field distribution $f_0(\mathbf{k})$, and according to Eq. (1.3), in the new equilibrium $f(\mathbf{k})$ under the applied electric field, the relaxation due to scattering is balanced by the electrons' acceleration by the applied field.

Combining Eqs. (1.3) and (1.4) allows us to expand $f(\mathbf{k})$ to linear order in the applied field,

$$f(\mathbf{k}) = f_0(\mathbf{k}) - \tau_{\mathbf{k}} \partial_{\mathbf{k}} f(\mathbf{k}) \cdot \mathbf{E} \approx f_0(\mathbf{k}) - \tau_{\mathbf{k}} \partial_{\mathbf{k}} f_0(\mathbf{k}) \cdot \mathbf{E}, \quad (1.5)$$

which then gives the average current,

$$\langle \mathbf{j} \rangle = \frac{1}{V} \sum_{\mathbf{k}} f(\mathbf{k}) \mathbf{v}_{\mathbf{k}} \approx \frac{1}{V} \sum_{\mathbf{k}} \left(-\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right) \Big|_{\varepsilon_{\mathbf{k}}} (\partial_{\mathbf{k}} \varepsilon_{\mathbf{k}}) (\partial_{\mathbf{k}} \varepsilon_{\mathbf{k}}) \tau_{\mathbf{k}} \cdot \mathbf{E}. \quad (1.6)$$

Here V is the volume of the system, and we have noted that the zero-field distribution is just the Fermi-Dirac distribution, $f_0(\mathbf{k}) = f(\varepsilon_{\mathbf{k}})$, assumed that the equilibrium current in the absence of the electric field is zero, $\langle \mathbf{j} \rangle_0 = \sum_{\mathbf{k}} f_0(\mathbf{k}) \mathbf{v}_{\mathbf{k}} = 0$, and remembered that the velocity is $\mathbf{v}_{\mathbf{k}} = \partial_{\mathbf{k}} \varepsilon_{\mathbf{k}}$. Comparing this to Eq. (1.1), we identify the conductivity as

$$\boldsymbol{\sigma} = \frac{1}{V} \sum_{\mathbf{k}} \left(-\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right) \Big|_{\varepsilon_{\mathbf{k}}} (\partial_{\mathbf{k}} \varepsilon_{\mathbf{k}}) (\partial_{\mathbf{k}} \varepsilon_{\mathbf{k}}) \tau_{\mathbf{k}}. \quad (1.7)$$

The last step is to calculate the relaxation time, which is done essentially by using Fermi's golden rule for the collision term together with the linear-order expansion of the distribution function, Eq. (1.5), a calculation which is omitted here for brevity and clarity of presentation. The result is

$$\frac{1}{\tau_{\mathbf{k}}} = 2\pi n_i \int \frac{d\mathbf{k}'}{(2\pi)^3} |\langle \mathbf{k}' | H_{i,1} | \mathbf{k} \rangle|^2 \delta(\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}}), \quad (1.8)$$

where we have assumed the scattering Hamiltonian H_i is composed of many single scatterers described by $H_{i,1}$ and present at a concentration n_i which is dilute enough that they can be treated through single scattering events. Provided the eigenstates $|\mathbf{k}\rangle$ and energies $\varepsilon_{\mathbf{k}}$ of the pristine periodic Hamiltonian without scattering H_0 are known, the last two equations, Eqs. (1.7) and (1.8), contain all the information necessary to calculate the conductivity.

This formalism is ubiquitous in *ab initio* codes for its simplicity and ease of use [5–7]. However, the description in terms of a semiclassical distribution function places two significant limits on it. First, it describes scattering in terms of independent single scattering events, between which electrons are assumed to decohere and return the semiclassical thermal distribution. This assumption of incoherent scattering is only valid provided that scatterers are sufficiently dilute and weak, so that Boltzmann transport theory is limited to the weak-scattering regime. As such, it cannot describe physics driven by coherent scattering, such as the metal-to-insulator transition.

Secondly, the semiclassical distribution function does not capture interband coherence. As a result, Eq. (1.7) for the conductivity only accounts for intraband motion, neglecting interband contributions to the conductivity. These contributions are relevant in systems with multiple bands close to the Fermi level, especially narrow-gap semiconductors, such as those found in infrared electronics and thermoelectrics, and semimetals, such as graphene. Furthermore, regardless of the material, interband contributions are important in calculations which use large supercells, as the density of bands is proportional to the size of the supercell. This holds even for simple materials traditionally thought of as single-band, since through the folded-zone scheme each band is subdivided into many smaller bands in a large supercell. This limits the Boltzmann formula for the conductivity to simple, effectively single-band materials in small supercells.

Boltzmann transport theory succeeds in making the macroscopic limit tractable by coarse-graining the microscopic physics so that the dynamics could be described in terms of a one-particle distribution function. Its limitations stem from the fact that this distribution function is semiclassical. Hence, the next step is to replace semiclassical statistics with quantum statistics. This is the approach of Kubo.

1.2 The Kubo formalism

To move from classical statistical mechanics to quantum statistical mechanics, in calculating the average of a macroscopic variable A , we replace the sum weighted with

the distribution function f by a trace weighted with the density matrix $\tilde{\rho}$,

$$\langle A \rangle = \sum_{\alpha} f_{\alpha} A_{\alpha} \quad \Rightarrow \quad \langle A \rangle = \text{Tr}(\tilde{\rho}A). \quad (1.9)$$

As before, we are interested in the linear-order coefficient between a quantity of interest and a perturbation. Kubo's linear response formalism solves this problem exactly by computing the linear-order coefficient as a correlation function of the operator of interest and the operator which couples to the applied field [8].

Given a system with a Hamiltonian H affected by an applied perturbation $F(t)$ which couples to the system through a Hermitian operator B , the new Hamiltonian in the presence of the perturbation is $H - BF(t)$. Note that H is the full Hamiltonian of the system, with both the periodic and scattering parts. To calculate the average of an operator of interest, A , in the presence of the applied perturbation, we need to find the new equilibrium in the presence of the perturbation. It can be prepared from the unperturbed equilibrium by adiabatically switching the perturbation on over a long time. The first step in this process is to obtain the time evolution operator in the presence of the perturbation, $U(t, t_0)$.

$U(t, t_0)$ itself is not known, but we can write its first-order expansion in the applied field in terms of the known unperturbed time evolution operator $e^{-iH(t-t_0)}$,

$$U(t, t_0) \approx e^{-iH(t-t_0)} \left(1 + i \int_{t_0}^t dt' B(t' - t_0) F(t') \right), \quad (1.10)$$

so that the density matrix time-evolved from the unperturbed equilibrium is

$$\begin{aligned} \tilde{\rho}(t) &= U(t, t_0) \tilde{\rho}_0 U^{\dagger}(t, t_0) \\ &\approx \tilde{\rho}_0 - ie^{-iH(t-t_0)} \left(\int_{t_0}^t dt' [\tilde{\rho}_0, B(t' - t_0)] F(t') \right) e^{iH(t-t_0)}. \end{aligned} \quad (1.11)$$

Here $B(t' - t_0) = e^{iH(t-t_0)} B e^{-iH(t-t_0)}$ is in the interaction picture, and $\tilde{\rho}(t)$ is the density matrix evolved with the perturbation while $\tilde{\rho}_0$ is the density matrix evolved in the absence of the perturbation. At the initial time the density matrices agree, $\tilde{\rho}(t_0) = \tilde{\rho}_0$. Defining the thermal averages in the perturbed and unperturbed equilibria respectively as $\langle A \rangle(t) = \text{Tr}(\tilde{\rho}(t)A)$ and $\langle A \rangle_0 = \text{Tr}(\tilde{\rho}_0 A)$, the response of the operator A to the perturbation is

$$\langle \Delta A \rangle(t) = \langle A \rangle(t) - \langle A \rangle_0 = i \int_{t_0}^t dt' \langle [A(t - t'), B] \rangle_0 F(t'). \quad (1.12)$$

For this process to be adiabatic, we must start in the distant past, which is accomplished by taking $t_0 = -\infty$, and we must turn the perturbation on very slowly so that it is at full strength at the time t when we make the measurement, which is accomplished by the replacement $F(t') \rightarrow e^{\eta(t'-t)}F(t')$. With these provisions, the response is

$$\begin{aligned}\langle \Delta A \rangle(t) &= i \int_{-\infty}^t dt' \langle [A(t-t'), B] \rangle_0 e^{\eta(t'-t)} F(t') \\ &= \int_{-\infty}^{\infty} dt' e^{\eta(t'-t)} i \Theta(t-t') \langle [A(t-t'), B] \rangle_0 F(t'),\end{aligned}\quad (1.13)$$

and its Fourier transform is

$$\begin{aligned}\langle \Delta A \rangle(\omega) &= \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' e^{i\omega t} e^{\eta(t'-t)} i \Theta(t-t') \langle [A(t-t'), B] \rangle_0 F(t') \\ &= \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' e^{i(\omega+i\eta)(t-t')} e^{i\omega t'} i \Theta(t-t') \langle [A(t-t'), B] \rangle_0 F(t') \\ &= \left(\int_0^{\infty} dt'' e^{i(\omega+i\eta)t''} i \langle [A(t''), B] \rangle_0 \right) \left(\int_{-\infty}^{\infty} dt' e^{i\omega t'} F(t') \right) = X_{A,B}(\omega + i\eta) F(\omega),\end{aligned}\quad (1.14)$$

where $F(\omega)$ is the Fourier transform of the perturbation, where the Fourier transform is defined as $F(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} F(t)$, and $X_{A,B}(z)$ is the Laplace transform of the response function, where the Laplace transform is defined as $X_{A,B}(z) = \int_0^{\infty} e^{izt} \chi_{A,B}(t)$. At the end of the calculation, we must take $\eta \rightarrow 0$ so that the perturbation will be switched on adiabatically. Since A is a measured response, it must be an observable and hence Hermitian, so we can take as the definition of the response function,

$$\chi_{A,B}(t) = i \langle [A^\dagger(t), B] \rangle, \quad X_{A,B}(z) = \int_0^{\infty} dt e^{izt} \chi_{A,B}(t). \quad (1.15)$$

The usefulness of this definition will be apparent later, in Sec. 2.2.2.

The Kubo formula gives the exact linear-order response function, as no approximations were made in this derivation. This exactitude is both its greatest strength and its greatest limitation. On one hand, it captures the quantum coherent effects that could not be captured by Boltzmann transport theory. On the other, time evolution in the Kubo formula is evaluated by tracking the full microscopic dynamics. Specifically, through the time evolution operator $e^{-iH(t-t_0)}$, the Kubo formula requires knowledge of the exact eigenstates and energies of the system with scattering. As a result, it is limited to systems small enough to be diagonalized. The behavior of these microscopic systems is not always an accurate representation of the behavior of the corresponding systems in the thermodynamic limit. In particular, the dc limit of the Kubo formula for the

conductivity is either zero or infinity depending on the supercell's boundary conditions, as we will soon see.

In the Kubo formula for the conductivity, the operator of interest responding to a perturbation is the uniform current density operator, which is $\hat{\mathbf{j}}(\mathbf{q} = 0)/V = \hat{\mathbf{v}}/V = \hat{\mathbf{p}}/mV$ where $\hat{\mathbf{v}}$ is the velocity operator and $\hat{\mathbf{p}}$ is the momentum operator since we have taken $e = 1$, and where m is the electron mass. The perturbation is an applied electric field \mathbf{E} which couples to the Hamiltonian as $H - \int_V d\mathbf{r} \hat{\mathbf{r}} \cdot \mathbf{E}$. Using $\hat{\mathbf{v}} = i[H, \hat{\mathbf{r}}]$, we can calculate the conductivity as a current-current correlation function [8, Eq. (5.10)]. The same result can also be derived by writing the electric field in terms of a vector potential which couples to the current [4, Sec. 3.8]. In this way we obtain the Kubo formula for the conductivity, which for a general system with eigenstates labeled by s, s' is

$$\sigma_{\alpha,\beta}(\omega) = \lim_{\eta \rightarrow 0} \sigma_{\alpha,\beta}(\omega + i\eta) = \lim_{\eta \rightarrow 0} \left[\frac{i}{V} \sum_{s,s'} \frac{f(\varepsilon_{s'}) - f(\varepsilon_s)}{\varepsilon_s - \varepsilon_{s'}} \frac{\langle s | \hat{v}_\alpha | s' \rangle \langle s' | \hat{v}_\beta | s \rangle}{\omega + i\eta + \varepsilon_s - \varepsilon_{s'}} \right], \quad (1.16)$$

where we have written the tensor in terms of its components labeled by α, β . The adiabatic limit $\eta \rightarrow 0$ can be evaluated as $\lim_{\eta \rightarrow 0} \left(\frac{1}{x+i\eta} \right) = \mathcal{P} \frac{1}{x} - i\pi\delta(x)$, so that the real part of the conductivity is

$$\text{Re } \sigma_{\alpha,\beta}(\omega) = \frac{\pi}{V} \sum_{s,s'} \frac{f(\varepsilon_{s'}) - f(\varepsilon_s)}{\varepsilon_s - \varepsilon_{s'}} \langle s | \hat{v}_\alpha | s' \rangle \langle s' | \hat{v}_\beta | s \rangle \delta(\omega + \varepsilon_s - \varepsilon_{s'}). \quad (1.17)$$

While the eigenstates of an infinite system are continuously indexed, so that the Dirac deltas integrate to a function with an analytic real part, the eigenstates of a supercell are discretely indexed, so that at any frequency the conductivity is either zero or infinity. In particular, the real part of the dc conductivity in a supercell is infinite if there are any pairs of eigenstates at equal energy having a nonzero velocity matrix element, or is zero otherwise. In a periodic system with plane-wave eigenstates, $s = s'$ contributes because plane waves have well-defined velocities, $\langle s | \hat{\mathbf{v}} | s \rangle > 0$, whereas in a supercell with open boundary conditions, all eigenstates are localized to the supercell and must have zero velocity, $\langle s | \hat{\mathbf{v}} | s \rangle = 0$. As a result, the dc conductivity in periodic supercells is always infinite, and in open supercells is always zero.

The latter case is illustrated in Fig. 1.1. In particular, Fig. 1.1(a) shows that the dc limit should be approached as a limit $\omega \rightarrow 0$ while taking increasingly large supercells for the calculation; it is not simply obtained by evaluation at $\omega = 0$. That is, rather than obtaining the dc limit from strictly zero-energy excitations, $\varepsilon_s = \varepsilon_{s'}$, we should approach the dc limit as a limit of the excitation energy tending to zero, $\varepsilon_s - \varepsilon_{s'} \rightarrow 0$. As

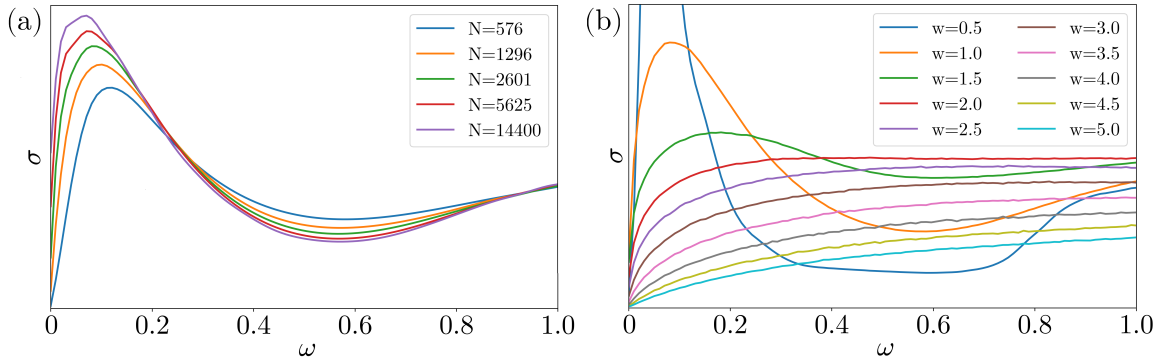


Figure 1.1. The longitudinal Kubo-Greenwood conductivity of a 2601-atom tight-binding graphene system with Anderson disorder with site energies in $[-w, w]$ illustrates the limitation of the Kubo-Greenwood approach in calculating the dc conductivity. (a) As system size increases, current-carrying excitations become available at lower frequencies, so that the low-frequency limit of the conductivity converges. However, the smallest excitation energy is still finitely large, so that the dc limit $\sigma(\omega = 0)$ remains zero. (b) By computing the conductivity as a function of disorder w for fixed system size, it is also clear that a metal-to-insulator transition is occurring as disorder increases, but since the dc conductivity is out of reach we cannot tell where. To regularize the Dirac deltas in the limit of Eq. (1.16), they are histogrammed along the ω axis with 100 bins. The dc limit appears nonzero merely because the bins are wide enough to capture Dirac deltas with $\varepsilon_s - \varepsilon_{s'} > 0$. In both plots the Fermi level is $\mu = 0.4t$ and in (a) the disorder strength is $w = t$, where t is the tight-binding hopping parameter. The frequency ω is likewise given in units of t .

increasingly large supercells are used, the set of eigenvalues becomes increasingly dense, so that the minimum excitation energy $\varepsilon_s - \varepsilon_{s'}$ for $s \neq s'$ becomes smaller and closer to zero. The same limit is necessary in systems with periodic boundary conditions as well, since there will still be a minimum excitation energy $\varepsilon_s - \varepsilon_{s'}$ for $s \neq s'$ just as with the case of open boundary conditions. Were Fig. 1.1 generated using supercells with periodic boundary conditions, it would only differ in the presence of an infinite Dirac delta peak exactly at zero frequency.

The problem of infinite or zero dc conductivity arises because the dc conductivity is the response over infinite time to a constant electric field. With periodic boundary conditions, electrons accelerate indefinitely as they cycle across the supercell boundary to the next periodic supercell, while with open boundary conditions, electrons will be stopped by the supercell boundary and current will not flow in the long-time limit. This can be demonstrated explicitly with the calculations of Greenwood, who calculated the current due to a constant electric field at finite times. In the long-time limit, his expression yields a conductivity formula identical to Eq. (1.17), so that it is often known as the Kubo-Greenwood formula for the conductivity [9, Eqs. (29) and (30)].

In practice, the most common resolution is to impart a small lifetime to the current-carrying excitations by keeping η finite as a numerical parameter to broaden them, changing the Dirac deltas in Eq. (1.17) to Lorentzians. Since scattering is the physical source of finite lifetimes, η mimics the effect of scattering. As long as the lifetime is short enough (η is large enough) that electrons scatter before crossing the supercell, the conductivity of the supercell will accurately represent that of the infinite system. However, if η is too large, it will dominate the calculation and obscure the physical effects we are trying to calculate. On the other hand, if η is too small, the dc conductivity tends toward zero or infinity as the finite-size effects of the supercell are restored, and the result is no longer representative of the dc conductivity in the thermodynamic limit.

In this way, the dc limit is extremely sensitive to η [10, 11]. The accuracy of the calculation is limited by the size of η , which is in turn limited by the size of the largest supercell we can diagonalize. This limitation is especially restrictive for computationally intensive *ab initio* calculations. As a result, the Kubo formula is impractical for all but the simplest calculations, such as those using the tight-binding model, but as Fig. 1.1 shows, even in this case the Kubo formula cannot overcome finite-size effects.

The Kubo formalism improved on Boltzmann transport theory by replacing classical statistical mechanics with quantum statistical mechanics, but did not include the coarse-graining of the microscopic dynamics which made Boltzmann transport theory tractable in the thermodynamic limit. Mori addressed this problem by devising a method of coarse-graining that is compatible with quantum statistical mechanics. Because the Kubo formalism is an exact quantum statistical mechanical description, it is a very useful starting point. Hence, Mori's approach is not so much a separate formalism so much as it is a reformulation of time evolution in the Kubo formalism that makes coarse-graining approximations natural.

1.3 The memory function formalism

The general coarse-graining procedure is to find the most relevant collective variables to describe a macroscopic system, to rewrite the equation of motion for the relevant variables by separating out contributions due to coupling with the irrelevant variables, and to approximate the dynamics due to the irrelevant variables. This leads to a macroscopic equation of motion that reproduces the most interesting results of microscopic physics. For example, the Navier–Stokes equation describes fluid behavior in terms of the collective variables pressure, density and flow rather than by tracking the positions and velocities

of individual molecules, and it is derived from microscopic physics such as conservation of particles and of momentum by focusing on an averaged density and flow that ignore microscopic fluctuations. Similarly, the Mori projection provides a means to separate relevant and irrelevant variables in the equation of motion within the framework of the Kubo formalism.

The starting point is the Heisenberg equation of motion, which is equivalent to the time evolution in the Kubo formalism through $e^{-iH(t-t_0)}$,

$$\frac{d}{dt}A(t) = i[H, A] = i[H_0, A] + i[H_i, A] , \quad (1.18)$$

where we have assumed that the operator A has no explicit time dependence. In general, the Hamiltonian is not written in terms of the relevant operators, but rather in terms of microscopic operators such as single-particle excitations. By projecting the action of the Hamiltonian into the relevant and irrelevant subspaces, Mori reformulates Eq. (1.18) to be in terms of the relevant operators and the correlation functions which contain the irrelevant operators' effects on their evolution. The result is a generalized Langevin equation known as Mori's projected equation of motion [12, Eq. (3.10)],

$$\frac{d}{dt}\underline{A}(t) = i\underline{\Omega}\underline{A}(t) - \int_0^t dt' \underline{M}(t-t') \underline{A}(t') + \underline{f}(t) . \quad (1.19)$$

Here $\underline{A}(t)$ is the vector of relevant dynamical variables, $\underline{\Omega}$ is a correlation function matrix describing their natural frequencies of oscillation, $\underline{M}(t)$ is the memory function and is a correlation function matrix through which the fluctuating force damps the natural oscillations, and $\underline{f}(t)$ is a fluctuating force vector perturbing the natural oscillations. The memory function and fluctuating force are due to the coupling between the relevant operators and the irrelevant ones. If the relevant variables completely described the system, the memory function and fluctuating force would be absent, and the relevant variables would evolve without relaxation.

Our original purpose in calculating the operators' equation of motion was to evaluate their correlation functions as they arise in the Kubo formalism, since these correlation functions are the macroscopic material properties such as the conductivity that we ultimately wish to calculate. By inserting Eq. (1.19) into such a correlation function, written as an inner product of operators $\phi_{\alpha,\beta}(t) = (A_\alpha(t), A_\beta)$, we obtain the equation of

motion for the correlation functions, written in matrix form as [12, Eq. (3.7)]

$$\frac{d}{dt}\underline{\phi}(t) = i\underline{\Omega}\underline{\phi}(t) - \int_0^t dt' \underline{M}(t-t')\underline{\phi}(t') , \quad (1.20)$$

where the fluctuating force is not present because it is orthogonal to the relevant operators with respect to the inner product that gives the correlation functions. Up to this point, no approximations have been made, so that Mori's projected equations of motion for the relevant operators and for the correlation functions are still exact. They are essentially reformulations of the Heisenberg equation of motion, Eq. (1.18), so they still contain the full complexity of the microscopic dynamics and are still prohibitively difficult to solve. The last step in the coarse-graining procedure is to address this complexity by approximating the dynamics of the irrelevant variables. In particular, if we are interested in low frequencies, then we can use the fact that the low-frequency or long-time dynamics are dominated by the slowest variables and their slow relaxations as the basis for the approximation [12, 13].

To proceed further, we must apply the so-far general discussion to the specific problem of interest. The correlation function we wish to study is the conductivity, a correlation function of the Fourier transformed current operator, $\hat{\mathbf{j}}(\mathbf{q})$. In a translationally invariant system, such as a periodic system or the free-electron gas, the current operator can be written as a collective excitation or fluctuation by a given wavevector \mathbf{q} , as can the density operator to which it is related by the continuity equation,

$$L\hat{\rho}(\mathbf{q}) = -\mathbf{q} \cdot \hat{\mathbf{j}}(\mathbf{q}) . \quad (1.21)$$

This suggests taking fluctuations of a given wavevector \mathbf{q} as our relevant variables and placing fluctuations of all other wavevectors $\mathbf{q}' \neq \mathbf{q}$ in the irrelevant subspace, a choice first proposed by Götze to describe the conductivity of the free-electron gas [14]. With this choice, the correlation functions or the relevant variables will be functions of wavevector with the form $\underline{\phi}(\mathbf{q}, t)$, as is typically the most natural way to describe correlations in translationally invariant systems.

To reinforce this choice further, recall that the memory function in Mori's projected equation of motion accounts for the relaxation of the relevant variables due to coupling to the irrelevant variables. With this choice, the memory function gives the relaxation due to coupling between fluctuations of different wavevectors. Scattering is responsible for coupling fluctuations of different wavevectors, as it does not conserve momentum. Hence, with this choice the memory function explicitly describes relaxation due to scattering.

With the relevant variables defined and the projected equation of motion derived, the last step in the coarse-graining process is to approximate the dynamics due to the irrelevant variables, i.e., to approximate the memory function. Following the idea that low-frequency dynamics are dominated by slow variables, Götze recognized that particle conservation prevents the density from instantaneous dissipation; instead, it can only disperse through a current as formalized in the continuity equation, Eq. (1.21). As a result, the density is a slow variable, and the current inherits its slow timescale. Of these two slow variables, only the current couples to fluctuations of other wavevectors, so that the dominant relaxations should be described by the memory function of the current. Hence, Götze’s approximation for the memory function in his work on the free-electron gas is to replace the nonzero relaxations by those of the current, and additionally the static correlation functions are approximated by their counterparts in the system without scattering.

Making these approximations allows Mori’s projected equation of motion to be solved for the density relaxation function with scattering in the free-electron gas. To obtain the conductivity with scattering, the last step is to relate the density relaxation function to the current relaxation function, or conductivity, by using the continuity equation to relate the density and the current. The result is a generalized Drude formula [14, Eq. (22a)],

$$\sigma(z) = \frac{n_e}{m} \frac{i}{z + M(z)}, \quad (1.22)$$

where n_e is the number density of electrons and $M(z)$ is the uniform limit of the frequency-dependent memory function.

The point at which this dissertation enters is the generalization of the memory function formalism for the electrical conductivity of the free-electron gas outlined above to periodic systems. This is possible because the key ideas of the formalism relied only on translational invariance, a property which the free-electron gas shares with periodic systems. As a result, the reasoning outlined above regarding labeling fluctuations by wavevectors with scattering coupling fluctuations of dissimilar wavevectors through the memory function carries over to the case of periodic systems. Our contribution is to derive the generalized formalism, which includes the free-electron gas as the special case of a single parabolic band, and to explore the results which follow from generalizing the formalism to all periodic systems. We place special emphasis on comparisons to Boltzmann transport theory and the Kubo formalism as leading computational approaches, and demonstrate the memory function formalism for periodic systems as a more robust alternative.

To derive the memory function formalism for general periodic systems, in Chapter 2 we set the stage by calculating our operators in the Bloch basis which describes periodic systems. Subsequently, we retrace the derivation of Mori’s projected equation of motion and Götze’s solution in the context of periodic systems. In Chapter 3, we use the solution to obtain the conductivity of the full system with scattering. The resulting equation,

$$\boldsymbol{\sigma}(z) = \boldsymbol{\sigma}^{(0)}(z + M(z)), \quad (1.23)$$

where $\boldsymbol{\sigma}^{(0)}$ is the conductivity of the pristine periodic system without scattering, is extremely simple yet substantially generalizes the Drude-like expression for the free-electron gas to an expression which describes non-parabolic bands and includes interband contributions and the anomalous conductivity. In the latter part of the chapter, we explore the implications of this formula, focusing on the new contributions and making comparisons to the free-electron gas, Boltzmann transport theory, and the Kubo formalism. In Chapter 4, to calculate the memory function explicitly, we specify the case of scattering due to disorder, and we obtain a pair of self-consistent equations for the frequency-dependent memory function. In the zero-frequency limit the self-consistent equations give an analytic equation for the memory function which demonstrates the existence of a metal-to-insulator transition and which our collaborators have implemented into their *ab initio* density-functional theory code `exciting` [1]. We apply our calculations for the memory function and the conductivity to the nearly-free-electron metal sodium as a benchmark and compare our results to those from Boltzmann transport theory in the relaxation time approximation and Götze’s memory function formalism for the free-electron gas. In Chapter 5, we conclude with a review of our results and possibilities for future work, including both refinements of approximations and further applications of the theory.

Chapter 2 |

The memory function formalism in a periodic system

In this chapter, we calculate the operators whose evolution and correlation functions we will study in the Bloch basis, a natural basis for the description of periodic systems. Then, we follow and discuss Mori's derivation of the projected equation of motion [12] and Götze's method to solve it for a free-electron gas [14] in the broader context of a generic periodic system.

2.1 The Bloch basis

2.1.1 Hamiltonian and Bloch basis states

The microscopic study of any quantum system begins with the Hamiltonian of the system and the basis which we use to study it. Here we will study a Hamiltonian H composed of a pristine periodic part H_0 and scattering part H_i ,

$$H = H_0 + H_i . \quad (2.1)$$

In the present case of a periodic system, the Hamiltonian of the pristine system can be diagonalized in the Bloch basis as

$$H_0 = \sum_{n,\mathbf{k}} \varepsilon_{n,\mathbf{k}} c_{n,\mathbf{k}}^\dagger c_{n,\mathbf{k}} , \quad (2.2)$$

where the summation over \mathbf{k} runs over vectors in the first Brillouin zone and we use periodic boundary conditions over the volume of the system $V = N\Omega$, where N is the

number of unit cells, each of volume Ω . In this dissertation, for simplicity of presentation we do not consider spin, as it is not affected by the forms of scattering we are interested in. The operator $c_{n,\mathbf{k}}^\dagger$ creates an electron in a Bloch state, defined as

$$\langle \mathbf{r} | c_{n,\mathbf{k}}^\dagger | \emptyset \rangle = \psi_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r}). \quad (2.3)$$

where $u_{n,\mathbf{k}}(\mathbf{r})$ has the periodicity of the lattice. With this definition, the Bloch state and its periodic part are normalized as

$$\int_V d\mathbf{r} \psi_{n',\mathbf{k}'}^*(\mathbf{r}) \psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} \delta_{\mathbf{k}-\mathbf{k}',\mathbf{G}} \delta_{n,n'}, \quad \int_{\Omega} d\mathbf{s} u_{n',\mathbf{k}}^*(\mathbf{s}) u_{n,\mathbf{k}}(\mathbf{s}) = \delta_{n,n'}, \quad (2.4)$$

as shown in Appendix A.1. As a result, within the unit cell the periodic part of the Bloch function forms a complete set for every band n and crystal momentum \mathbf{k} ,

$$\sum_n u_{n,\mathbf{k}}^*(\mathbf{s}) u_{n,\mathbf{k}}(\mathbf{s}') = \sum_{\mathbf{R}} \delta(\mathbf{s} - \mathbf{s}' + \mathbf{R}) \quad \text{or equivalently} \quad \sum_n |u_{n,\mathbf{k}}\rangle \langle u_{n,\mathbf{k}}| = 1. \quad (2.5)$$

2.1.2 Density and Current Operators

2.1.2.1 Density operator

With the microscopic quantities of the system defined, we now express global quantities in terms of them, beginning with the particle density and current. The density operator is

$$\hat{\rho}(\mathbf{r}) = \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}) \quad (2.6)$$

in real space, where the field operator can be expanded in the Bloch basis as

$$\hat{\psi}(\mathbf{r}) = \sum_{n,\mathbf{k}} \psi_{n,\mathbf{k}}(\mathbf{r}) c_{n,\mathbf{k}}. \quad (2.7)$$

The Fourier transformed density operator is

$$\hat{\rho}(\mathbf{q}) = \int_V d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} \hat{\rho}(\mathbf{r}) = \sum_{n,n',\mathbf{k}} M_{n',n,\mathbf{k}}(\mathbf{q}) c_{n',\mathbf{k}-\mathbf{q}}^\dagger c_{n,\mathbf{k}}, \quad (2.8)$$

where the matrix element, evaluated in Appendix A.2, is

$$M_{n',n,\mathbf{k}}(\mathbf{q}) = \langle \psi_{n',\mathbf{k}-\mathbf{q}} | e^{-i\mathbf{q}\cdot\hat{\mathbf{r}}} | \psi_{n,\mathbf{k}} \rangle = \int_V \psi_{n',\mathbf{k}'-\mathbf{q}}^*(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} \psi_{n,\mathbf{k}}(\mathbf{r})$$

$$= \int_{\Omega} d\mathbf{s} u_{n',k-\mathbf{q}}^*(\mathbf{s}) u_{n,k}(\mathbf{s}) = \langle u_{n',k-\mathbf{q}} | u_{n,k} \rangle . \quad (2.9)$$

Since $\hat{\rho}(\mathbf{r})$ is Hermitian, it follows from the definition, Eq. (2.8), that $(\hat{\rho}(\mathbf{q}))^\dagger = \hat{\rho}(-\mathbf{q})$.

From this calculation we can see that the density operator $\hat{\rho}(\mathbf{q})$ is a linear combination of electron-hole excitations or fluctuations of the same wavevector \mathbf{q} . To underscore and utilize this, we define a fluctuation operator,

$$\xi_{n',n,k}(\mathbf{q}) = c_{n',k-\mathbf{q}}^\dagger c_{n,k} , \quad (2.10)$$

and then we can write the density operator as

$$\hat{\rho}(\mathbf{q}) = \sum_{n,n',\mathbf{k}} M_{n',n,k}(\mathbf{q}) \xi_{n',n,k}(\mathbf{q}) . \quad (2.11)$$

The commutator between the fluctuation operators, which we will need later, is

$$\begin{aligned} & [\xi_{l,l',k'}(-\mathbf{q}'), \xi_{n,n',k}(\mathbf{q})] \\ &= [c_{l,k'+\mathbf{q}'}^\dagger c_{l',k'}, c_{n,k-\mathbf{q}}^\dagger c_{n',k}] \\ &= \delta_{l',n} \delta_{k',k-\mathbf{q}} c_{l,k-\mathbf{q}+\mathbf{q}'}^\dagger c_{n',k} - \delta_{l,n'} \delta_{k'+\mathbf{q}',k} c_{n,k-\mathbf{q}}^\dagger c_{l',k-\mathbf{q}'} \\ &= \delta_{l',n} \delta_{k',k-\mathbf{q}} \xi_{l,n',k}(\mathbf{q} - \mathbf{q}') - \delta_{l,n'} \delta_{k'+\mathbf{q}',k} \xi_{n,l',k-\mathbf{q}'}(\mathbf{q} - \mathbf{q}') \end{aligned} \quad (2.12)$$

Also note that the pristine part of the Hamiltonian, H_0 , can be written in terms of zero-wavevector fluctuations,

$$H_0 = \sum_{n,\mathbf{k}} \varepsilon_{n,\mathbf{k}} \xi_{n,n,\mathbf{k}}(0) . \quad (2.13)$$

2.1.2.2 Current operator

The current operator expanded in a single particle basis of Bloch waves is

$$\hat{\mathbf{j}}(\mathbf{q}) = \sum_{\substack{n,\mathbf{k} \\ n',\mathbf{k}'}} \langle \psi_{n',\mathbf{k}'} | \hat{\mathbf{j}}(\mathbf{q}) | \psi_{n,\mathbf{k}} \rangle c_{n',\mathbf{k}'}^\dagger c_{n,\mathbf{k}} , \quad (2.14)$$

where, taking $\hbar = 1$ and the electron charge $e = 1$, writing the electron mass as m , and using Eq. (2.9), the matrix element is

$$\begin{aligned} \langle \psi_{n',k'} | \hat{\mathbf{j}}(\mathbf{q}) | \psi_{n,k} \rangle &= \int_V d\mathbf{r} \psi_{n',k'}^*(\mathbf{r}) \frac{1}{2m} \left(\hat{\mathbf{p}} e^{-i\mathbf{q}\cdot\mathbf{r}} + e^{-i\mathbf{q}\cdot\mathbf{r}} \hat{\mathbf{p}} \right) \psi_{n,k}(\mathbf{r}) \\ &= \sum_G \delta_{\mathbf{k}-\mathbf{k}'-\mathbf{q},\mathbf{G}} \left\{ \frac{1}{m} \left[\left(\mathbf{k} - \frac{\mathbf{q}}{2} \right) M_{n',n,k}(\mathbf{q}) + \mathbf{P}_{n',n,k}(\mathbf{q}) \right] \right\}. \end{aligned} \quad (2.15)$$

Here

$$\mathbf{P}_{n',n,k}(\mathbf{q}) = \langle u_{n',k-\mathbf{q}} | \hat{\mathbf{p}} | u_{n,k} \rangle = \int_{\Omega} d\mathbf{s} u_{n',k-\mathbf{q}}^*(\mathbf{s}) \hat{\mathbf{p}} u_{n,k}(\mathbf{s}). \quad (2.16)$$

All together, then,

$$\hat{\mathbf{j}}(\mathbf{q}) = \sum_{n,n',\mathbf{k}} \mathbf{J}_{n',n,k}(\mathbf{q}) \xi_{n',n,k}(\mathbf{q}), \quad (2.17)$$

with

$$\begin{aligned} \mathbf{J}_{n',n,k}(\mathbf{q}) &= \frac{1}{m} \left\langle u_{n',k-\mathbf{q}} \left| \mathbf{k} - \frac{\mathbf{q}}{2} + \hat{\mathbf{p}} \right| u_{n,k} \right\rangle \\ &= \frac{1}{m} \left[\left(\mathbf{k} - \frac{\mathbf{q}}{2} \right) M_{n',n,k}(\mathbf{q}) + \mathbf{P}_{n',n,k}(\mathbf{q}) \right]. \end{aligned} \quad (2.18)$$

2.1.3 Disorder potential

In Chapter 4, we will focus on the specific case in which H_i describes scattering due to disorder. The disorder is defined by a real-space potential or equivalently its Fourier transform,

$$U(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} U(\mathbf{q}), \quad U(\mathbf{q}) = \int_V d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} U(\mathbf{r}), \quad (2.19)$$

so that the disorder part of the Hamiltonian is

$$H_i = \int_V d\mathbf{r} U(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}) = \int_V d\mathbf{r} U(\mathbf{r}) \hat{\rho}(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{q}} U(\mathbf{q}) \hat{\rho}(-\mathbf{q}). \quad (2.20)$$

We can check that H_i has the correct units by recalling that the Fourier transform imparts units of volume and the inverse Fourier transform imparts units of inverse volume, so that $\left[\frac{1}{V} \right] [U(\mathbf{q})] [\hat{\rho}(-\mathbf{q})] = (V^{-1})(EV)(1) = E$, and that it has the correct scaling with system size by checking the simple case of a constant potential, $U(\mathbf{r}) = U_0$, in which case $U(\mathbf{q}) = VU_0\delta_{\mathbf{q},\mathbf{0}}$ so that $H_i = U_0\hat{\rho}(0) = U_0 \sum_{n,\mathbf{k}} c_{n,\mathbf{k}}^\dagger c_{n,\mathbf{k}} = U_0 \hat{N}$ correctly gives one

U_0 per particle. Of course, in practical calculations the zero of energy is arbitrary, so we will always take $U(\mathbf{q} = 0) = 0$.

2.2 Dynamics

2.2.1 Time evolution of the operators

We will work in the Heisenberg picture, where time evolution of operators is determined by the equation of motion with $\hbar = 1$

$$\frac{d}{dt}A(t) = i[H, A] + \frac{\partial A}{\partial t}. \quad (2.21)$$

No operators considered in this dissertation have explicit time evolution, so the last term will always be zero for us, and therefore time evolution will be determined strictly by commutation with the Hamiltonian. To evaluate this time evolution, we use Eq. (2.12), which shows that the commutator of two fluctuations of wavevector \mathbf{q} and $-\mathbf{q}'$ yields a fluctuation with the sum of their wavevectors $\mathbf{q} - \mathbf{q}'$. According to Eq. (2.13), the pristine part of the Hamiltonian is composed only of zero-wavevector fluctuations and therefore does not mix the dynamics of different wavevectors. On the other hand, the scattering Hamiltonian is composed only of nonzero-wavevector fluctuations and therefore exclusively mixes the dynamics of different wavevectors, as shown in Eq. (2.20) for the case of disorder. In other words, the subspace of fluctuations of wavevector \mathbf{q} is invariant under the action of H_0 but not of H_i .

This becomes explicit as we evaluate the commutators using Eq. (2.12) with Eqs. (2.13) and (2.20), yielding

$$[H_0, \xi_{m,n,\mathbf{k}}(\mathbf{q})] = (\varepsilon_{m,\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}})\xi_{m,n,\mathbf{k}}(\mathbf{q}) = \varepsilon_{m,n,\mathbf{k}}(\mathbf{q})\xi_{m,n,\mathbf{k}}(\mathbf{q}), \quad (2.22)$$

where we defined the excitation energy $\varepsilon_{m,n,\mathbf{k}}(\mathbf{q}) = \varepsilon_{m,\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}}$, and

$$[H_i, \xi_{m,n,\mathbf{k}}(\mathbf{q})] = \frac{1}{V} \sum_{\mathbf{q}'} U(\mathbf{q}') \sum_l \left(M_{l,m,\mathbf{k}-\mathbf{q}}(-\mathbf{q}') \xi_{l,n,\mathbf{k}}(\mathbf{q} - \mathbf{q}') \right. \\ \left. - M_{n,l,\mathbf{k}-\mathbf{q}'}(-\mathbf{q}') \xi_{m,l,\mathbf{k}-\mathbf{q}'}(\mathbf{q} - \mathbf{q}') \right), \quad (2.23)$$

where the wavevector of the fluctuations is preserved in the case of H_0 but not of H_i . Eq. (2.23) is a multiband generalization of the fluctuating force of the free-electron

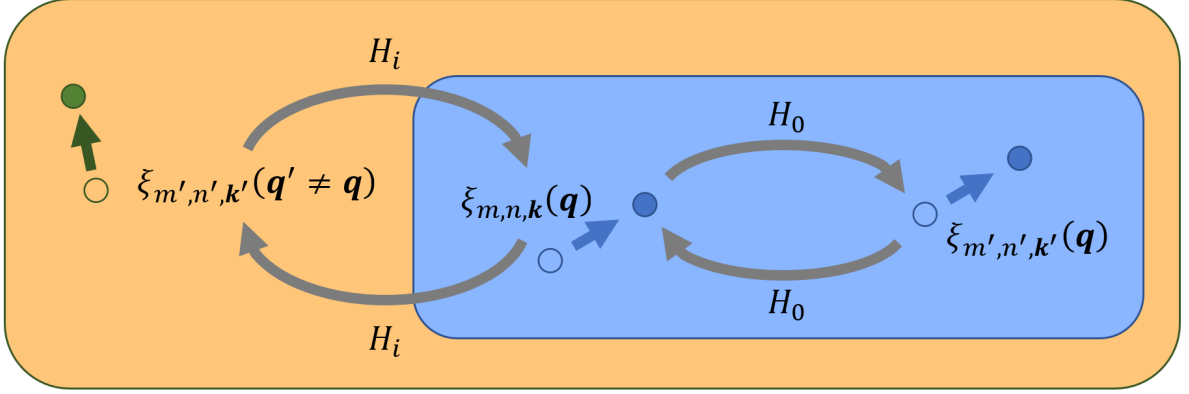


Figure 2.1. Pictorially we can divide the space of all fluctuations into those with wavevector \mathbf{q} and those with a different wavevector. The pristine part of the Hamiltonian, H_0 , preserves wavevector, whereas the scattering part, H_i , does not. This is because wavevector is a good eigenstate label in a pristine system, where translational symmetry is present, but the scattering breaks translational symmetry so that the eigenstates can no longer be labeled by wavevector. Hence, scattering gives a finite lifetime to the states labeled by wavevector.

gas [14, Eq. (8d)].

The labeling of fluctuations by wavevectors and the mixing of subspaces by scattering are the foundation for the Mori projection that yields the memory function, as used by Götze in the case of the disordered solid [12, 14]. Fluctuations labeled by \mathbf{q} comprise the operators labeled by \mathbf{q} which are our dynamical variables, and the projected equation of motion separates out terms which couple these operators to operators of the same wavevector \mathbf{q} and terms which couple them to operators of other wavevectors $\mathbf{q}' \neq \mathbf{q}$. As shown above, the former are due to the pristine system and the latter are due to the disorder, so that projecting based on wavevector distinguishes the disorder's contributions to the operators' evolution. This relationship, which we have demonstrated explicitly for the case in which H_i represents disorder, holds more generally for any scattering which does not conserve momentum. Fig. 2.1 illustrates this separation based on wavevector, where H_0 couples the dynamics of different wavevectors but H_i does not.

The equation of motion for the operators yields the equation of motion for the response and relaxation functions of the system as well, for these functions are obtained directly from the operators. This is our goal, as the conductivity is the relaxation function of the current, which can be constructed from fluctuations of the same wavevector as shown in Sec. 2.1.2.

Specifically, we can define a set of operators as

$$A_\alpha(\mathbf{q}) = \sum_{m,n,\mathbf{k}} a_{m,n,\mathbf{k}}^{(\alpha)}(\mathbf{q}) \xi_{m,n,\mathbf{k}}(\mathbf{q}). \quad (2.24)$$

Since the commutator is bilinear, using Eqs. (2.22) and (2.23) these operators inherit the property that in the equation of motion they are coupled to operators of the same wavevector by H_0 and operators of different wavevector by H_i . As noted in Sec. 2.1.2, both the density and the current are of this form.

It is worth reiterating that this approach applies more generally than only to disorder. We can use the projected equation of motion for any periodic system with momentum-nonconserving scattering, of which disorder is only one example. Other important examples include the Coulomb and electron-phonon interactions.

2.2.2 From operators to correlation functions

Before proceeding to the equation of motion for the operators, we introduce several definitions that will clarify our calculations. First, we can convert from the equation of motion for operators to the equation of motion for relaxation functions by means of an inner product of operators [8, 12, 14, 15],

$$(A, B) = \int_0^\beta d\lambda \left\langle e^{\lambda H} (A - \langle A \rangle)^\dagger e^{-\lambda H} (B - \langle B \rangle) \right\rangle, \quad (2.25)$$

where $\langle \dots \rangle$ denotes the thermodynamic average and $\beta = 1/k_B T$ is the inverse temperature, so that the inner product imparts units of inverse energy. By its nature as an inner product, it measures the overlap of A and B . Therefore, an inner product of the form $(A(t), A)$ measures the overlap of A with itself at a time t later. In other words, it measures the relaxation of the operator A over time, hence the terminology as a relaxation function. We denote these relaxation functions by

$$\phi_{\alpha,\beta}(\mathbf{q}, t) = \left(e^{iLt} A_\alpha(\mathbf{q}), A_\beta(\mathbf{q}) \right). \quad (2.26)$$

That Eq. (2.25) defines an inner product is demonstrated in Appendix B.1, where we also prove three properties which are useful in calculating the time evolution of the

relaxation functions. These are

$$(A, LB) = (LA, B) , \quad (2.27a)$$

$$(A, LB) = \langle [A^\dagger, B] \rangle , \quad (2.27b)$$

$$(e^{iLt}A, B) = (A, e^{-iLt}B) . \quad (2.27c)$$

Here L is the Liouvillian, a superoperator defined by

$$L \circ = [H, \circ] = L_0 \circ + L_i \circ = [H_0, \circ] + [H_i, \circ] . \quad (2.28)$$

Written in terms of the Liouvillian, the Heisenberg equation of motion for our operators reads

$$\frac{d}{dt}A(t) = iLA , \quad (2.29)$$

with the solution

$$A(t) = e^{iLt}A . \quad (2.30)$$

Rather than work in the time domain, we will use Eq. (2.27c) and take Laplace transforms to work in the frequency domain. The Laplace transform definition and the transform we need are

$$F(z) = \int_0^\infty dt e^{izt} f(t) , \quad R(z) = \int_0^\infty dt e^{izt} e^{-iLt} = \frac{i}{z - L} , \quad (2.31)$$

where $\text{Im}(z) > 0$. We use the counterpropagator $R(z)$ rather than the propagator merely for the convenience of avoiding complex conjugation in later calculations. We denote the Laplace-transformed relaxation functions of our operators by

$$\Phi_{\alpha,\beta}(\mathbf{q}, z) = \int_0^\infty dt e^{izt} \phi_{\alpha,\beta}(\mathbf{q}, t) = (A_\alpha(\mathbf{q}), R(z)A_\beta(\mathbf{q})) . \quad (2.32)$$

We will often write $R(z)B = B(z)$. In this dissertation, we refer to the general class of functions calculated as thermal averages over operators as correlation functions. Of these, two cases are especially relevant. The first are the relaxation functions, which as above have the form

$$\phi_{A,B}(t) = (A(t), B) , \quad \Phi_{A,B}(z) = \int_0^\infty dt e^{izt} \phi_{A,B}(t) = (A, B(z)) , \quad (2.33)$$

as obtained through Eqs. (2.26) and (2.27c). As described above, these measure the overlap between A and B . The second are the response functions, which have the form

$$\chi_{A,B}(t) = i\langle[A^\dagger(t), B]\rangle, \quad X_{A,B}(z) = \int_0^\infty dt e^{izt} \chi_{A,B}(t) = i\langle[A^\dagger, B(z)]\rangle, \quad (2.34)$$

as obtained through Eqs. (2.27b) and (2.27c). These measure how the system responds with A to a perturbation which couples to B [8].

2.2.3 Time evolution of the correlation functions

To keep the equation of motion simple, we will further require that the operators which are our dynamical variables, Eq. (2.24), are orthonormal with respect to the inner product, $(A_\alpha, A_\beta) = \delta_{\alpha,\beta}$. This is already the case for the density and current, which as we will soon show follows from the continuity equation.

Mori's projected equation of motion has the form of a generalized Langevin equation, in which an object evolves in time with contributions of a natural frequency, damping by memory function, and a fluctuating force; cf. Eqs. (1.19) and (1.20). The definition of the inner product taken in Eq. (2.25) is useful not only for directly constructing an equation of motion for the correlation functions, but also because it minimizes the average random force acting on the projected time evolution of operators [13, p. 155]. Specifically, the fluctuating force is not present in the correlation functions' equation of motion because it is orthogonal to the dynamical variables [12], as we show by rederiving the equation of motion.

Mori's projected equation of motion [12] is rederived fully in Appendix B.2 and reads

$$\sum_\beta \Phi_{\gamma,\beta}(\mathbf{q}, z) (z\delta_{\beta,\alpha} - \Omega_{\beta,\alpha}(\mathbf{q}) + M_{\beta,\alpha}(\mathbf{q}, z)) = i\delta_{\gamma,\alpha}. \quad (2.35)$$

It is derived by defining projectors into, $P(\mathbf{q})$, and out of, $Q(\mathbf{q})$, the space of fluctuations of wavevector \mathbf{q} ,

$$P(\mathbf{q})\bullet = \sum_\alpha A_\alpha(\mathbf{q}) (A_\alpha(\mathbf{q}), \bullet), \quad Q(\mathbf{q}) = 1 - P(\mathbf{q}), \quad (2.36)$$

and using these projectors to split the equation of motion for the counterpropagator into terms which separate the time evolution due to the fluctuations of the same wavevector from those due to coupling to other wavevectors. As described in Sec. 2.2.1, this

equivalently separates out evolution due to the dynamics of the pristine system from that due the effects of scattering.

Here

$$\Omega_{\beta,\alpha}(\mathbf{q}) = (A_{\beta}(\mathbf{q}), LA_{\alpha}(\mathbf{q})) \quad (2.37)$$

is the frequency of oscillations in the subspace labeled by wavevector \mathbf{q} , and

$$M_{\beta,\alpha}(\mathbf{q}, z) = i \left(Q(\mathbf{q})LA_{\beta}(\mathbf{q}), R_{Q(\mathbf{q})}(z)Q(\mathbf{q})LA_{\alpha}(\mathbf{q}) \right) \quad (2.38)$$

is the eponymous memory function, which encodes evolution projected into the space of dissimilar wavevectors $\mathbf{q}' \neq \mathbf{q}$ through the projected counterpropagator $R_{Q(\mathbf{q})}(z) = i(z - Q(\mathbf{q})L)^{-1}$. The meaning of its name can be seen through the Laplace transform convolution rule, which takes $\Phi_{\gamma,\beta}(\mathbf{q}, z)M_{\beta,\alpha}(\mathbf{q}, z) \rightarrow \int_0^t dt' \phi_{\gamma,\beta}(\mathbf{q}, t')M_{\beta,\alpha}(\mathbf{q}, t-t')$, so that the memory function imparts to the relaxation function a dependence on its history, i.e., a memory. In this way the memory function is the relaxation function of the fluctuating force in the Langevin dynamics. With this definition, the imaginary part of the memory function describes relaxation effects, rather than the real part as in Eq. (1.19)

Up to this point we have made no approximations and the equation of motion is still exact, so it is no surprise that the projected counterpropagator (corresponding to projected time evolution $e^{iQ(\mathbf{q})Lt}$) is beyond our ability to work with directly. As such, our first step is to derive its series expansion in terms of the full counterpropagator, and then to truncate the series at an acceptable point. To do this we will follow an approach described by Mazenko [16, Sec. 5.3.7].

The expansion is derived in Appendix B.3 and reads

$$\begin{aligned} M_{\gamma,\alpha}(\mathbf{q}, z) &= i (L_i A_{\gamma}(\mathbf{q}), R(z)L_i A_{\alpha}(\mathbf{q})) \\ &\quad - i \sum_{\beta,\eta} (L_i A_{\gamma}(\mathbf{q}), R(z)A_{\beta}(\mathbf{q})) \Phi_{\beta,\eta}^{-1}(\mathbf{q}, z) (A_{\eta}(\mathbf{q}), R(z)L_i A_{\alpha}(\mathbf{q})) . \end{aligned} \quad (2.39)$$

This series expansion is still exact, and by including only evolution through L_i , reiterates that the memory function includes only the effect of scattering on the time evolution, so that in a pristine system the memory function would be zero. We can construct approximations by truncating the series at a given point. In this work, we will be content to use only the first term, so that for us the memory function is given by

$$M_{\gamma,\alpha}(\mathbf{q}, z) = i (L_i A_{\gamma}(\mathbf{q}), R(z)L_i A_{\alpha}(\mathbf{q})) . \quad (2.40)$$

Because $Q(\mathbf{q})LA_\alpha(\mathbf{q}) = L_iA_\alpha(\mathbf{q})$, this expression is identical to Eq. (2.38) except that the projected counterpropagator, $R_{Q(\mathbf{q})}(z)$, has been replaced with the full one, $R(z)$. This means that we allow fluctuations of wavevector $\mathbf{q}' \neq \mathbf{q}$ to couple to one another through fluctuations of wavevector \mathbf{q} , in contrast to Eq. (2.38), which treats strictly their evolution due to coupling with other $\mathbf{q}' \neq \mathbf{q}$. The second term of Eq. (2.39) removes the effects of this coupling when the full counterpropagator is used.

2.2.4 Continuity and slow variables

The projected equation of motion, Eq. (2.35), and expression for the memory function, Eq. (2.40), still involve many degrees of freedom and functions we do not know. To solve the former problem, we will judiciously approximate the memory function by the most important of its matrix elements. To solve the latter, we will retain the effects of scattering only in dynamical functions and neglect them in static ones, i.e., we will replace the static functions of the full system by their counterparts of the pristine system. These approximations were originally employed by Götze to describe conductivity in the disordered free-electron gas [14].

We will discuss implications and refinements of the former approximation when we make it explicit later in this section. As a result of the latter, we model the full system with scattering in terms of the density of states of the pristine system, and in terms of its bands with broadening. We will give an example where this is relevant in Sec. 3.2.2.2. This approximation can be relaxed by using other methods, e.g., the coherent potential approximation, to capture modifications to the density of states [14, p. 222].

The memory function imparts a history dependence to the relaxation functions, so that for long-time or equivalently low-frequency physics, the most important matrix elements of the memory function will be those coupling operators which vary slowly. As formalized in the continuity equation,

$$-\frac{d}{dt}\hat{\rho}(\mathbf{r}) = \nabla \cdot \hat{\mathbf{j}}(\mathbf{r}), \quad (2.41)$$

which upon a Fourier transform and use of Eq. (2.29) reads

$$L\hat{\rho}(\mathbf{q}) = -\mathbf{q} \cdot \hat{\mathbf{j}}(\mathbf{q}), \quad (2.42)$$

particle density cannot simply disappear but must dissipate through a current. Hence,

the density is a slow variable, and so we choose it for our first orthonormal variable,

$$A_0(\mathbf{q}) = \frac{1}{\sqrt{(\hat{\rho}(\mathbf{q}), \hat{\rho}(\mathbf{q}))}} \hat{\rho}(\mathbf{q}) . \quad (2.43)$$

The continuity equation shows that current is generated when and only when density changes. As a result, the current inherits its time scale from the density, and is hence also a slow variable. The natural choice for our second orthonormal variable is therefore an operator proportional to the current. Using the continuity equation, we see that this variable will have the form

$$A_1(\mathbf{q}) = \frac{1}{\sqrt{(L\hat{\rho}(\mathbf{q}), L\hat{\rho}(\mathbf{q}))}} L\hat{\rho}(\mathbf{q}) . \quad (2.44)$$

The continuity equation shows that $L\hat{\rho}(\mathbf{q})$ is still in the space of fluctuations with wavevector \mathbf{q} . That $A_0(\mathbf{q})$ and $A_1(\mathbf{q})$ are orthonormal follows the properties of the inner product, Eq. (2.27). Therefore, $A_1(\mathbf{q})$ is valid as an orthonormal variable of wavevector \mathbf{q} . We can define additional dynamical variables as long as we can think of more operators labeled by a wavevector \mathbf{q} in the form in Eq. (2.24), orthonormalising them with the Gram-Schmidt procedure if necessary. In this dissertation, we will use an approximation that focuses on these most relevant variables, so that the others will not be necessary; inclusion of additional variables is left to future study.

We intend to approximate the memory function in such a way that we will be able to solve for the relaxation function in the equation of motion, Eq. (2.35). Following Götze [14], we can define a sequence of approximations by, at order N , preserving only the first $N \times N$ block of the memory function matrix and replacing the entries with row or column indices exceeding N by $M_{\alpha,\beta}(\mathbf{q}, z) = \delta_{\alpha,\beta} M_{N,N}(\mathbf{q}, z)$. Provided we label our dynamical variables in descending order of their significance, this means approximating the remaining operators with the least significant contribution included to order N and neglecting mixing between them. Before making our choice of N , we note that $M_{\alpha,0}(\mathbf{q}, z) = 0 = M_{0,\alpha}(\mathbf{q}, z)$ since

$$Q(\mathbf{q})LA_0(\mathbf{q}) = Q(\mathbf{q})L_0A_0(\mathbf{q}) = 0 . \quad (2.45)$$

Hence, the $N = 0$ approximation neglects the memory function. As we are replacing all static correlation functions (namely, $\Omega_{\beta,\alpha}(\mathbf{q})$) with their pristine counterparts, Eq. (2.35) would then be the equation of motion for the pristine system, and its solution would be

the pristine relaxation function.

Eq. (2.45) indicates that the density does not couple to itself through scattering. However, the current is also a slow variable on the same time scale as the density, so that the memory function of the current should dominate long-time dynamics. With this in mind, we take the $N = 1$ approximation, so that the memory function is approximated to have matrix elements given by

$$M_{\alpha,\beta}(\mathbf{q}, z) = M(\mathbf{q}, z)\delta_{\alpha,\beta} - M(\mathbf{q}, z)\delta_{\alpha,0}\delta_{0,\beta}, \quad (2.46)$$

where we have taken

$$M(\mathbf{q}, z) = M_{1,1}(\mathbf{q}, z) = (L_i A_1(\mathbf{q}), R(z) L_i A_1(\mathbf{q})), \quad (2.47)$$

and dropped the subscripts which are no longer necessary after we have specified the $\alpha, \beta = 1$ case of our approximate matrix elements of the memory function given in Eq. (2.40).

Placing our focus on the slow variables implies that this approximation for the memory function is valid for low frequencies. The choice to focus on only one or a few collective variables in the memory function also constitutes a coarse-graining description of the dynamics [17, Appendix 3]. By transforming to the orthonormal basis, Eq. (2.24), we chose to focus on collective fluctuations rather than individual electron-hole excitations, Eq. (2.10). By subsequently focusing on only a few collective fluctuations, we relinquish the ability to describe independently the relaxations of fluctuations with different wavevectors \mathbf{k} . In exchange, we receive a tractable calculation which describes a coarse-grained lifetime.

If we insert the approximation for the memory function of Eq. (2.46) into the equation of motion of the relaxation function, we obtain

$$\sum_{\mu} \Phi_{\alpha,\mu}(\mathbf{q}, z) [(z + M(\mathbf{q}, z)) \delta_{\mu,\beta} - \Omega_{\mu,\beta}(\mathbf{q})] = i\delta_{\alpha,\beta} + \Phi_{\alpha,0}(\mathbf{q}, z) M(\mathbf{q}, z) \delta_{0,\beta}. \quad (2.48)$$

To simplify this equation further, we denote the relaxation function of the pristine system by $\Phi_{\alpha,\beta}^{(0)}(\mathbf{q}, z)$ and give its equation of motion, remembering that because $\Omega_{\beta,\alpha}(\mathbf{q})$ is a static correlation function we evaluate it in the pristine system in both cases,

$$\sum_{\mu} \Phi_{\alpha,\mu}^{(0)}(\mathbf{q}, z) [z\delta_{\mu,\beta} + \Omega_{\mu,\beta}(\mathbf{q})] = \sum_{\mu} [z\delta_{\alpha,\mu} + \Omega_{\alpha,\mu}(\mathbf{q})] \Phi_{\mu,\beta}^{(0)}(\mathbf{q}, z) = i\delta_{\alpha,\beta}. \quad (2.49)$$

We then multiply Eq. (2.48) by $\Phi_{\beta,\nu}^{(0)}(\mathbf{q}, z + M(\mathbf{q}, z))$ from the right, and we sum over β to find that

$$i\Phi_{\alpha,\nu}(\mathbf{q}, z) = i\Phi_{\alpha,\nu}^{(0)}(\mathbf{q}, z + M(\mathbf{q}, z)) - \Phi_{\alpha,0}(\mathbf{q}, z)M(\mathbf{q}, z)\Phi_{0,\nu}^{(0)}(\mathbf{q}, z + M(\mathbf{q}, z)). \quad (2.50)$$

Focusing on the $\alpha, \nu = 0$ case, we obtain an expression for the normalized relaxation function,

$$\Phi_{0,0}(\mathbf{q}, z) = \frac{\Phi_{0,0}^{(0)}(\mathbf{q}, z + M(\mathbf{q}, z))}{1 + iM(\mathbf{q}, z)\Phi_{0,0}^{(0)}(\mathbf{q}, z + M(\mathbf{q}, z))}. \quad (2.51)$$

The above relaxation function is not quite the usual density relaxation function because it incorporates the normalization with respect to the inner product,

$$(\hat{\rho}(\mathbf{q}), \hat{\rho}(\mathbf{q})) = i(\hat{\rho}(\mathbf{q}), LR(0)\hat{\rho}(\mathbf{q})) = i\langle[\hat{\rho}(-\mathbf{q}), \hat{\rho}(\mathbf{q}, \mathbf{0})]\rangle = VX(\mathbf{q}, 0), \quad (2.52)$$

where we have used $1 = iL(i/(0-L)) = iLR(0)$ and recognized the static density response function of the Kubo formalism, $X(\mathbf{q}, 0) = i\langle[\hat{\rho}(-\mathbf{q})/V, \hat{\rho}(\mathbf{q}, \mathbf{0})]\rangle$ as in Eq. (2.34). The density response function given by Eq. (2.52) is intensive, as shown in its derivation in the case of the pristine periodic system in Appendix C.1.1. The other correlation functions representing physically measurable quantities will similarly be defined so that they are intensive. The subscripted relaxation functions $\Phi_{\alpha,\beta}(\mathbf{q}, z)$ and $\Phi_{\alpha,\beta}^{(0)}(\mathbf{q}, z)$ are intensive due to the normalization of the orthonormal variables.

The density relaxation function is then given in terms of the orthonormal variable relaxation function by

$$\Phi(\mathbf{q}, z) = \frac{1}{V}(\hat{\rho}(\mathbf{q}), R(z)\hat{\rho}(\mathbf{q})) = \frac{1}{V}(\hat{\rho}(\mathbf{q}), \hat{\rho}(\mathbf{q}))\Phi_{0,0}(\mathbf{q}, z) = X(\mathbf{q}, 0)\Phi_{0,0}(\mathbf{q}, z), \quad (2.53)$$

and similarly for $\Phi^{(0)}(\mathbf{q}, z)$. Recalling our approximation of static correlation functions by their counterparts in the pristine system and making the replacement $X(\mathbf{q}, 0) \rightarrow X^{(0)}(\mathbf{q}, 0)$, the resulting equation for the density relaxation function is

$$\Phi(\mathbf{q}, z) = \frac{\Phi^{(0)}(\mathbf{q}, z + M(\mathbf{q}, z))}{1 + iM(\mathbf{q}, z)\Phi^{(0)}(\mathbf{q}, z + M(\mathbf{q}, z))/X^{(0)}(\mathbf{q}, 0)}, \quad (2.54)$$

as was obtained by Götze for the free-electron gas [14, 18, 19].

Chapter 3 |

The Electrical Conductivity

In this chapter, we derive a formula for the conductivity of the full system in the presence of scattering through the density relaxation function of the full system. We show that it agrees with and generalizes Boltzmann transport theory, the Drude model, and Götze's free-electron gas conductivity formula. We then explore the implications of our conductivity formula, including its ability to capture the thermodynamic limit and interband contributions to the conductivity.

3.1 Conductivity from the evolution of the density

From the density relaxation function of the full system, we can derive the Kubo formula conductivity tensor. Written as a relaxation function, it is [8, Eq. (5.11)]

$$\boldsymbol{\sigma}(\mathbf{q}, t) = \frac{1}{V} \left(\hat{\mathbf{j}}(\mathbf{q}, t), \hat{\mathbf{j}}(\mathbf{q}) \right) . \quad (3.1)$$

We can project the conductivity tensor in the direction of \mathbf{q} to obtain the longitudinal component of the tensor, and use the continuity equation, Eq. (2.42), to relate the current to the density operator,

$$\mathbf{q} \cdot \boldsymbol{\sigma}(\mathbf{q}, t) \cdot \mathbf{q} = \frac{1}{V} \left(\mathbf{q} \cdot \hat{\mathbf{j}}(\mathbf{q}, t), \hat{\mathbf{j}}(\mathbf{q}) \cdot \mathbf{q} \right) = \frac{1}{V} (L\hat{\rho}(\mathbf{q}, t), L\hat{\rho}(\mathbf{q})) . \quad (3.2)$$

Then, performing a Laplace transform, using self-adjointness of the Liouvillian, observing $(\hat{\rho}(\mathbf{q}), L\hat{\rho}(\mathbf{q})) = 0$ which follows from

$$(\hat{\rho}(\mathbf{q}), L\hat{\rho}(\mathbf{q})) = \langle [\hat{\rho}(-\mathbf{q}), \hat{\rho}(\mathbf{q})] \rangle = \int_V d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}'} \int_V d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} \langle [\hat{\rho}(\mathbf{r}'), \hat{\rho}(\mathbf{r})] \rangle = 0 , \quad (3.3)$$

because the density operator $\hat{\rho}(\mathbf{r}) = \psi^\dagger(\mathbf{r})\psi(\mathbf{r})$ commutes with itself, and using $L^2R(z) = -iL + z(-i + zR(z))$ which follows from $R(z) = i(z - L)^{-1}$,

$$\begin{aligned}
\mathbf{q} \cdot \boldsymbol{\sigma}(\mathbf{q}, z) \cdot \mathbf{q} &= \frac{1}{V} (L\hat{\rho}(\mathbf{q}), LR(z)\hat{\rho}(\mathbf{q})) \\
&= \frac{1}{V} (\hat{\rho}(\mathbf{q}), L^2\hat{\rho}(\mathbf{q})) \\
&= \frac{z}{V} [-i(\hat{\rho}(\mathbf{q}), \hat{\rho}(\mathbf{q})) + z(\hat{\rho}(\mathbf{q}), R(z)\hat{\rho}(\mathbf{q}))] \\
&= z [z\Phi(\mathbf{q}, z) - iX^{(0)}(\mathbf{q}, 0)] .
\end{aligned} \tag{3.4}$$

We can use a similar algebraic identity to relate the density relaxation function to the density response function; namely, by using $R(z) = \frac{1}{z}(LR(z) - LR(0))$ we find that

$$\Phi(\mathbf{q}, z) = -\frac{i}{z} (X(\mathbf{q}, z) - X^{(0)}(\mathbf{q}, 0)) . \tag{3.5}$$

Substituting this into Eq. (3.4), we find another expression for the conductivity,

$$\mathbf{q} \cdot \boldsymbol{\sigma}(\mathbf{q}, z) \cdot \mathbf{q} = -izX(\mathbf{q}, z) . \tag{3.6}$$

Analogous versions of Eqs. (3.6), (3.5), and (3.6) hold for the pristine system.

To evaluate the conductivity, we write it in terms of the known correlation functions of the pristine system. Using Eq. (2.54) in Eq. (3.4), and expanding Eq. (2.54) using Eq. (3.5) for the case of the pristine system, we have

$$\begin{aligned}
\Phi(\mathbf{q}, z) &= \frac{1}{\frac{1}{\Phi^{(0)}(\mathbf{q}, z+M(\mathbf{q}, z))} + i\frac{M(\mathbf{q}, z)}{X^{(0)}(\mathbf{q}, 0)}} \\
&= \frac{1}{\frac{z+M(\mathbf{q}, z)}{-i(X^{(0)}(\mathbf{q}, 0) - X^{(0)}(\mathbf{q}, z+M(\mathbf{q}, z)))} + i\frac{M(\mathbf{q}, z)}{X^{(0)}(\mathbf{q}, 0)}} \\
&= i\frac{(X^{(0)}(\mathbf{q}, 0))^2 - X^{(0)}(\mathbf{q}, 0)X^{(0)}(\mathbf{q}, z+M(\mathbf{q}, z))}{zX^{(0)}(\mathbf{q}, 0) + M(\mathbf{q}, z)X^{(0)}(\mathbf{q}, z+M(\mathbf{q}, z))} .
\end{aligned} \tag{3.7}$$

Inserting this expression into the equation for the conductivity, Eq. (3.4),

$$\begin{aligned}
\mathbf{q} \cdot \boldsymbol{\sigma}(\mathbf{q}, z) \cdot \mathbf{q} &= iz \left(z\frac{(X^{(0)}(\mathbf{q}, 0))^2 - X^{(0)}(\mathbf{q}, 0)X^{(0)}(\mathbf{q}, z+M(\mathbf{q}, z))}{zX^{(0)}(\mathbf{q}, 0) + M(\mathbf{q}, z)X^{(0)}(\mathbf{q}, z+M(\mathbf{q}, z))} - X^{(0)}(\mathbf{q}, 0) \right) \\
&= iz \left(\frac{-X^{(0)}(\mathbf{q}, 0)X^{(0)}(\mathbf{q}, z+M(\mathbf{q}, z)) [z+M(\mathbf{q}, z)]}{zX^{(0)}(\mathbf{q}, 0) + M(\mathbf{q}, z)X^{(0)}(\mathbf{q}, z+M(\mathbf{q}, z))} \right) .
\end{aligned} \tag{3.8}$$

Comparing this to Eq. (3.6), we can likewise write the full response function, $X(\mathbf{q}, z)$, in terms of its pristine counterpart, $X^{(0)}(\mathbf{q}, z)$, as

$$X(\mathbf{q}, z) = \frac{X^{(0)}(\mathbf{q}, 0)X^{(0)}(\mathbf{q}, z + M(\mathbf{q}, z)) [z + M(\mathbf{q}, z)]}{zX^{(0)}(\mathbf{q}, 0) + M(\mathbf{q}, z)X^{(0)}(\mathbf{q}, z + M(\mathbf{q}, z))}. \quad (3.9)$$

We are primarily interested in the optical conductivity $\sigma(z)$, which is the uniform or $q \rightarrow 0$ limit of $\sigma(\mathbf{q}, z)$. In the limit of small \mathbf{q} we can approximate $X^{(0)}(\mathbf{q}, z) \approx \mathbf{q} \cdot \mathbf{X}^{(0)}(z) \cdot \mathbf{q}$, where the tensor $\mathbf{X}^{(0)}(z)$ is the dipole-dipole response function or dynamical polarizability [20, Eq. (4)], while on the other hand $X^{(0)}(\mathbf{q}, 0)$ approaches the density of states at the Fermi level as $q \rightarrow 0$, a positive constant. Hence, in the limit $q \rightarrow 0$,

$$\begin{aligned} \mathbf{q} \cdot \boldsymbol{\sigma}(\mathbf{q}, z) \cdot \mathbf{q} &= iz \left(\frac{-X^{(0)}(\mathbf{q}, 0) [z + M(\mathbf{q}, z)] [\mathbf{q} \cdot \mathbf{X}^{(0)}(z + M(\mathbf{q}, z)) \cdot \mathbf{q}]}{zX^{(0)}(\mathbf{q}, 0) + M(\mathbf{q}, z) [\mathbf{q} \cdot \mathbf{X}^{(0)}(z + M(\mathbf{q}, z)) \cdot \mathbf{q}]} \right) \\ &\rightarrow \mathbf{q} \cdot [-i(z + M(\mathbf{q}, z)) \mathbf{X}^{(0)}(z + M(\mathbf{q}, z))] \cdot \mathbf{q}. \end{aligned} \quad (3.10)$$

Therefore, with $M(z) = \lim_{q \rightarrow 0} M(\mathbf{q}, z)$, the conductivity tensor is

$$\boldsymbol{\sigma}(z) = -i[z + M(z)] \mathbf{X}^{(0)}(z + M(z)). \quad (3.11)$$

Since the conductivity for the pristine system can be written as

$$\boldsymbol{\sigma}^{(0)}(z) = -iz\mathbf{X}^{(0)}(z), \quad (3.12)$$

we see that the conductivity of the full system within our approximations is

$$\boldsymbol{\sigma}(z) = \boldsymbol{\sigma}^{(0)}(z + M(z)). \quad (3.13)$$

The validity of this result is independent of the approximation used to calculate the memory function, such as the neglect of all but the first term in the series expression for the memory function in terms of the relaxation function, Eq. (2.39), or the type of scattering described by H_i and any approximations used following the choice of H_i . It only depends on the expression obtained for the relaxation function in terms of the memory function and the relaxation function without scattering, Eq. (2.54), which was derived using the approximate matrix elements of the memory function, Eq. (2.46), and the approximation of that we can replace static correlation functions of the full system with those of the pristine system.

In Appendix C.2 we calculate the pristine conductivity tensor explicitly and show that

$$\begin{aligned} \sigma_{\alpha,\beta}^{(0)}(z) = & \frac{i}{zV} \sum_{n,\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \partial_{k_\alpha} \partial_{k_\beta} \varepsilon_{n,\mathbf{k}} - \frac{1}{V} \sum_{n,\mathbf{k},\gamma} f(\varepsilon_{n,\mathbf{k}}) \varepsilon_{\alpha,\beta,\gamma} \Omega_{n,\mathbf{k};\gamma} \\ & - \frac{iz}{V} \sum_{n,n',\mathbf{k}} \frac{f(\varepsilon_{n',\mathbf{k}}) - f(\varepsilon_{n,\mathbf{k}})}{z + \varepsilon_{n,\mathbf{k}} - \varepsilon_{n',\mathbf{k}}} X_{n',n,\mathbf{k};\alpha}^* X_{n',n,\mathbf{k};\beta} , \end{aligned} \quad (3.14)$$

where $\mathbf{X}_{n',n,\mathbf{k}} = i \langle u_{n',\mathbf{k}} | \partial_{\mathbf{k}} u_{n,\mathbf{k}} \rangle$ is the Berry connection and $\boldsymbol{\Omega}_{n,\mathbf{k}} = \nabla \times \mathbf{X}_{n,\mathbf{k}}$ is the Berry curvature. In particular, its longitudinal components may be written as

$$\begin{aligned} \sigma_{\alpha,\alpha}^{(0)}(z) = & \quad (3.15) \\ = & \frac{i}{zV} \sum_{n,\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \partial_{k_\alpha}^2 \varepsilon_{n,\mathbf{k}} - \frac{i}{V} \left(\sum_{n',n,\mathbf{k}} (f(\varepsilon_{n,\mathbf{k}}) - f(\varepsilon_{n',\mathbf{k}})) \frac{z(\varepsilon_{n',\mathbf{k}} - \varepsilon_{n,\mathbf{k}})}{(\varepsilon_{n',\mathbf{k}} - \varepsilon_{n,\mathbf{k}})^2 - z^2} |X_{n',n,\mathbf{k};\alpha}|^2 \right) . \end{aligned}$$

These formulae, together with the role of $M(z)$ as a complex frequency shift, already has important implications for evaluations of the conductivity based on the Kubo formula. We will comment on the implications of Eqs. (3.13) and (3.14) further in Sec. 3.2.1.

3.1.1 Analogies with the Drude model and Boltzmann transport theory

For some insight into the role of the memory function, compare the dc limit of the intraband term of the memory function formalism conductivity, Eqs. (3.13) and (3.14), to the Boltzmann expression for the conductivity, Eq. (1.7). They read as

$$\sigma_{\alpha,\beta}^{\text{BTT}} = \frac{1}{V} \sum_{\mathbf{k}} f(\varepsilon_{\mathbf{k}}) \partial_{k_\alpha} \partial_{k_\beta} \varepsilon_{\mathbf{k}} \tau_{\mathbf{k}} , \quad \sigma_{\alpha,\beta}^{\text{MFF}} = \frac{1}{M(0)V} \sum_{n,\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \partial_{k_\alpha} \partial_{k_\beta} \varepsilon_{n,\mathbf{k}} . \quad (3.16)$$

We rewrote the Boltzmann expression using Eq. (C.26) for ease of comparison. It is clear that if the wavevector dependence of the relaxation time is ignored, the imaginary part of the memory function parallels the inverse relaxation time. We can similarly compare to the Drude model. In the case of a single parabolic band, i.e., a free electron gas, $\varepsilon_{\mathbf{k}} = k^2/2m^*$ where m^* is the effective mass, so the memory function gives the optical conductivity at frequency ω as

$$\sigma_{\alpha,\beta}(\omega) = \frac{n_e}{m^*} \frac{i}{\omega + M(\omega)} \delta_{\alpha,\beta} . \quad (3.17)$$

This is the special case that was obtained by Götze [14, 21]. Similarly, classical Drude theory gives

$$\sigma_{\alpha,\beta}(\omega) = \frac{n_e}{m^*} \frac{i}{\omega + i/\tau} \delta_{\alpha,\beta}. \quad (3.18)$$

In the dc limit and ignoring any wavevector dependence on the relaxation time, the memory function theory, Drude theory, and Boltzmann transport theory all agree, giving $\sigma_{\alpha,\beta} = \frac{n_e \tau}{m^*} \delta_{\alpha,\beta}$. Hence, the imaginary part of the memory function parallels the inverse relaxation time. Indeed, Götze and Wölfle showed that to lowest order in scattering, the present memory function theory coincides with Boltzmann transport theory in the relaxation time approximation, with the imaginary part of the memory function replacing the inverse relaxation time [21]. In fact, the parallel between the memory function and the inverse relaxation time holds more generally, as $M(z=0) = M(\mathbf{q}=0, z=0)$ is in general purely imaginary [15]. We will often write this as $M(z=0) = iM''$, where M'' is real.

From the arguments above together with Eqs. (3.17) and (3.18), we see that the parallel between the memory function and the inverse relaxation time is simply $M'' \leftrightarrow 1/\tau$. This parallel explains how the memory function is able to capture the physics of the thermodynamic limit even in a finite supercell. As long as electrons scatter before crossing the finite supercell, it will be indistinguishable from the infinite system. In the formulae for the correlation functions, this means that M'' , which acts as a Lorentzian broadening, should exceed the excitation energies of the supercell. We demonstrate this correspondence when discussing numerical implementations in Appendix C.3.1.

Using this parallel, Eq. (3.14) can already be implemented into existing Boltzmann transport theory codes by the replacement $M(0) = iM'' \rightarrow i/\tau$. Evaluating the dc conductivity as $\sigma_{\alpha,\beta}^{BT} = \sigma_{\alpha,\beta}^{(0)}(i/\tau)$ with $\sigma_{\alpha,\beta}^{(0)}$ as given in Eq. (3.14) would enable these codes to capture the interband contributions to the conductivity which are normally neglected in Boltzmann transport theory. We will discuss the importance of these terms in Sec. 3.2.2. This approach does, however, keep Boltzmann transport theory limited to the weak-scattering regime due to the semiclassical evaluation of the relaxation time τ . We will address this in Chapter 4 with an explicit evaluation of the memory function that respects quantum coherence.

The parallel $M'' \leftrightarrow 1/\tau$ also makes clear the meaning of “coarse-graining” in Sec. 2.2.4. M'' has no wavevector dependence, in contrast to the relaxation time given in Eq. (1.8). By transforming the collective orthonormal variables of Eq. (2.24) and tracking only one

collective variable in the memory function, we have traded away the ability to describe the lifetimes of all wavevectors \mathbf{k} independently, keeping instead a coarse-grained lifetime on the most relevant time scale. In exchange, we have obtained a memory function which describes coherent scattering of electrons.

This ability enables the memory function formalism to describe physics which is out of reach in Boltzmann transport theory. In particular, the memory function can capture the metal-to-insulator transition, which follows from the large- M'' limit of Eq. (3.13) taken using Eq. (3.15). In this limit we have $\sigma_{\alpha,\alpha}(0) = \sigma_{\alpha,\alpha}^{(0)}(iM'') \sim 1/M'' \rightarrow 0$, so that a metal-to-insulator transition occurs where M'' diverges. The existence of such a transition at finite scattering strength will be demonstrated in Sec. 4.1.2, where we calculate the memory function for the case in which scattering is due to disorder, and where we explicitly demonstrate a purely imaginary solution for the memory function at zero frequency. First, we will explore further implications of Eqs. (3.14) and (3.15) in Sec. 3.2.2.

3.2 Implications of the conductivity

From the preceding calculations, we have seen that the effects of scattering on the conductivity can be described by the memory function as a complex frequency shift. We also showed that in the dc limit, the complex frequency shift is purely imaginary, i.e., a pure Lorentzian broadening.

In the following we delineate two important consequences of these results. One is the physical and parameter-free derivation of the broadening as coming from M , which is relevant to evaluations of the Kubo formula. The other is the presence of interband contributions to the conductivity which are not accounted for in Boltzmann transport theory. We also briefly mention a third implication regarding the anomalous term which remains for future study.

3.2.1 Physical origin of broadening

First we describe further how the memory function formalism circumvents the problems which calculations based on the Kubo formula face in the dc limit. We showed in Sec. 1.2 that the Kubo formula for the conductivity yields zero dc conductivity for finite systems, i.e., large supercells with open boundary conditions, and infinite dc conductivity for supercells with periodic boundary conditions. We also explained that the broadening

η imparts a finite lifetime to current-carrying excitations, which obscures the actual relaxation effects of the system, and that to minimize these we must take the ill-behaved limit $\eta \rightarrow 0$. Now we are able to show how the memory function resolves the problem.

In Eq. (3.15), we gave $\sigma_{\alpha,\beta}^{(0)}(z)$, which is an expression for the conductivity of a periodic system. Within the memory function formalism, only the pristine system is periodic, since scattering in H_i breaks periodicity. However, this formula also describes the conductivity of periodic supercells with random disorder, as are often used in Kubo formula calculations, since the random disorder also has the periodicity of the supercell. As a result, Eq. (3.15) will still apply, and the conductivity will be

$$\begin{aligned} \sigma_{\alpha,\alpha}(\omega) &= \lim_{\eta \rightarrow 0} \sigma_{\alpha,\alpha}(\omega + i\eta) \\ &= \lim_{\eta \rightarrow 0} \left[\frac{i}{(\omega + i\eta)V} \sum_{n,\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \partial_{k_\alpha} \partial_{k_\beta} \varepsilon_{n,\mathbf{k}} \right. \\ &\quad \left. - \frac{i(\omega + i\eta)}{V} \sum_{n,n',\mathbf{k}} \frac{f(\varepsilon_{n,\mathbf{k}}) - f(\varepsilon_{n',\mathbf{k}})}{\omega + i\eta + \varepsilon_{n',\mathbf{k}} - \varepsilon_{n,\mathbf{k}}} (X_{n',n,\mathbf{k};\alpha})(X_{n',n,\mathbf{k};\beta}^*) \right], \end{aligned} \quad (3.19)$$

where now the energies and Berry connections are those of the supercell. Regardless, taking the limit $\eta \rightarrow 0$ the dc conductivity will be infinite due to the Lorentzian approaching a Dirac delta at zero frequency in the intraband term.

As discussed in Sec. 1.2, in numerical evaluations of the Kubo formula, the broadening η must be kept finite as a numerical parameter for a finite dc conductivity to be calculated, regardless of the supercell boundary conditions. Eq. (3.19) shows that if η is too small, the dc conductivity will tend infinity in a periodic supercell. Moreover, comparing Eq. (3.19) to Eqs. (3.13) and (3.15) shows that from the perspective of the present memory function formalism, the parameter η is a substitute for $M(z)$. While $M(z)$ has physical meaning in the context of broadening due to scattering, η does not. Hence, η obscures the true dc conductivity, necessitating the limit $\eta \rightarrow 0$, as much as it can be taken without the supercell boundary conditions dictating that the result tends to either 0 or infinity. This balance is too sensitive to be practical for all but the largest supercells when no other consideration is given to the thermodynamic limit [10, 11].

The memory function formalism circumvents this with a physical broadening, $M(z)$. We demonstrated in Sec. 3.1.1 that in the zero-frequency limit the memory function is purely imaginary, $M(0) = iM''$, so that it always provides a broadening to the dc limit of the conductivity. As a result of this broadening, the correlation functions of a finite supercell converge to those of an infinite system as long as the broadening M'' is larger than the excitation energies available to the supercell. We show in Appendix C.3.1, this is

equivalent to the requirement that electrons scatter before traversing the finite supercell. This condition is relatively straightforward to meet. In particular, it is readily achieved in the strong-scattering regime where the memory function formalism is necessary. In the limit of weak scattering, where the memory function formalism and Boltzmann transport theory coincide [21], the latter formalism may be used if necessary.

3.2.2 Interband contributions to the dc conductivity

To study the interband contributions to the dc conductivity, we insert $M(0) = iM''$ as derived in Sec. 3.1 into the explicit expression for the longitudinal component of the dc conductivity, Eq. (3.15). We find

$$\begin{aligned} \sigma_{\alpha,\alpha}(0) &= \sigma_{\alpha,\alpha}^{(0)}(iM'') & (3.20) \\ &= \frac{1}{M''V} \sum_{n,\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \partial_{\mathbf{k}\alpha}^2 \varepsilon_{n,\mathbf{k}} \\ &\quad + \frac{1}{V} \left(\sum_{n',n,\mathbf{k}} (f(\varepsilon_{n,\mathbf{k}}) - f(\varepsilon_{n',\mathbf{k}})) \frac{M'' (\varepsilon_{n',\mathbf{k}} - \varepsilon_{n,\mathbf{k}})}{(\varepsilon_{n',\mathbf{k}} - \varepsilon_{n,\mathbf{k}})^2 + (M'')^2} |X_{n',n,\mathbf{k};\alpha}|^2 \right). \end{aligned}$$

As commented in Sec. 3.1, upon the correspondence $M'' \leftrightarrow 1/\tau_{\mathbf{k}}$ the first term is the familiar Drude-like intraband term, matching the expression in Eq. (1.7) upon integration by parts. It gives the contribution to the conductivity of electrons traveling with a velocity $\mathbf{v}_{n,\mathbf{k}} = \partial_{\mathbf{k}} \varepsilon_{n,\mathbf{k}}$ within a band. However, the second term, which is the interband term, distinguishes our result Eq. (3.20) from the typical Boltzmann form Eq. (1.7), where interband contributions are typically assumed to be unimportant and are neglected [5].

The recovery of these missing contributions, combined with a clear means to calculate them, is a major consequence of our derivations. In addition to providing a means to explore the importance of the interband contributions, it explains how supercell size affects the memory function and likewise the relaxation time, and demonstrates that in certain situations conductivity may actually increase with scattering.

Clearly, the interband term is most important when there are multiple bands close to the Fermi level. This can happen in two ways. One is in the conventional sense, in which the bands are defined for a single unit cell, and are e.g., the conduction and valence band of a semiconductor, or the upper and lower Dirac cones of graphene. In this case, Eq. (3.20) shows that the interband term contributes significantly when the broadening is on the order of the energy gap between filled valence band states and empty conduction band states.

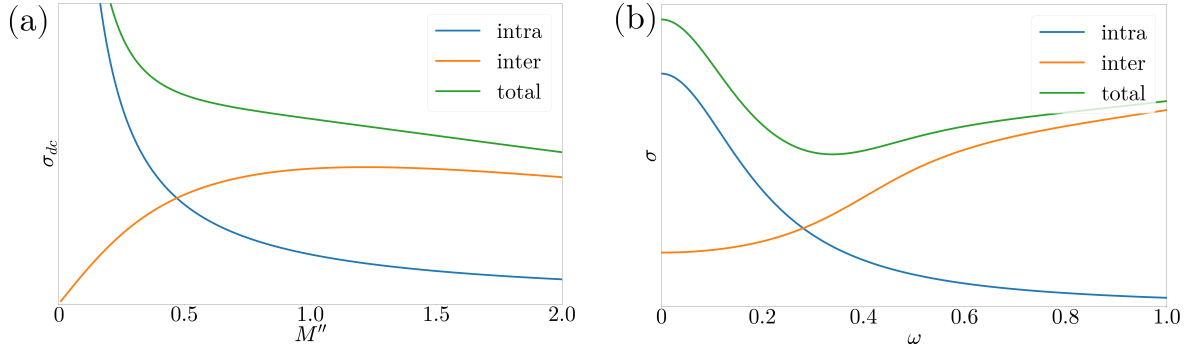


Figure 3.1. Here we plot (a) the dc conductivity of graphene versus M'' , and (b) the optical conductivity for a fixed model broadening $M(\omega) = 0.2i$ to show that when the Fermi level is small, the interband term is important even for small broadening. In particular, in graphene interband transitions have minimum energy 2μ , so that the interband term becomes important around $M'' \sim 2\mu$. In both plots we measure energy in units of the hopping t and use a Fermi level of $\mu = 0.2$.

Using graphene as an example, Fig. 3.1(a) shows that the interband term becomes the dominant term in the dc conductivity as the scattering and hence broadening M'' increase. Though only zero-energy excitations contribute to the dc conductivity, M'' broadens excitations so that even interband excitations can contribute at zero energy. From weak to moderate scattering, when the broadening M'' is less than or on the order of the band separation, the interband term grows linearly as M'' as the interband excitations are broadened and made increasingly available at zero energy. Only in the limit of very strong scattering, when M'' is on the order of the combined band width of both bands, does the interband term decay as $1/M''$. In contrast, the intraband term decays as $1/M''$ for all M'' . As a result, when both terms are present, the intraband term dominates for weak scattering, while the interband term dominates for stronger scattering. The crossover point is determined by the Fermi level and the separation between occupied and unoccupied states.

To demonstrate how broadened interband excitations contribute at zero energy, consider that in pristine graphene, the optical conductivity has a well-separated Drude peak at zero frequency and optical shoulder at $\omega = 2\mu$, which is the lowest energy at which interband transitions become available. As illustrated in Fig. 3.1(b), however, when scattering is present the interband excitations are broadened and contribute even at zero energy. The broadening flattens the Drude peak, decreasing the intraband contribution to the dc conductivity, while simultaneously extending the interband shoulder to zero frequency, increasing the interband contribution.

After the case of multiband materials, the other case in which the interband term is

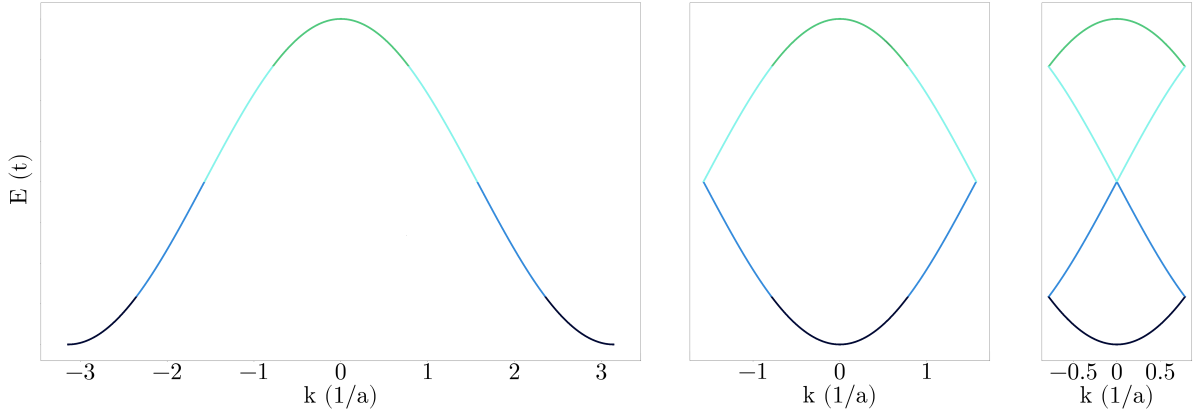


Figure 3.2. The band structure of a pristine linear chain is shown for one-atom, two-atom, and four-atom unit cells. These yield one band, two bands, and four bands, obtained by folding the outer quarters of the original band inward zero, one, and two times, respectively. At each step the size of the first Brillouin zone is halved while the number of bands is doubled. The overall number of states, which is proportional to the size of the system, is unchanged.

important is that of large supercells. In this case, even a simple, effectively single-band material can be made multiband through the band-folding scheme.

3.2.2.1 Large supercells

Large supercells are often used in *ab initio* calculations, e.g., to include many unit cells each with random disorder, or for systems with complex geometries. Such a system will have a larger number of bands in proportion to the size of the supercell, and a smaller first Brillouin zone in inverse proportion, as the bands are folded into the reduced first Brillouin zone of the larger supercell. More specifically, as is illustrated in Fig. 3.2, the number of bands scales with the number of atoms in the supercell, and the width of the Brillouin zone scales inversely with the width of the supercell. As a result, large supercells have more bands and shorter bands than small supercells.

Now recall that the separation in energy between bands determines the broadening M'' at which interband contributions become important. Therefore, for larger supercells which have shorter bands, the level of scattering at which interband contributions become important becomes lower. This further limits the range of validity of any transport calculation which neglects the interband term, a problem which is avoided in the present formalism.

Moreover, the folding of bands transfers weight from the intraband term to the interband term. To see this, note that the intraband term in Eqs. (3.14) and (3.20) is a sum over occupied states in the conduction band. As the size of the supercell is

increased, the original conduction band is cut into many smaller bands, most of which will be fully occupied or fully unoccupied and will no longer contribute. As a result, the sum is smaller, and the weight of the intraband term decreases. On the other hand, cutting the partially occupied conduction band into smaller fully occupied and fully unoccupied bands allows for new interband transitions between them. Because these transitions were originally intraband transitions within the conduction band, they are the same transitions that were lost from the intraband term upon folding the original band. In this way, increasing supercell size transfers weight from the intraband term to the intraband term.

As an aside, this analysis complements the motivation for the need for large supercells in the Kubo formalism that we gave in Secs. 1.2 and 3.2.1. Large supercells aid Kubo formula calculations by transferring weight from the ill-behaved intraband term to the well-behaved interband term.

Considering for a moment the application of this formalism specifically to disorder, large supercells can explicitly include random disorder throughout the supercell, e.g., by substitutions, adatoms, or site energies, in addition to representing these through the disorder potential $U(\mathbf{q})$. While in a pristine system the response and relaxation functions and hence the memory function are independent of supercell size, this is not generally the case when explicit disorder is present. Explicit disorder manifests in the response and relaxation functions and thus affects the memory function calculation, so that the memory function should be recalculated for each supercell with unique disorder. Furthermore, the level of the disorder in the system is given by the combination of explicit disorder in the supercell and the disorder potential $U(\mathbf{q})$, so that the level of disorder is now given by a sum over U and the explicit disorder parameters. While generally the explicit disorder and $U(\mathbf{q})$ will represent the same physical impurities or defects, $U(\mathbf{q})$ is necessary to provide the macroscopic randomness that cannot be captured in a finite supercell, breaking the translational symmetry that would otherwise be present as discussed in Sec. 3.2.1.

3.2.2.2 Conductivity enhanced by scattering

A situation which underscores the importance of the interband term is that in which the Fermi level is in the gap. Traditional Boltzmann transport theory would tell us that the dc conductivity is zero regardless of scattering in this case, because then Eq. (1.7) is zero regardless of $\tau_{\mathbf{k}}$. Likewise, the intraband term in Eqs. (3.14), (3.15), and (3.20) is always zero. However, the interband term is nonzero for any $M'' > 0$, growing linearly

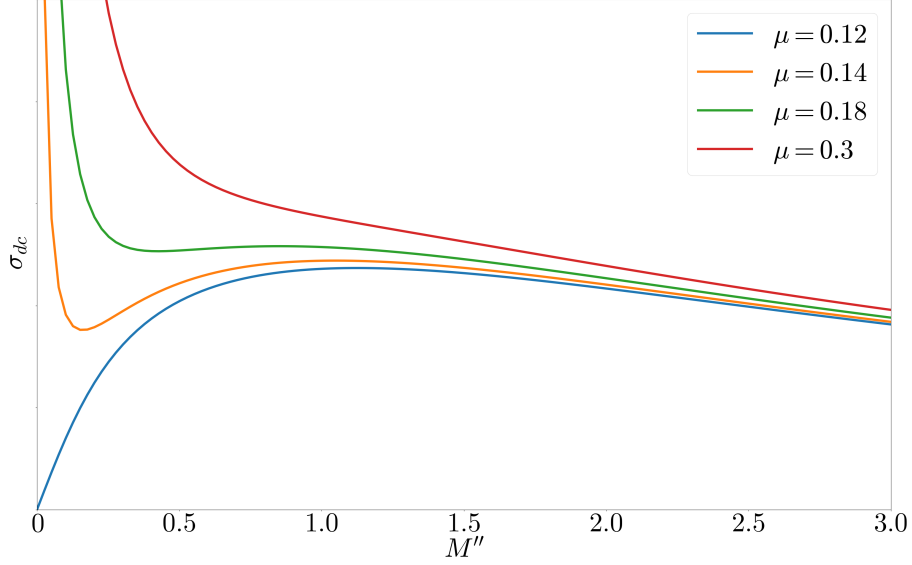


Figure 3.3. A dimerized honeycomb lattice with its Fermi level in its gap shows an increase in conductivity with scattering. Energies are measured in units of the hopping t , and the energy gap is induced by a site energy imbalance of $\Delta = 0.25$. The lowest-energy conduction band states have energy $\frac{1}{2}\Delta$, so that when the Fermi level is above this energy, the Drude peak is present and visible for small M'' .

with M'' for small M'' and decaying as $1/M''$ for large M'' . Therefore, when the Fermi level is in a band gap, the conductivity will initially increase with scattering. This cannot be reproduced with the intraband term alone, as it is always zero when the Fermi level is in the gap.

The physical explanation for this effect is simple. In the pristine system, all transitions are sharp, and no zero-energy transitions exist between separate bands. However, scattering broadens excitations so that even interband excitations become available at zero energy. When the Fermi level is in the gap, there are no electrons in the conduction band and so the intraband term vanishes, leaving only the interband term. The interband contribution to the dc conductivity increases with M'' for weak scattering as interband transitions become increasingly available at zero energy, until in the strong-scattering limit the conductivity decreases as $1/M''$. The latter is the typical behavior for scattering as we recall from the original Drude formula in which $\sigma = \frac{ne\tau}{m} \propto \tau \leftrightarrow 1/\tau$, where scattering is treated without involving broadening since the theory is classical.

The increase in conductivity with scattering is demonstrated in Fig. 3.3 for a honeycomb lattice which has been dimerized to give it a gap. A Fermi level in the gap is a sufficient condition for the conductivity to increase with scattering, but as this figure shows, it is not a necessary one. Even when the Fermi level is in the band, scattering

may still increase conductivity if the Fermi level is not too far into the band. In Fig. 3.3, there is a range of broadening M'' for which the dc conductivity increases with scattering for Fermi levels not only in the gap but also in the band up to approximately $\mu = 0.18$, noting that the bottom of the conduction band lower at 0.125. In this range of Fermi levels, there are few enough electrons in the conduction band that the interband term dominates over the intraband term for all but the smallest broadening M'' . For higher Fermi levels, the intraband term is large enough to hide the growth of the interband term with scattering, so that the conductivity strictly decreases with scattering.

A common situation where this result is relevant is in extrinsic semiconductors, where dopants can increase conductivity both by providing charge carriers and by broadening excitations. The standard approach to conduction in a doped extrinsic semiconductor is to consider dopants forming donor levels just below the bottom of the conduction band, or similarly for acceptor levels above the valence band, and to consider Drude-like conductivity in terms of the number of carriers thermally excited into the neighboring band [22]. When scattering is included, it is typically addressed in the framework of Boltzmann transport theory [23].

This standard approach overlooks the broadening of the bands into the gap by scattering. As a result, at zero temperature where no carriers are thermally excited, the donor/acceptor level model predicts zero conductivity, in contrast with the memory function formalism. On the other hand, in our level of approximation the memory function formalism only treats the donor or acceptor atoms as a disorder potential, so that it does not account for presence of the donor/acceptor level in the gap in the occupation factors $f(\varepsilon_{n,\mathbf{k}})$ in Eq. (3.20). As a result, it does not account for the well-defined excitation energy from the donor/acceptor level to the band and hence may not capture the correct temperature dependence of the conductivity.

As noted in Sec. 2.2.4, this is a result of our approximating static correlation functions in the full system with scattering by their counterparts in the pristine system. This approximation neglects the effects of the dopants on the density of states, and hence neglects the appearance of the donor/acceptor level in the gap. It can be relaxed by calculating the static correlation functions with other methods which address modification of the density of states by the dopants [14].

3.2.3 Anomalous conductivity

As we show in Appendix C.2, inclusion of multiple bands also gives rise to the anomalous Hall term of the conductivity. According to Eq. (3.14), this term is frequency-

independent,

$$\sigma_{\alpha,\beta}^{(0),\text{anom}}(z) = -\frac{1}{V} \sum_{n,\mathbf{k},\gamma} f(\varepsilon_{n,\mathbf{k}}) \epsilon_{\alpha,\beta,\gamma} \Omega_{n,\mathbf{k};\gamma} . \quad (3.21)$$

Since scattering only manifests through a frequency shift as the memory function, the anomalous term is therefore scattering-independent. This is suggestive of topological protection. At present, however, we are content to focus on the conductivity of the bulk and leave conductivity of the edge states for future study.

3.3 Publications of this work

We have reported a summary of these results in Ref. 24 and its companion publication Ref. 1. The former principally focuses on Eq. (3.13) and its implications discussed throughout Sec. 3.2. The latter describes the calculation of the memory function in the case of scattering due to disorder and the implementation of the memory function formalism into *ab initio* code, as we will discuss in Chapter 4.

Chapter 4 |

The memory function formalism for disordered systems

In this chapter, we specialize to the case of scattering due to disorder to obtain an explicit formula for the memory function. Through this formula we show that the memory function captures the metal-to-insulator transition. We implement the memory function formalism into the density-functional theory code `exciting` [25] and evaluate it for disordered sodium, a nearly-free-electron gas chosen for benchmarking with Götze’s free-electron gas results [14], and we compare our results to Boltzmann transport theory.

4.1 Calculating the memory function of a disordered system

So far we have derived our results for a general scattering Hamiltonian H_i . To give additional concreteness to the meaning of $M(z)$ and to explore an important application, here we calculate it in the case in which H_i is the disorder potential in Eq. (2.20), following the mode-coupling approach described by Götze [14]. Other methods which have been used to calculate memory functions such as ours include continued fraction expansions [26, 27], Monte Carlo methods [28], and diagrammatic approaches [29]. The advantage of the mode-coupling approach is that it is a self-consistent approach which leads to an analytic formula for the memory function that is valid at all scattering strengths.

Deriving the conductivity of the full system, Eq. (3.13), required only the approximations on the matrix elements $M_{\alpha,\beta}(\mathbf{q}, z)$ and on the static correlation functions. Our approach to evaluate the memory function requires two additional approximations, which

are the truncated series expansion already introduced in Eq. (2.39) and the mode-coupling approximation.

To evaluate the memory function, given by Eq. (2.47), and considering the definition of $A_1(\mathbf{q})$, given in Eq. (2.44), we must evaluate

$$L_i A_1(\mathbf{q}) = \frac{1}{\sqrt{(L_0 \hat{\rho}(\mathbf{q}), L_0 \hat{\rho}(\mathbf{q}))_0}} L_i L_0 \hat{\rho}(\mathbf{q}). \quad (4.1)$$

The two quantities involved in this expression are

$$\begin{aligned} L_i L_0 \hat{\rho}(\mathbf{q}) &= -\mathbf{q} \cdot L_i \hat{\mathbf{j}}(\mathbf{q}) \\ &= -\mathbf{q} \cdot \frac{1}{V} \sum_{\mathbf{q}'} U(\mathbf{q}') [\hat{\rho}(-\mathbf{q}'), \hat{\mathbf{j}}(\mathbf{q})], \end{aligned} \quad (4.2)$$

where we used the continuity equation, and the normalization

$$\begin{aligned} (L_0 \hat{\rho}(\mathbf{q}), L_0 \hat{\rho}(\mathbf{q}))_0 &= \langle [\hat{\rho}^\dagger(\mathbf{q}), L_0 \hat{\rho}(\mathbf{q})] \rangle_0 \\ &= -\mathbf{q} \cdot \langle [\hat{\rho}(-\mathbf{q}), \hat{\mathbf{j}}(\mathbf{q})] \rangle_0. \end{aligned} \quad (4.3)$$

Here the subscript 0s in $(\dots)_0$ and in $\langle \dots \rangle_0$ indicate that the thermal average is taken in the pristine system since these are static correlation functions. We have also recognized that $L \hat{\rho}(\mathbf{q}) = L_0 \hat{\rho}(\mathbf{q})$ because $L_i \hat{\rho}(\mathbf{q}) = [H_i, \hat{\rho}(\mathbf{q})] = \frac{1}{V} \sum_{\mathbf{q}'} U(\mathbf{q}') [\hat{\rho}(-\mathbf{q}'), \hat{\rho}(\mathbf{q})] = 0$, as noted in Eq. (3.3).

Both quantities we wish to evaluate require the commutator

$$[\hat{\rho}(-\mathbf{q}'), \hat{\mathbf{j}}(\mathbf{q})] = -\frac{1}{m} \mathbf{q}' \hat{\rho}(\mathbf{q} - \mathbf{q}'), \quad (4.4)$$

which is proved as follows. First we calculate

$$\begin{aligned} &[\hat{\rho}(-\mathbf{q}'), \hat{\mathbf{j}}(\mathbf{q})] = \\ &= \sum_{\substack{n, n', k \\ l, l', k'}} M_{l, l', k'}(-\mathbf{q}') \mathbf{J}_{n, n', k}(\mathbf{q}) [\xi_{l, l', k'}(-\mathbf{q}'), \xi_{n, n', k}(\mathbf{q})] \\ &= \left[\sum_{n, n', l, k} M_{l, n, k - \mathbf{q}}(-\mathbf{q}') \mathbf{J}_{n, n', k}(\mathbf{q}) \xi_{l, n', k}(\mathbf{q} - \mathbf{q}') \right. \\ &\quad \left. - \sum_{n, l, l', k} M_{l, l', k - \mathbf{q}'}(-\mathbf{q}') \mathbf{J}_{n, l, k}(\mathbf{q}) \xi_{n, l', k - \mathbf{q}'}(\mathbf{q} - \mathbf{q}') \right] \end{aligned}$$

$$\begin{aligned}
&= \sum_{n,n',l,k} \xi_{l,n',k}(\mathbf{q} - \mathbf{q}') [M_{l,n,k-\mathbf{q}}(-\mathbf{q}') \mathbf{J}_{n,n',k}(\mathbf{q}) - M_{n,n',k}(-\mathbf{q}') \mathbf{J}_{l,n,k+\mathbf{q}'}(\mathbf{q})] \\
&= \frac{1}{m} \sum_{n,n',l,k} \xi_{l,n',k}(\mathbf{q} - \mathbf{q}') \times \left[\langle u_{l,k-\mathbf{q}+\mathbf{q}'} | u_{n,k-\mathbf{q}} \rangle \langle u_{n,k-\mathbf{q}} | \mathbf{k} + \frac{\mathbf{q}}{2} + \mathbf{p} | u_{n',k} \rangle \right. \\
&\quad \left. - \langle u_{l,k-\mathbf{q}+\mathbf{q}'} | \mathbf{k} + \mathbf{q}' + \frac{\mathbf{q}}{2} + \mathbf{p} | u_{n,k+\mathbf{q}'} \rangle \langle u_{n,k+\mathbf{q}'} | u_{n',k} \rangle \right] \\
&= \frac{1}{m} \sum_{l,n',k} \xi_{l,n',k}(\mathbf{q} - \mathbf{q}') \left[\langle u_{l,k-\mathbf{q}+\mathbf{q}'} | \mathbf{k} + \frac{\mathbf{q}}{2} + \mathbf{p} | u_{n',k} \rangle - \langle u_{l,k-\mathbf{q}+\mathbf{q}'} | \mathbf{k} + \mathbf{q}' + \frac{\mathbf{q}}{2} + \mathbf{p} | u_{n',k} \rangle \right] \\
&= -\frac{1}{m} \mathbf{q}' \sum_{l,n',k} M_{l,n',k}(\mathbf{q} - \mathbf{q}') \xi_{l,n',k}(\mathbf{q} - \mathbf{q}') \\
&= -\frac{1}{m} \mathbf{q}' \hat{\rho}(\mathbf{q} - \mathbf{q}') . \tag{4.5}
\end{aligned}$$

In the second equality we used the commutator Eq. (2.12), in the third we shifted indices, and in the fifth we used the resolution of the identity Eq. (2.5). Note that the latter requires a complete set of bands, so to be consistent with the formalism, numerical calculations should also include enough bands to describe the physics of the system fully. In practice, this can be checked by obtaining results as a function of the size of the basis set, and steadily expanding the basis set until calculations have converged with respect to it; see also Appendix C.3 and Ref. 1.

Using this result, we find that the fluctuating force is

$$L_i L_0 \hat{\rho}(\mathbf{q}) = \frac{1}{mV} \sum_{\mathbf{q}'} \mathbf{q} \cdot \mathbf{q}' U(\mathbf{q}') \hat{\rho}(\mathbf{q} - \mathbf{q}') , \tag{4.6}$$

as was the case in the free-electron gas [14, Eq. (11)], and that the normalization squared is

$$(L_0 \hat{\rho}(\mathbf{q}), L_0 \hat{\rho}(\mathbf{q}))_0 = \frac{q^2}{m} \langle \hat{\rho}(0) \rangle_0 = \frac{q^2}{m} \sum_{n,k} f(\varepsilon_{n,k}) = \frac{q^2}{m} N_e = \frac{q^2}{m} n_e V , \tag{4.7}$$

where N_e is the number of electrons in the volume V of the periodic boundary conditions, with density $n_e = N_e/V$. This result is a form of the f -sum rule.

Now we have all the required elements to evaluate the memory function from its definition in Eq. (2.47), and we find that

$$\begin{aligned}
M(\mathbf{q}, z) &= i (L_i A_1(\mathbf{q}), R(z) L_i A_1(\mathbf{q})) \\
&= \frac{i}{(L_0 \hat{\rho}(\mathbf{q}), L_0 \hat{\rho}(\mathbf{q}))} (L_i L_0 \hat{\rho}(\mathbf{q}), R(z) L_i L_0 \hat{\rho}(\mathbf{q}))
\end{aligned}$$

$$\begin{aligned}
&= \frac{m}{n_e V q^2} \frac{i}{m^2 V^2} \sum_{\mathbf{q}', \mathbf{q}''} U^*(\mathbf{q}') U(\mathbf{q}'') (\mathbf{q} \cdot \mathbf{q}') (\mathbf{q} \cdot \mathbf{q}'') \\
&\quad \times (\hat{\rho}(\mathbf{q} - \mathbf{q}'), R(z) \hat{\rho}(\mathbf{q} - \mathbf{q}'')) \\
&= \frac{i}{n_e m V^3} \sum_{\mathbf{q}', \mathbf{q}''} U^*(\mathbf{q}') U(\mathbf{q}'') \left(\frac{\mathbf{q} \cdot \mathbf{q}'}{q} \right) \left(\frac{\mathbf{q} \cdot \mathbf{q}''}{q} \right) \\
&\quad \times (\hat{\rho}(\mathbf{q} - \mathbf{q}'), R(z) \hat{\rho}(\mathbf{q} - \mathbf{q}'')) . \tag{4.8}
\end{aligned}$$

Note that the two terms $\mathbf{q}' U(\mathbf{q}')$ and $\mathbf{q}'' U(\mathbf{q}'')$ are the Fourier transforms of the force or the disorder potential, $F(\mathbf{r}) = -\nabla U(\mathbf{r})$, up to unit-magnitude constants. This makes explicit our earlier statement in Sec. 2.2.3 that the memory function is the relaxation function of the fluctuating force as which the disorder potential manifests in the Langevin equation.

4.1.1 Mode coupling

Our final step is the mode-coupling approximation, in which we keep only terms with the same wavevector, $\mathbf{q}' = \mathbf{q}''$, in Eq. (4.8). This corresponds to taking

$$\begin{aligned}
(\hat{\rho}(\mathbf{q} - \mathbf{q}'), R(z) \hat{\rho}(\mathbf{q} - \mathbf{q}'')) &= \delta_{\mathbf{q}', \mathbf{q}''} (\hat{\rho}(\mathbf{q} - \mathbf{q}'), R(z) \hat{\rho}(\mathbf{q} - \mathbf{q}')) \\
&= \delta_{\mathbf{q}', \mathbf{q}''} V \Phi(\mathbf{q} - \mathbf{q}', z), \tag{4.9}
\end{aligned}$$

i.e., assuming that there is zero overlap for density fluctuations of different modes, or that only fluctuations of the same mode couple, hence the name “mode coupling”.

To validate this approximation, note that if we take a configurational average $\langle \dots \rangle_c$ over disorder with translationally symmetric correlations, $\langle U(\mathbf{r}') U(\mathbf{r}'') \rangle_c = U_2(\mathbf{r}' - \mathbf{r}'')$ for some $U_2(\mathbf{r}' - \mathbf{r}'')$, we find

$$\begin{aligned}
\langle U^*(\mathbf{q}') U(\mathbf{q}'') \rangle_c &= \int_V d\mathbf{r}' \int_V d\mathbf{r}'' e^{i(\mathbf{q}' \cdot \mathbf{r}' - \mathbf{q}'' \cdot \mathbf{r}'')} \langle U(\mathbf{r}') U(\mathbf{r}'') \rangle_c \\
&= \int_V d\mathbf{r}' \int_V d\mathbf{r}'' e^{i(\mathbf{q}' \cdot (\mathbf{r}' - \mathbf{r}'') + (\mathbf{q}' - \mathbf{q}'') \cdot \mathbf{r}'')} U_2(\mathbf{r}' - \mathbf{r}'') \\
&= \int_V d(\mathbf{r}' - \mathbf{r}'') e^{i\mathbf{q}' \cdot (\mathbf{r}' - \mathbf{r}'')} U_2(\mathbf{r}' - \mathbf{r}'') \int_V d\mathbf{r}'' e^{i(\mathbf{q}' - \mathbf{q}'') \cdot \mathbf{r}''} \\
&= V \delta_{\mathbf{q}', \mathbf{q}''} U_2(-\mathbf{q}'), \tag{4.10}
\end{aligned}$$

so that in this case mode coupling is actual and not approximate. Since a large system mimics the effect of the configurational average, and most forms of disorder are distributed with no preferred origin, the mode-coupling approximation is reasonable.

The result is an equation for $M(\mathbf{q}, z)$ in terms of $\Phi(\mathbf{q}, z)$,

$$M(\mathbf{q}, z) = \frac{i}{n_e m V^2} \sum_{\mathbf{q}'} \left(\frac{\mathbf{q} \cdot \mathbf{q}'}{q} \right)^2 |U(\mathbf{q}')|^2 \Phi(\mathbf{q} - \mathbf{q}', z), \quad (4.11)$$

complementing Eq. (2.54) which gives $\Phi(\mathbf{q}, z)$ in terms of $M(\mathbf{q}, z)$. Together the two equations can be solved self-consistently to determine $M(\mathbf{q}, z)$, which is finally used in Eq. (3.13) to calculate the conductivity.

In the weak-disorder limit, this equation shows that $M(\mathbf{q}, z) \propto U^2$, upholding the parallel between $M(\mathbf{q}, z)$ and the inverse relaxation time. This is because as $U(\mathbf{q}') \rightarrow 0$ the relaxation function $\Phi(\mathbf{q} - \mathbf{q}', z) \rightarrow \Phi^{(0)}(\mathbf{q} - \mathbf{q}', z)$, so that to lowest order in U the right side is U^2 .

As is clear from Eq. (3.13), $M(\mathbf{q}, z)$ has units of energy and should not depend on system size. We can confirm that Eq. (4.11) obeys both of these with a few observations. First, we check units. From Sec. 2.2.2, the inner product has units of inverse energy, and our normalization of the Fourier transform in Sec. 2.1 imparts units of V , so that $[\Phi] = \frac{1}{E} [\hat{\rho}(q)^2 R] = \frac{1}{E^2}$, $[U(\mathbf{q})] = EV$, and $\left[\frac{q^2}{m} \right] = E$ because we are using units where $\hbar = 1$. All together, $[M] = E$ as it should be.

Now we check scaling with V , which we denote by braces. $\{1/n_e m V^2\} = V^{-2}$, $\{\sum_{\mathbf{q}'}\} = V$, the example of Eq. (4.10) shows that $\{|U(\mathbf{q}')|^2\} = V$, and $\{\Phi\} = \{\Phi^{(0)}\} = \{X^{(0)}\} = 1$ because they have been defined to be intensive as shown in Appendix C.1.1. Together, $\{M\} = 1$, i.e., the memory function is intensive as it should be.

To simplify the solution, we make one final approximation, which is to take the $\mathbf{q} \rightarrow 0$ limit of Eq. (4.11) and to neglect the \mathbf{q} dependence of the memory function by replacing

$$M(\mathbf{q}, z) \rightarrow M(0, z) = M(z) \quad (4.12)$$

in $\Phi(-\mathbf{q}', z)$. This yields the self-consistent equations

$$M(z) = \frac{i}{n_e m V^2} \sum_{\mathbf{q}'} (\hat{\mathbf{n}} \cdot \mathbf{q}')^2 |U(-\mathbf{q}')|^2 \Phi(\mathbf{q}', z), \quad (4.13a)$$

$$\Phi(\mathbf{q}', z) = \frac{\Phi^{(0)}(\mathbf{q}', z + M(z))}{1 + iM(z)\Phi^{(0)}(\mathbf{q}', z + M(z))/X^{(0)}(\mathbf{q}', 0)}, \quad (4.13b)$$

where $\hat{\mathbf{n}}$ was the direction of \mathbf{q} , a choice which we ignore as we expect a continuous limit $M(\mathbf{q} \rightarrow 0, z)$, and where we reindexed $\mathbf{q}' \rightarrow -\mathbf{q}'$. This approximation was introduced by Götze, who showed that this only slightly affects the slope of $\sigma(\omega)$ in the dc limit and leads to a slight underestimation of the memory function [14, App. B]. This is acceptable for the present case, although it should be treated more carefully in two dimensions [19].

There are no adjustable or fitted parameters in the theory. The only physical inputs enter through the density response function $X^{(0)}(\mathbf{q}, z)$, which characterizes the pristine system, and the disorder potential $U(\mathbf{q})$, which characterizes the disorder.

4.1.2 Zero-frequency conducting-phase solution

In time-reversal-symmetric systems such as the present case given in Eqs. (2.2) and (2.20), by ansatz we can calculate the zero-frequency limit of the memory function and hence also the dc conductivity directly without self-consistency. To begin, we specialize Eq. (2.54) to the zero-frequency case and use Eq. (3.5),

$$\begin{aligned}\Phi(\mathbf{q}, 0) &= \frac{\Phi^{(0)}(\mathbf{q}, M(\mathbf{q}, 0))}{1 + iM(\mathbf{q}, 0) \frac{\Phi^{(0)}(\mathbf{q}, M(\mathbf{q}, 0))}{X^{(0)}(\mathbf{q}, 0)}} \\ &= -\frac{i}{M(\mathbf{q}, 0)} \frac{X^{(0)}(\mathbf{q}, M(\mathbf{q}, 0)) - X^{(0)}(\mathbf{q}, 0)}{1 + \frac{X^{(0)}(\mathbf{q}, M(\mathbf{q}, 0)) - X^{(0)}(\mathbf{q}, 0)}{X^{(0)}(\mathbf{q}, 0)}} \\ &= -i \frac{X^{(0)}(\mathbf{q}, 0)}{M(\mathbf{q}, 0)} \left(1 - \frac{X^{(0)}(\mathbf{q}, 0)}{X^{(0)}(\mathbf{q}, M(\mathbf{q}, 0))} \right).\end{aligned}\quad (4.14)$$

Using this and the approximation $M(\mathbf{q}, z) \rightarrow M(0, z) = M(z)$ with Eq.(4.13), and ansatzing a purely imaginary solution, i.e., $M(0) = iM''$ with real M'' , we obtain

$$U^{-2} = \frac{1}{n_e m V^2} \sum_{\mathbf{q}'} (\hat{\mathbf{n}} \cdot \mathbf{q}')^2 |F(-\mathbf{q}')|^2 \frac{X^{(0)}(\mathbf{q}', 0)}{(M'')^2} \left(\frac{X^{(0)}(\mathbf{q}', 0)}{X^{(0)}(\mathbf{q}', iM'')} - 1 \right), \quad (4.15)$$

Here we have factored the disorder potential $U(\mathbf{q}) = UF(\mathbf{q})$ into a disorder strength U and its \mathbf{q} dependence $F(\mathbf{q})$, and we have divided through by $iM''U^2$.

With a few observations, we can see that this ansatz is a valid solution within a certain range $0 < U < U_c$, where the critical disorder U_c will be defined later. First, we observe that the static response function,

$$X^{(0)}(\mathbf{q}, 0) = \frac{1}{V} \sum_{n', n, \mathbf{k}} \frac{f(\varepsilon_{n, \mathbf{k}}) - f(\varepsilon_{n', \mathbf{k}-\mathbf{q}})}{\varepsilon_{n', \mathbf{k}-\mathbf{q}} - \varepsilon_{n, \mathbf{k}}} |M_{n', n, \mathbf{k}}(\mathbf{q})|^2, \quad (4.16)$$

derived in Appendix C.1.1, is positive in any system since the numerator and denominator always have opposite signs.

Second, we observe that in time-reversal-symmetric systems, the response for purely imaginary frequency,

$$X^{(0)}(\mathbf{q}, iM'') = \frac{1}{V} \sum_{n', n, \mathbf{k}} \frac{(f(\varepsilon_{n, \mathbf{k}}) - f(\varepsilon_{n', \mathbf{k}-\mathbf{q}})) (\varepsilon_{n', \mathbf{k}-\mathbf{q}} - \varepsilon_{n, \mathbf{k}})}{(M'')^2 + (\varepsilon_{n', \mathbf{k}-\mathbf{q}} - \varepsilon_{n, \mathbf{k}})^2} |M_{n', n, \mathbf{k}}(\mathbf{q})|^2, \quad (4.17)$$

is always positive for similar reasons to the static response, as derived in Appendix C.1.2.

Finally, by comparing Eqs. (4.16) and (4.17), it is clear that $X^{(0)}(\mathbf{q}, iM'') \leq X^{(0)}(\mathbf{q}, 0)$ with equality only at $M'' = 0$, so that every factor on the right side of Eq. (4.15) is positive. Because the right side is positive, there is a real disorder strength U solving Eq. (4.15). Hence we have demonstrated explicitly that the memory function is purely imaginary at zero frequency as indicated in Sec. 3.1.1. In this way we have demonstrated that Eq. (4.15) gives the disorder strength as a function of the self-consistent memory function. By evaluating Eq. (4.15) numerically over a range of values for the memory function and inverting the result, we can obtain the memory function as a function of the disorder.

There are two obvious limits of interest, $M'' \rightarrow 0$ and $M'' \rightarrow \infty$. The former limit is the weak disorder limit and, as discussed in Sec. 4.1.1, yields $M'' \propto U^2$ just as $1/\tau \propto U^2$. The second limit, in contrast, gives the critical disorder U_c at which a formerly conducting system becomes an insulator. This can be seen from the expression for the longitudinal conductivity, Eq. (3.15), where for large M'' we have $\sigma_{\alpha, \alpha}(0) = \sigma_{\alpha, \alpha}^{(0)}(iM'') \sim 1/M'' \rightarrow 0$. Using the large- M'' limit of the response function,

$$\begin{aligned} \lim_{M'' \rightarrow \infty} (M'')^2 X^{(0)}(\mathbf{q}, iM'') &= \\ &= \frac{1}{V} \sum_{n', n, \mathbf{k}} (f(\varepsilon_{n, \mathbf{k}}) - f(\varepsilon_{n', \mathbf{k}-\mathbf{q}})) (\varepsilon_{n', \mathbf{k}-\mathbf{q}} - \varepsilon_{n, \mathbf{k}}) |M_{n', n, \mathbf{k}}(\mathbf{q})|^2 = \frac{n_e q^2}{m}, \end{aligned} \quad (4.18)$$

where the last equality is proven in Appendix C.1.2, we identify the critical disorder as the $M'' \rightarrow \infty$ limit of Eq. (4.15),

$$U_c^{-2} = \frac{1}{n_e^2 V^2} \sum_{\mathbf{q}'} (\hat{\mathbf{n}} \cdot \hat{\mathbf{q}}')^2 |F(-\mathbf{q}')|^2 \left(X^{(0)}(\mathbf{q}', 0) \right)^2. \quad (4.19)$$

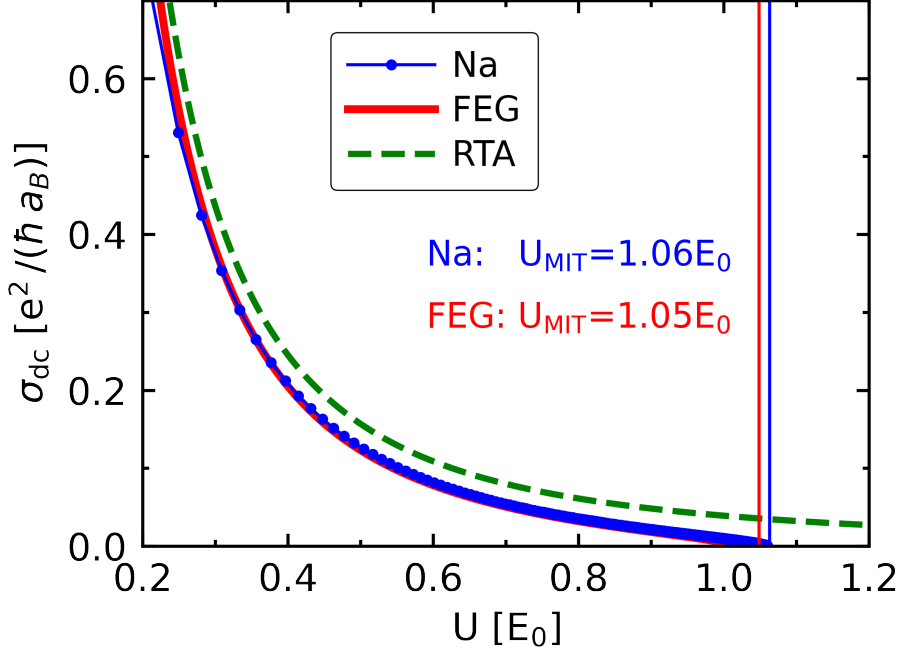


Figure 4.1. We have calculated the dc conductivity as a function of disorder of sodium using the memory function formalism in `exciting`, and of the free-electron gas using the memory function formalism as well as Boltzmann transport theory in the relaxation time approximation. The figure is reproduced from Ref. 1. The disorder potential strength is measured in units of $E_0 = \hbar^2 q_0^2 / 2m$ with $q_0 = 0.55 a_B^{-1}$. q_0 is the range of the step-function disorder potential $|U(\mathbf{q})|^2 = U^2 \frac{6\pi^2}{q_0^3} \Theta(|q_0 - q|)$, which is used as a continuous-space analogue of Anderson disorder. The critical disorder which we generally denote by U_c is written here as U_{MIT} and is about 4.3 eV. Sodium’s effective mass, $m^* = 1.038m$ where m is the electron mass, was calculated *ab initio* and used for the free-electron gas calculations.

4.2 Evaluation and comparison to previous methods and models

Our collaborators in the Draxl group have implemented Eqs. (3.14), (4.15), and (4.19) into the density functional theory code `exciting` [25] and then applied to sodium, chosen for comparison to free-electron gas calculations where the analytic response function is known. Fig. 4.1 shows the result and a comparison to the free-electron gas in the memory function formalism and Boltzmann transport theory, and the overlay of band structures in Fig. 4.2 demonstrates that sodium and the free-electron gas are comparable [1]. The Boltzmann transport result is evaluated as the lowest-order expansion of the memory function in terms of the disorder strength, since this is identical to Boltzmann transport theory in the relaxation time approximation [21] as mentioned earlier in Sec. 3.1.

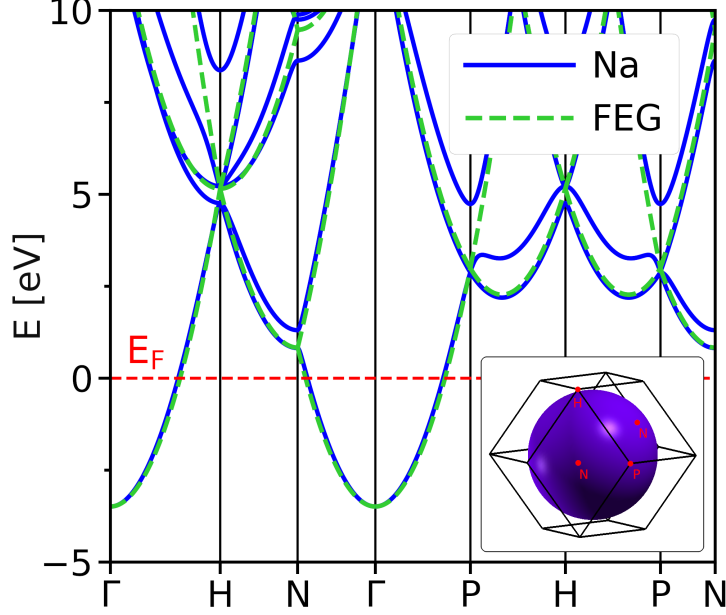


Figure 4.2. The band structures of sodium and of the free-electron gas are superimposed above. Sodium is well-suited as a comparison on equal footing to the free-electron gas because its sodium is highly parabolic with an effective mass close to the free-electron mass, so they are a close comparison. It is similarly well-suited and on equal footing to Boltzmann transport theory because the conduction band is relatively isolated, so that the interband contributions to the conductivity will be small. Sodium’s effective mass is $m^* = 1.038m$, its lattice parameter is 4.0598\AA , and its Fermi wavevector is $k_F = 0.51a_B^{-1}$. All were calculated ab initio and the mass and wavevector were also used for the free-electron gas bands. The sphere in the inset shows the range of the disorder potential in the first Brillouin zone.

Note that in Fig. 4.1 the memory function predicts a finite critical disorder, whereas Boltzmann transport theory predicts an asymptotic decrease due to $\sigma_{dc} \approx \frac{n_e \tau}{m}$ with $\tau \sim \frac{1}{U^2}$. For low disorder, the two agree because (1) in this limit the semiclassical approximation of incoherent scattering used in Boltzmann transport theory is valid and (2) in sodium the other bands are not close to the Fermi level, so that the interband contributions to the conductivity discussed in Sec. 3.2.2 are not significant.

The only inputs for this evaluation are the density response function of the pristine system, $X^{(0)}(\mathbf{q}, z)$, and the disorder potential, $U(\mathbf{q})$. The pristine and full density relaxation functions can be found from the pristine density response function using Eqs. (3.5) and (2.54), and to reduce the number of separately calculated correlation functions, it suffices to evaluate the conductivity as a numerical limit of small $\mathbf{q} = q\hat{\mathbf{n}}$

where $\hat{\mathbf{n}}$ is in the α direction,

$$\sigma_{\alpha,\alpha}(z) = -i \lim_{q \rightarrow 0} \frac{1}{q^2} [z + M(z)] X^{(0)}(q\hat{\mathbf{n}}, z + M(z)), \quad (4.20)$$

following Eq. (3.11). The density response function is already present in the excited states package of `exciting` and was used for these calculations [30, 31].

The disorder potential can be any potential function, such as the screened Coulomb potentials of impurity charges, vacancy potentials, or in two dimensions adsorbates or surface roughness potentials. We chose $|U(\mathbf{q})|^2 = U^2 \frac{6\pi^2}{q_0^3} \Theta(|q_0 - q|)$ as a continuous representation of Anderson disorder, for which $|U(\mathbf{q})|^2$ is a step function in the first Brillouin zone. To see this, define the discrete tight-binding analogues of the disorder potential and its Fourier transform,

$$U_{\mathbf{R}} = \frac{1}{N} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{R}} U_{\mathbf{q}}, \quad U_{\mathbf{q}} = \sum_{\mathbf{R}} e^{-i\mathbf{q}\cdot\mathbf{R}} U_{\mathbf{R}}, \quad (4.21)$$

where the $U_{\mathbf{R}}$ are real site energies uniformly and randomly distributed in $[-w, w]$. It follows that the average over disorder configurations of $|U(\mathbf{q})|^2$ is

$$\langle |U(\mathbf{q})|^2 \rangle = \sum_{\mathbf{R}, \mathbf{R}'} e^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} \langle U_{\mathbf{R}} U_{\mathbf{R}'} \rangle = \sum_{\mathbf{R}, \mathbf{R}'} e^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} \frac{w^2}{3} \delta_{\mathbf{R}, \mathbf{R}'} = N \frac{w^2}{3}, \quad (4.22)$$

so that the disorder potential is constant with respect to \mathbf{q} up to the cutoff q_0 . In tight-binding the cutoff is implicit because smallest spatial scale is the lattice length, and hence it provides a natural cutoff. For our continuous analogue we take $q_0 = 0.55a_B^{-1}$ which defines a sphere inside the unit cell of sodium, as shown in Fig. 4.2.

We make a few additional comments regarding numerical implementations in general in Appendix C.3. These address considerations such as the basis set used to calculate the Bloch energies and matrix elements and the grid of reciprocal lattice vectors \mathbf{k} and \mathbf{q} .

4.3 Critical scaling of the dc conductivity

In addition to numerical results, the calculations of Sec. 4.1.2 yield the scaling of the longitudinal dc conductivity at the critical point,

$$\sigma_{\alpha,\alpha}(0) \sim \left(1 - \frac{U}{U_c}\right)^s, \quad (4.23)$$

where s is the critical exponent. To do this, we begin by expanding Eq. (4.15) in powers of $1/M''$ for large M'' . The expression for the critical disorder, Eq. (4.19), can be thought of as the lowest-order term in this expansion.

As derived in Appendix C.1.2.1, for large M'' the density response function can be expanded in powers of $1/M''$ as

$$X^{(0)}(\mathbf{q}, iM'') = \frac{1}{(M'')^2} K_1^{(0)}(\mathbf{q}) + \frac{1}{(M'')^4} K_3^{(0)}(\mathbf{q}) + O\left((M'')^{-6}\right), \quad (4.24)$$

where

$$K_j^{(0)}(\mathbf{q}) = \frac{1}{V} \sum_{n', n, \mathbf{k}} (f(\varepsilon_{n, \mathbf{k}}) - f(\varepsilon_{n', \mathbf{k}-\mathbf{q}})) (\varepsilon_{n', \mathbf{k}-\mathbf{q}} - \varepsilon_{n, \mathbf{k}})^j |M_{n', n, \mathbf{k}}(\mathbf{q})|^2. \quad (4.25)$$

We then use this to expand the M'' -dependent part of Eq. (4.19),

$$\begin{aligned} \frac{\Phi(\mathbf{q}, 0)}{M''} &= \frac{X^{(0)}(\mathbf{q}, 0)}{(M'')^2} \left(\frac{X^{(0)}(\mathbf{q}, 0)}{X^{(0)}(\mathbf{q}, iM'')} - 1 \right) = \\ &= \frac{(X^{(0)}(\mathbf{q}, 0))^2}{K_1^{(0)}(\mathbf{q})} + \frac{1}{(M'')^2} \left(\frac{(X^{(0)}(\mathbf{q}, 0))^2 K_3^{(0)}(\mathbf{q})}{(K_1^{(0)}(\mathbf{q}))^2} - X^{(0)}(\mathbf{q}, 0) \right) + O\left((M'')^{-4}\right). \end{aligned} \quad (4.26)$$

Although we have the analytic expression $K_1^{(0)}(\mathbf{q}) = n_e q^2 / m$ as in Eq. (4.18), here we keep it in terms of the expansion coefficients $K_j^{(0)}(\mathbf{q})$ to keep the presentation consistent and clear. Substituting the expansion into Eq. (4.15) after division by M'' , we have

$$\begin{aligned} U^{-2} &= \frac{1}{n_e m} \frac{1}{V^2} \sum_{\mathbf{q}} (\hat{\mathbf{n}} \cdot \mathbf{q})^2 |F(\mathbf{q})|^2 \frac{(X^{(0)}(\mathbf{q}, 0))^2}{K_1^{(0)}(\mathbf{q})} \\ &+ \frac{1}{(M'')^2} \frac{1}{n_e m} \frac{1}{V^2} \sum_{\mathbf{q}} (\hat{\mathbf{n}} \cdot \mathbf{q})^2 |F(\mathbf{q})|^2 \left(\frac{(X^{(0)}(\mathbf{q}, 0))^2 K_3^{(0)}(\mathbf{q})}{(K_1^{(0)}(\mathbf{q}))^2} - X^{(0)}(\mathbf{q}, 0) \right) \\ &+ O\left((M'')^{-4}\right). \end{aligned} \quad (4.27)$$

The first term yields the critical disorder as in Eq. (4.19), and the second gives the critical scaling. Define

$$A(\mathbf{q}) = \frac{1}{n_e m} \frac{1}{V^2} \sum_{\mathbf{q}} (\hat{\mathbf{n}} \cdot \mathbf{q})^2 |F(\mathbf{q})|^2 \left(\frac{(X^{(0)}(\mathbf{q}, 0))^2 K_3^{(0)}(\mathbf{q})}{(K_1^{(0)}(\mathbf{q}))^2} - X^{(0)}(\mathbf{q}, 0) \right) \quad (4.28)$$

so that Eq. (4.27) becomes

$$U^{-2} = U_c^{-2} + \frac{1}{(M'')^2} A(\mathbf{q}) + O((M'')^{-4}) , \quad (4.29)$$

and rearrange to solve for $1/M''$,

$$\begin{aligned} \frac{1}{M''} &= (A(\mathbf{q}))^{-\frac{1}{2}} \left(\frac{1}{U^2} - \frac{1}{U_c^2} + O((M'')^{-4}) \right)^{\frac{1}{2}} \\ &= \frac{1}{(A(\mathbf{q}))^{1/2} U} \left(\left(1 - \frac{U}{U_c}\right) \left(1 + \frac{U}{U_c}\right) + O((M'')^{-4}) \right)^{\frac{1}{2}} . \end{aligned} \quad (4.30)$$

Since M'' must be positive and real, we take the positive branch of the square root, and we confirm that $A(\mathbf{q})$ is positive in Appendix C.1.2.1.

As we observed earlier, from Eq. (3.15) in the large- M'' limit the conductivity scales as $\sigma_{\alpha,\alpha}(0) \sim 1/M''$, so by focusing on the zero at $U = U_c$ in Eq. (4.30), we find that the critical exponent of the conductivity is $s = 1/2$,

$$\sigma_{\alpha,\alpha}(0) \sim \frac{1}{M''} \sim \left(1 - \frac{U}{U_c}\right)^{1/2} . \quad (4.31)$$

The critical exponent is independent of the dimensionality of the system, provided that a conducting phase exists. The conducting phase generally exists for dimension $d \geq 3$, but $d = 2$ is marginal and $d = 1$ is strictly localized [14, 32, 33]. Our result corroborates the findings of Götze for the free-electron gas and Prelovšek using a tight-binding adaptation of the present memory function formalism for the hypercubic lattice, demonstrating that, as is typical of critical phenomena, the scaling is irrelevant of the microscopic details of the system. By describing the scaling of the conductivity with disorder, our result complements typical scaling analyses of metal-to-insulator transitions, which give the scaling of the conductivity with the Fermi level [32, 34].

Chapter 5 |

Conclusion and outlook

5.1 Summary of this dissertation

We have derived an expression for the conductivity in a memory function formalism which addresses the relaxation effects due to scattering within the framework of quantum statistical mechanics. The approach is derived for a general periodic system, and by allowing for quantum coherence between scattering events, it is valid for any level of scattering. In this way, the memory function formalism goes beyond Boltzmann transport theory in the relaxation time approximation. It is also capable of describing physics in the thermodynamic limit, which addresses the limitation of the Kubo formula to microscopic models systems.

In Chapter 2, we discussed Mori's projected equation of motion in the context of periodic systems [12]. The Mori projection isolates the relaxation effects due to scattering in the time evolution of the operators, yielding a generalized Langevin equation for their relaxation functions. These relaxation effects are described by a complex memory function. To solve this equation, we showed that the method of Götze, which is to approximate the relaxation in the memory term by that of the slowest collective variables, generalizes to multiband systems [14]. This yields the density relaxation function of the full system in terms of that of the pristine system and the memory function. The continuity relation between density and current then relate this relaxation function to the conductivity.

In Chapter 3, we extended Götze's work on the free-electron gas by deriving a conductivity formula general to any periodic system. We derived the conductivity of the full system with scattering,

$$\sigma(z) = \sigma^{(0)}(z + M(z)), \quad (5.1)$$

in terms of the conductivity of the pristine system, $\sigma^{(0)}$, with a broadening and frequency shift respectively due to the imaginary and real parts of the memory function, M . In the dc limit of the conductivity, the memory function is a pure imaginary broadening, $M(0) = iM''$, giving a finite lifetime to the current-carrying excitations, analogous to the inverse of the Boltzmann transport theory relaxation time. This broadening resolves the problem of the dc limit of the Kubo formula evaluated in supercells, where the dc conductivity was either zero for open boundary conditions or infinity for periodic boundary conditions. Our formula also includes interband contributions to the dc conductivity which are absent from Boltzmann transport theory. These contributions are important not only for systems with multiple bands near the Fermi level, such as semimetals and narrow-bandgap semiconductors, but also for more general systems when the calculation uses a large supercell. Furthermore, when the Fermi level is in or near a gap, we find remarkably that low or moderate scattering can increase the conductivity by broadening the bands into the gap. Using the parallel with the inverse relaxation time, our formula is easy to implement into existing Boltzmann transport theory *ab initio* codes by making the replacement $M'' \rightarrow 1/\tau$, recovering the missing multiband contributions. These results are discussed in our publication Ref. 24.

In Chapter 4, we applied the mode-coupling approach of Götze in the context of periodic systems to derive a self-consistent formula for the memory function in the case of scattering due to disorder [14]. In the zero-frequency limit, this became an analytic formula for the memory function, which shows that the memory function diverges at finite disorder. Taking the limit of large $M(0)$, we obtained an explicit formula for the critical disorder. Since the only inputs for these formulae are the density response function of the pristine system and the disorder potential, they are easy to implement into *ab initio* codes, and our collaborators implemented them into their density-functional theory code `exciting`, where the former has already been implemented [25, 30, 31]. Taking as a demonstrative case the nearly-free-electron metal sodium and a disorder potential which is the continuous-space adaptation of Anderson disorder, we evaluated the memory function and dc conductivity of disordered sodium, and found that it undergoes a metal-to-insulator transition at finite disorder. We compared our results to Boltzmann transport theory, showing that the two agree for low disorder where the semiclassical approximation is valid, whereas only the memory function captures the metal-to-insulator transition when the disorder is strong. Finally, we calculated the critical exponent for the variation of the longitudinal dc conductivity with respect to disorder and find it to be $s = 1/2$ regardless of dimension, provided the conducting phase exists. The implementation and

the formulae for the memory function are discussed in our publication Ref. 1.

5.2 Approximations and refinements

Future work in the memory function formalism can address refinements of the approximations we have made so far or applications we have not yet explored. Here we will discuss the approximations, which were first used by Götze to derive the memory function formalism for the free-electron gas [14]. Two were made to derive the expression for the density relaxation function, Eq. (2.54), and current relaxation function or conductivity, Eq. (3.13), of the full system with scattering.

First, we approximated the static correlation functions of the full system by their counterparts in the pristine system without scattering, e.g., replacing $X(\mathbf{q}, 0)$ with $X^{(0)}(\mathbf{q}, 0)$. This enabled us to write the correlation functions of the full system in terms of the correlation functions of the pristine system and the memory function. As a result, at our level of approximation the correlation functions of the full system, in particular the conductivity, are given in terms of the density of states and broadened band structure and of the pristine system. For example, we pointed out in Sec. 3.2.2.2 that this prevents the memory function formalism from recognizing the presence of the donor/acceptor level in doped semiconductors, so that the conductivity does not have the correct temperature dependence. This approximation can be relaxed by using another method, e.g., the coherent potential approximation, to calculate the static correlation functions of the full system [14, p. 222].

We also replaced the exact memory function matrix in Eq. (2.46) by

$$M_{\alpha,\beta}(\mathbf{q}, z) = M(\mathbf{q}, z)\delta_{\alpha,\beta} - M(\mathbf{q}, z)\delta_{\alpha,0}\delta_{0,\beta} \quad \text{where} \quad M(\mathbf{q}, z) = M_{1,1}(\mathbf{q}, z). \quad (5.2)$$

That is, on the grounds that the density and current are slow variables and should therefore dominate the long-time or low-frequency dynamics, we replaced the memory functions of all other variables by that of the current. In physical terms, we assumed that all dynamical variables relax with the same rate as the current. Choosing only one or a few collective variables to track in this way is a form of coarse-graining [17]. We explained in Sec. 3.1.1 that this is why the memory function $M(\mathbf{q}, z)$ has no wavevector dependence while its parallel $1/\tau_k$, the inverse relaxation time of Boltzmann, does. As discussed in Sec. 2.2.4, we can refine this approximation by defining additional orthonormal variables $A_\alpha(\mathbf{q})$ and including their memory functions explicitly in the memory function matrix.

This would capture their relaxation more accurately, expanding the frequency range over which the memory function formalism is valid and more accurately representing the relaxation of excitations of different wavevectors.

To calculate the memory function explicitly, we made two further approximations. First, we replaced the projected counterpropagator $R_{Q(\mathbf{q})}(z)$ with the full one $R(z)$ in Eq. (2.38). Equivalently, we truncated the series expansion for the memory function, Eq. (2.39), at the first term. From this equation, we see that refinements of this approximation require the matrix elements of the inverse relaxation function matrix $\underline{\Phi}^{-1}(z)$. Calculating these would require an approximate form for the entire relaxation function matrix $\underline{\Phi}(z)$. Presumably such an approximation would be built on similar grounds as that for the memory function matrix, but we will not explore this possibility further here.

We also replaced the memory function $M(\mathbf{q}, z)$ by its uniform limit $M(z) = M(\mathbf{q} = 0, z)$. For the uniform conductivity we only need the uniform limit of the memory function, but inserting Eq. (2.54) into Eq. (4.11) shows that $M(\mathbf{q} = 0, z)$ is calculated as a sum over all $M(\mathbf{q}, z)$. As noted by Götze in his treatment of the three-dimensional free-electron gas, this leads to only a slight underestimation of the memory function, and a slight deviation in the slope $d\sigma/d\omega$ in the dc limit $\omega \rightarrow 0$ [14, App. B]. It is appropriate for the present case but should be treated more carefully for, e.g., the two-dimensional case [19]. This approximation was made purely to simplify computations, so that it may be relaxed with either higher computer power or an appropriate ansatz for the variation of the memory function with \mathbf{q} .

5.3 Future applications

We derived the memory function formalism and conductivity in Chapters 2 and 3 for a general scattering Hamiltonian H_i , and in Chapter 4 studied the specific case of scattering due to disorder. Equally important sources of scattering are the Coulomb and electron-phonon interactions, which remain to be treated in a self-consistent way for general periodic systems. This is perhaps the most outstanding direction for future study.

For the purpose of demonstration, we evaluated the memory function and dc conductivity only for a model potential representing Anderson disorder in a three-dimensional nearly-free-electron metal. It will be illuminating to compare this case to other materials, e.g., systems with reduced dimensionality, multiple bands, or nonparabolic dispersion.

For example, the memory function formalism applied to the disordered two-dimensional free-electron gas predicts that at finite low disorder a quasi-conducting regime and at strong disorder a transition to an insulating regime [19]. The effects of dispersion and other aspects of band structure remain to be explored.

In addition to conductivity, the memory function formalism also describes the insulating regime, and has been used to this end for the free-electron gas [14, 19]. In our derivation we chose to focus on the conducting regime, but through Eq. (3.9), our extension of the memory function formalism to periodic systems also describes dielectric behavior and localization in the insulating regime. As with the conductivity, the density response function's behavior in the presence of disorder varies strongly with dimension; with its static uniform limit diverging exponentially with inverse disorder strength in two dimensions but polynomially in three. Therefore, the dielectric properties, too, warrant exploration in low-dimensional materials and complex materials. Regarding localization, the localization length and participation ratio can be calculated using a tight-binding adaptation of the present memory function formalism for hypercubic lattices [33]. Deriving these localization metrics from the present formalism would be useful as an analytic complement to their typical use in numerical experiments.

In Sec. 3.2.3, we noted that the anomalous Hall conductivity is frequency-independent and hence, within the present theory, unaffected by scattering. This may indicate topological protection. At present, we have been content to study the dc conductivity in the bulk without examining edge states, so this question remains open.

Since the forms of scattering we are most interested in are not sensitive to spin, we have not included it in our calculations. Spin would be simple to reintroduce and may be relevant for magnetic materials and magnetic impurities. This should be kept in mind when applying the memory function formalism to more complex materials.

5.4 Conclusion

We now have a memory function formalism for the electrical conductivity of a periodic system with scattering which is built within the framework of quantum statistical mechanics and captures the thermodynamic limit. Specifically, this formalism describes the evolution of operators in terms of a memory function that gives relaxation due to scattering. Constructing dynamical correlation functions the dynamical operators and focusing the slowest relaxations yields a solution for the long-time dynamics of the slow variables. In this way we derived an expression for the conductivity which accounts

for coherent scattering while accomplishing the coarse-graining necessary to describe macroscopic systems.

Capturing quantum coherence for a general periodic system allows the memory function formalism to build on Boltzmann transport theory by going beyond the weak-scattering limit and to describe multiband systems. Capturing the thermodynamic limit allows the memory function formalism to circumvent the finite-size problems faced by the Kubo formula. As a result, the memory function formalism allows for a more complete description of conductivity in systems with scattering. With this, in the dc limit we were able to describe the metal-to-insulator transition and scattering-enhanced conductivity, which otherwise would have been out of reach. We also derived analytic formulae for the memory function in the case of scattering due to disorder, and our collaborators implemented them into their *ab initio* code and evaluated them for a model system to demonstrate the theory [1].

The memory function formalism has opportunities for many valuable developments and extensions. We have pointed out its immediate application to other sources of scattering, dielectric behavior in the insulating regime, and complex materials. Furthermore, the theory of the Mori projection, conserved quantities, and slow variables are all of a very broad nature [12, 14]. In this way, the present theory can serve as a template for self-consistent memory function treatments of other correlation functions in periodic systems, such as spin or thermal correlation functions [12].

Appendix A

The Bloch basis

To evaluate the Bloch matrix elements, we will use the relation for the Dirac comb. Writing out the unit cell vectors

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \quad \mathbf{k} = \frac{2\pi}{N_1 a_1} m_1 \mathbf{b}_1 + \frac{2\pi}{N_2 a_2} m_2 \mathbf{b}_2 + \frac{2\pi}{N_3 a_3} m_3 \mathbf{b}_3, \quad (\text{A.1})$$

with the lattice vectors and reciprocal lattice vectors which obey $\mathbf{a}_\mu \cdot \mathbf{b}_\nu = 2\pi \delta_{\mu,\nu}$ and where there are N_μ unit cells in the direction of lattice vector \mathbf{a}_μ , we have

$$\begin{aligned} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} &= \sum_{n_1, n_2, n_3} e^{i \left(\frac{2\pi}{N_1} m_1 n_1 + \frac{2\pi}{N_2} m_2 n_2 + \frac{2\pi}{N_3} m_3 n_3 \right)} \\ &= \left(\sum_{n_1} e^{i \frac{2\pi}{N_1} m_1 n_1} \right) \left(\sum_{n_2} e^{i \frac{2\pi}{N_2} m_2 n_2} \right) \left(\sum_{n_3} e^{i \frac{2\pi}{N_3} m_3 n_3} \right) \\ &= \left(N_1 \sum_{j_1} \delta_{m_1, j_1 N_1} \right) \left(N_2 \sum_{j_2} \delta_{m_2, j_2 N_2} \right) \left(N_3 \sum_{j_3} \delta_{m_3, j_3 N_3} \right) = N \sum_{\mathbf{G}} \delta_{\mathbf{k}, \mathbf{G}}. \end{aligned} \quad (\text{A.2})$$

A.1 Normalization

The normalization of the Bloch wavefunctions is given by

$$\int_V d\mathbf{r} \psi_{n', \mathbf{k}'}^*(\mathbf{r}) \psi_{n, \mathbf{k}}(\mathbf{r}) = \frac{1}{N} \int_V d\mathbf{r} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} u_{n', \mathbf{k}'}^*(\mathbf{r}) u_{n, \mathbf{k}}(\mathbf{r}) \quad (\text{A.3})$$

$$= \frac{1}{N} \sum_{\mathbf{R}} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}} \int_{\Omega} d\mathbf{s} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{s}} u_{n', \mathbf{k}'}^*(\mathbf{s}) u_{n, \mathbf{k}}(\mathbf{s}) \quad (\text{A.4})$$

$$= \sum_{\mathbf{G}} \delta_{\mathbf{k}-\mathbf{k}', \mathbf{G}} \int_{\Omega} d\mathbf{s} u_{n', \mathbf{k}}^*(\mathbf{s}) u_{n, \mathbf{k}}(\mathbf{s}) = \sum_{\mathbf{G}} \delta_{\mathbf{k}-\mathbf{k}', \mathbf{G}} \delta_{n, n'}. \quad (\text{A.5})$$

In the last line we used Eq. (A.2), and defined the periodic part of the Bloch wavefunction to be normalized by its integral over a unit cell,

$$\int_{\Omega} d\mathbf{s} u_{n',k}^*(\mathbf{s}) u_{n,k}(\mathbf{s}) = \delta_{n,n'} . \quad (\text{A.6})$$

A.2 Density matrix element

The density operator matrix elements are evaluated as

$$\begin{aligned} \int_V d\mathbf{r} \psi_{n',\mathbf{k}'}^*(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} \psi_{n,\mathbf{k}}(\mathbf{r}) &= \frac{1}{N} \int_V d\mathbf{r} e^{i(\mathbf{k}-\mathbf{q}-\mathbf{k}')\cdot\mathbf{r}} u_{n',\mathbf{k}'}^*(\mathbf{r}) u_{n,\mathbf{k}}(\mathbf{r}) \\ &= \frac{1}{N} \sum_{\mathbf{R}} e^{i(\mathbf{k}-\mathbf{q}-\mathbf{k}')\cdot\mathbf{R}} \int_{\Omega} d\mathbf{s} e^{i(\mathbf{k}-\mathbf{q}-\mathbf{k}')\cdot\mathbf{s}} u_{n',\mathbf{k}'}^*(\mathbf{s}) u_{n,\mathbf{k}}(\mathbf{s}) \\ &= \sum_{\mathbf{G}} \delta_{\mathbf{k}-\mathbf{q}-\mathbf{k}',\mathbf{G}} \int_{\Omega} d\mathbf{s} e^{i\mathbf{G}\cdot\mathbf{s}} u_{n',\mathbf{k}-\mathbf{q}-\mathbf{G}}^*(\mathbf{s}) u_{n,\mathbf{k}}(\mathbf{s}) \\ &= \sum_{\mathbf{G}} \delta_{\mathbf{k}-\mathbf{q}-\mathbf{k}',\mathbf{G}} \int_{\Omega} d\mathbf{s} u_{n',\mathbf{k}-\mathbf{q}}^*(\mathbf{s}) u_{n,\mathbf{k}}(\mathbf{s}) \\ &= \sum_{\mathbf{G}} \delta_{\mathbf{k}-\mathbf{q}-\mathbf{k}',\mathbf{G}} M_{n',n,\mathbf{k}}(\mathbf{q}) . \end{aligned} \quad (\text{A.7})$$

In the third line we used Eq. (A.2) and in the fourth we used $u_{n,\mathbf{k}+\mathbf{G}}(\mathbf{r}) = e^{-i\mathbf{G}\cdot\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r})$. The current operator matrix element as written in Eq. (2.18) follows easily from this matrix element. A more explicit expression requires the momentum matrix element in the Bloch basis.

A.3 Position and momentum matrix elements

To evaluate the momentum matrix elements we use $\hat{\mathbf{p}}/m = -i[\hat{\mathbf{r}}, H]$ which follows from the Heisenberg equation of motion with $H = \hat{\mathbf{p}}^2/2m + V(\mathbf{r})$. We see that

$$\begin{aligned} \langle n', \mathbf{k}' | \hat{\mathbf{p}}/m | n, \mathbf{k} \rangle & \quad (\text{A.8}) \\ &= -i \langle n', \mathbf{k}' | \hat{\mathbf{r}} H - H \hat{\mathbf{r}} | n, \mathbf{k} \rangle \\ &= -i (\varepsilon_{n,\mathbf{k}} - \varepsilon_{n',\mathbf{k}'}) \frac{1}{N} \int_V d\mathbf{r} u_{n',\mathbf{k}'}^*(\mathbf{r}) e^{-i\mathbf{k}'\cdot\mathbf{r}} r e^{i\mathbf{k}\cdot\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r}) \\ &= (\varepsilon_{n',\mathbf{k}'} - \varepsilon_{n,\mathbf{k}}) \left[\frac{1}{N} \int_V d\mathbf{r} u_{n',\mathbf{k}'}^*(\mathbf{r}) e^{-i\mathbf{k}'\cdot\mathbf{r}} \partial_{\mathbf{k}} \left(e^{i\mathbf{k}\cdot\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r}) \right) - \frac{1}{N} \int_V d\mathbf{r} u_{n',\mathbf{k}'}^*(\mathbf{r}) \partial_{\mathbf{k}} u_{n,\mathbf{k}}(\mathbf{r}) \right] \end{aligned}$$

$$= \left[\delta_{n,n'} (\varepsilon_{n',\mathbf{k}} - \varepsilon_{n,\mathbf{k}}) \partial_{\mathbf{k}} \delta_{\mathbf{k},\mathbf{k}'} - \delta_{\mathbf{k},\mathbf{k}'} (\varepsilon_{n',\mathbf{k}} - \varepsilon_{n,\mathbf{k}}) \int_{\Omega} d\mathbf{s} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} u_{n',\mathbf{k}}^*(\mathbf{s}) \partial_{\mathbf{k}} u_{n,\mathbf{k}}(\mathbf{s}) \right].$$

In the fourth line, in the first term we used $\partial_{\mathbf{k}} \langle n', \mathbf{k}' | n, \mathbf{k} \rangle = \delta_{n,n'} \partial_{\mathbf{k}} \delta_{\mathbf{k},\mathbf{k}'}$, and in the second we used

$$\begin{aligned} & \frac{1}{N} \int_V d\mathbf{r} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} u_{n',\mathbf{k}'}^*(\mathbf{r}) \partial_{\mathbf{k}} u_{n,\mathbf{k}}(\mathbf{r}) \\ &= \left(\frac{1}{N} \sum_R e^{i(\mathbf{k}-\mathbf{k}')\cdot R} \right) \int_{\Omega} d\mathbf{s} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{s}} u_{n',\mathbf{k}'}^*(\mathbf{s}) \partial_{\mathbf{k}} u_{n,\mathbf{k}}(\mathbf{s}) \\ &= \int_{\Omega} d\mathbf{s} u_{n',\mathbf{k}}^*(\mathbf{s}) \partial_{\mathbf{k}} u_{n,\mathbf{k}}(\mathbf{s}), \end{aligned} \quad (\text{A.9})$$

where we only need the single $\delta_{\mathbf{k},\mathbf{k}'}$ and not the full Dirac comb when considering \mathbf{k}, \mathbf{k}' in the unit cell. Using also

$$0 = \partial_{\mathbf{k}}(0) = \partial_{\mathbf{k}} ((\varepsilon_{n',\mathbf{k}} - \varepsilon_{n,\mathbf{k}}) \delta_{\mathbf{k},\mathbf{k}'}) \Rightarrow (\varepsilon_{n',\mathbf{k}} - \varepsilon_{n,\mathbf{k}}) \partial_{\mathbf{k}} \delta_{\mathbf{k},\mathbf{k}'} = \delta_{\mathbf{k},\mathbf{k}'} \partial_{\mathbf{k}} \varepsilon_{n,\mathbf{k}}, \quad (\text{A.10})$$

we find that the momentum operator is diagonal in the Bloch basis, with

$$\langle n', \mathbf{k} | \hat{\mathbf{p}}/m | n, \mathbf{k} \rangle = \partial_{\mathbf{k}} \varepsilon_{n,\mathbf{k}} + i (\varepsilon_{n',\mathbf{k}} - \varepsilon_{n,\mathbf{k}}) \mathbf{X}_{n',n,\mathbf{k}}, \quad (\text{A.11})$$

where $\mathbf{X}_{n',n,\mathbf{k}} = i \langle u_{n',\mathbf{k}} | \partial_{\mathbf{k}} u_{n,\mathbf{k}} \rangle$ is the Berry connection.

Appendix B | Operator Algebra and the Projected Equation of Motion

B.1 Inner product of operators

Here we repeat the definition of our inner product,

$$(A, B) = \int_0^\beta d\lambda \left\langle e^{\lambda H} (A - \langle A \rangle)^\dagger e^{-\lambda H} (B - \langle B \rangle) \right\rangle, \quad (\text{B.1})$$

and demonstrate that it constitutes an inner product and also has three useful properties.

The proposed inner product satisfies linearity because it is constructed from linear operations. It satisfies conjugate symmetry since

$$\left\langle \left(e^{\lambda H} A^\dagger e^{-\lambda H} B \right)^\dagger \right\rangle = \left\langle B^\dagger e^{-\lambda H} A e^{\lambda H} \right\rangle = \left\langle e^{\lambda H} B^\dagger e^{-\lambda H} A \right\rangle. \quad (\text{B.2})$$

Here and in the following calculations, for brevity we have suppressed the mean values which do not affect the calculations. We have also used the fact that the thermal average $\langle \dots \rangle = \frac{1}{Z} \text{Tr}(e^{-\beta H} \dots)$ is cyclic for functions of the Hamiltonian due to trace cyclicity, a property we will use this several more times. Finally, the proposed inner product satisfies positive definiteness since, expanding in the eigenstate basis,

$$\begin{aligned} \left\langle e^{\lambda H} A^\dagger e^{-\lambda H} A \right\rangle &= \frac{1}{Z} \sum_{mn} \left(e^{-\beta \varepsilon_m} e^{\lambda \varepsilon_m} (A^\dagger)_{mn} e^{-\lambda \varepsilon_n} A_{nm} \right) \\ &= \frac{1}{Z} \sum_{mn} \left(e^{-\beta \varepsilon_m + \lambda(\varepsilon_m - \varepsilon_n)} |A_{mn}|^2 \right), \end{aligned} \quad (\text{B.3})$$

which is positive as long as not all matrix elements of A are zero, i.e., as long as $A \neq 0$.

It is easy to show that L is self-adjoint with respect to this inner product,

$$\begin{aligned}
(A, LB) &= \int_0^\beta d\lambda \langle e^{\lambda H} A^\dagger e^{-\lambda H} [H, B] \rangle \\
&= \int_0^\beta d\lambda \langle (e^{\lambda H} A^\dagger e^{-\lambda H} HB - e^{\lambda H} A^\dagger e^{-\lambda H} BH) \rangle \\
&= \int_0^\beta d\lambda \langle (e^{\lambda H} A^\dagger H e^{-\lambda H} B - e^{\lambda H} H A^\dagger e^{-\lambda H} B) \rangle \\
&= \int_0^\beta d\lambda \langle e^{\lambda H} [H, A]^\dagger e^{-\lambda H} B \rangle \\
&= (LA, B) .
\end{aligned} \tag{B.4}$$

Note that self-adjointness of superoperators such as L is in respect to the inner product of operators given above. It should not be confused with self-adjointness of operators which is in respect to the usual inner product of states. To avoid confusion, we refer to the latter as Hermiticity.

Also, we can show that

$$\begin{aligned}
(A, LB) &= \int_0^\beta d\lambda \langle e^{\lambda H} A^\dagger e^{-\lambda H} [H, B] \rangle \\
&= \int_0^\beta d\lambda \langle (e^{\lambda H} A^\dagger e^{-\lambda H} HB - e^{\lambda H} A^\dagger e^{-\lambda H} BH) \rangle \\
&= \int_0^\beta d\lambda \langle (e^{\lambda H} A^\dagger H e^{-\lambda H} B - e^{\lambda H} H A^\dagger e^{-\lambda H} B) \rangle \\
&= - \int_0^\beta d\lambda \frac{d}{d\lambda} \langle e^{\lambda H} A^\dagger e^{-\lambda H} B \rangle \\
&= - \langle e^{\beta H} A^\dagger e^{-\beta H} B \rangle + \langle A^\dagger B \rangle \\
&= - \frac{1}{Z} \text{Tr} (e^{-\beta H} e^{\beta H} A^\dagger e^{-\beta H} B) + \langle A^\dagger B \rangle \\
&= - \frac{1}{Z} \text{Tr} (e^{-\beta H} B A^\dagger) + \langle A^\dagger B \rangle \\
&= \langle [A^\dagger, B] \rangle .
\end{aligned} \tag{B.5}$$

With this we can relate the time derivative of the time evolution of a variable projected on its initial value, $(d/dt)(A(t), A)$, with the correlation function of the variables displaced in time, $i\langle [A(t)^\dagger, A] \rangle$.

Finally, by using Eq. (2.30) and also solving the Heisenberg equation of motion in terms of H , we have

$$e^{iLt} A = A(t) = e^{iHt} A e^{-iHt} . \tag{B.6}$$

From this it follows that

$$\begin{aligned}
(e^{iLt} A, B) &= \int_0^\beta d\lambda \langle e^{\lambda H} (e^{iHt} A e^{-iHt})^\dagger e^{-\lambda H} B \rangle \\
&= \int_0^\beta d\lambda \langle e^{\lambda H} e^{iHt} A^\dagger e^{-iHt} e^{-\lambda H} B \rangle \\
&= \int_0^\beta d\lambda \langle e^{\lambda H} A^\dagger e^{-\lambda H} e^{-iHt} B e^{iHt} \rangle = (A, e^{-iLt} B) .
\end{aligned} \tag{B.7}$$

This identity is a special case of the more general property that

$$(A(t - t'), B) = (A(t), B(t')) = (A, B(-(t - t'))), \tag{B.8}$$

which states that the time dependence of two operators' inner product depends only on the relative time between them. This is the behavior we expect from operators and a Hamiltonian which do not depend explicitly on time.

B.2 Deriving the projected equation of motion

The projectors into and out of the subspace of wavevector \mathbf{q} can respectively be written in terms of the orthonormal variables as

$$P(\mathbf{q})\bullet = \sum_\alpha A_\alpha(\mathbf{q}) (A_\alpha(\mathbf{q}), \bullet) \tag{B.9}$$

and $Q(\mathbf{q}) = 1 - P(\mathbf{q})$. In the following we will suppress the argument \mathbf{q} for clarity. The projector is self-adjoint with respect to the operator inner product, since

$$\begin{aligned}
(B, PC) &= \sum_\alpha (B, A_\alpha(A_\alpha, C)) \\
&= \sum_\alpha (B, A_\alpha)(A_\alpha, C) \\
&= \sum_\alpha (A_\alpha(A_\alpha, B), C) = (PB, C),
\end{aligned} \tag{B.10}$$

and the same property follows for Q .

We start with the counterpropagator $R(z) = i(z - L)^{-1}$ and its counterpart for evolution in the bath subspace $R_Q(z) = i(z - QL)^{-1}$. Expand the full counterpropagator

as

$$\begin{aligned}
R(z) &= \frac{i}{z-L} [i(QL - z)] \frac{i}{z-QL} \\
&= \frac{1}{L-z} (L - PL - z) R_Q(z) \\
&= \left(1 - \frac{1}{L-z} PL\right) R_Q(z) \\
&= R_Q(z) - i \frac{i}{z-L} PL R_Q(z) \\
&= R_Q(z) - i R(z) PL R_Q(z). \tag{B.11}
\end{aligned}$$

Then from the identity $R(z)(z-L) = i$ we get the equation of motion for the counter-propagator ($zR(z)$ is the Laplace transform of $\frac{d}{dt}e^{iLt}$)

$$\begin{aligned}
zR(z) &= i + R(z)L \\
&= i + R(z)PL + R(z)QL \\
&= i + R(z)PL + R_Q(z)QL - iR(z)PLR_Q(z)QL. \tag{B.12}
\end{aligned}$$

We now apply this operator to one of the dynamical variables, A_α , and use the definition of the projector P , Eq. (B.9), to obtain

$$\begin{aligned}
zR(z)A_\alpha &= iA_\alpha + R(z)PLA_\alpha + R_Q(z)QLA_\alpha - iR(z)PLR_Q(z)QLA_\alpha \\
&= iA_\alpha + \sum_{\beta} (A_\beta, LA_\alpha) R(z)A_\beta + R_Q(z)QLA_\alpha \\
&\quad - i \sum_{\beta} (A_\beta, LR_Q(z)QLA_\alpha) R(z)A_\beta. \tag{B.13}
\end{aligned}$$

It is convenient to define the frequency of oscillations in the subspace of wavevector \mathbf{q}

$$\Omega_{\beta,\alpha} = (A_\beta, LA_\alpha) \tag{B.14}$$

and the Laplace transform of the memory function

$$M_{\beta,\alpha}(z) = i (A_\beta, LR_Q(z)QLA_\alpha) = i (QLA_\beta, R_Q(z)QLA_\alpha). \tag{B.15}$$

In the last equation we used the self-adjoint property of the Liouvillian and Q together with the fact that $R_Q(z) = QR_Q(z)$, which can be seen by a power series expansion and idempotency. This expression makes clear that the memory function is the correlation

of the random force QLA_α with projected dynamics. The equation for the relaxation function $\Phi_{\gamma,\alpha}(z) = (A_\gamma, R(z)A_\alpha)$ is obtained by taking an internal product of an evolved dynamical variable with another at time zero. Recalling the suppressed label \mathbf{q} on the dynamical variables and that Q projects out of this space, the third term vanishes due to $(A_\gamma, R_Q(z)QLA_\alpha) = (QA_\gamma, R_Q(z)QLA_\alpha) = 0$, meaning that the random force is orthogonal to the dynamical variables. As a result, we obtain

$$z\Phi_{\gamma,\alpha}(z) = i\delta_{\gamma,\alpha} + \sum_{\beta} \Phi_{\gamma,\beta}(z)\Omega_{\beta,\alpha} - \sum_{\beta} \Phi_{\gamma,\beta}(z)M_{\beta,\alpha}(z). \quad (\text{B.16})$$

Reinstating the suppressed wavevector and reorganizing terms,

$$\sum_{\beta} \Phi_{\gamma,\beta}(\mathbf{q}, z) (z\delta_{\beta,\alpha} - \Omega_{\beta,\alpha}(\mathbf{q}) + M_{\beta,\alpha}(\mathbf{q}, z)) = i\delta_{\gamma,\alpha}. \quad (\text{B.17})$$

B.3 Series expansion for the memory function

Since the projected counterpropagator $R_{Q(\mathbf{q})}(z)$ required to evaluate the memory function as written in (B.15) is prohibitive for us to attempt to evaluate, here we derive an expansion which allows us to write the memory function solely in terms solely of the full counterpropagator $R(z)$. We will follow the approach described by Mazenko [16, Sec. 5.3.7] and invert the equation of motion for the relaxation function, Eq. (B.17). For brevity we will continue to suppress the wavevector argument \mathbf{q} until the final result. We begin by noticing that, because $zR(z) = i + LR(z) = i + R(z)L$,

$$z\Phi_{\gamma,\alpha}(z) = i\delta_{\gamma,\alpha} + (A_\gamma, LR(z)A_\alpha) = i\delta_{\gamma,\alpha} + (A_\gamma, R(z)LA_\alpha). \quad (\text{B.18})$$

Inserting this into the equation of motion, Eq. (B.16), we get

$$(A_\gamma, LR(z)A_\alpha) = \sum_{\beta} \Phi_{\gamma,\beta}(z) [\Omega_{\beta,\alpha} - M_{\beta,\alpha}(z)], \quad (\text{B.19})$$

and multiplying by z we obtain

$$z(A_\gamma, LR(z)A_\alpha) = \sum_{\beta} z\Phi_{\gamma,\beta}(z) [\Omega_{\beta,\alpha} - M_{\beta,\alpha}(z)]. \quad (\text{B.20})$$

Here, once again we use $zR(z) = i + R(z)L$ to obtain

$$\begin{aligned} i\Omega_{\gamma,\alpha} + (LA_\gamma, R(z)LA_\alpha) &= i\Omega_{\gamma,\alpha} - iM_{\gamma,\alpha}(z) + \sum_{\beta} (LA_\gamma, R(z)A_\beta) [\Omega_{\beta,\alpha} - M_{\beta,\alpha}(z)] \\ \Rightarrow M_{\gamma,\alpha}(z) &= i(LA_\gamma, R(z)LA_\alpha) - i \sum_{\beta} (LA_\gamma, R(z)A_\beta) [\Omega_{\beta,\alpha} - M_{\beta,\alpha}(z)] , \end{aligned} \quad (\text{B.21})$$

and eliminate the last square bracket by inverting Eq. (B.19) as a matrix equation for the relaxation functions, $(A, LR(z)A) = \underline{\Phi}(z) [\underline{\Omega} - \underline{M}] \Rightarrow [\underline{\Omega} - \underline{M}] = \underline{\Phi}^{-1}(z)(A, LR(z)A)$, yielding

$$M_{\gamma,\alpha}(z) = i(LA_\gamma, R(z)LA_\alpha) - i \sum_{\beta,\eta} (LA_\gamma, R(z)A_\beta) \Phi_{\beta,\eta}^{-1}(z) (A_\eta, R(z)LA_\alpha) . \quad (\text{B.22})$$

Reinstating the suppressed wavevector \mathbf{q} , we can take this one step further by expanding $L = P(\mathbf{q})L + Q(\mathbf{q})L$ in the above equation. Using \mathbf{u}, \mathbf{v} as collective indices representing the tuple of bands and wavevector on the electron-hole excitation operators $\xi_{m,n,\mathbf{k}}(\mathbf{q})$ and corresponding excitation energies $\varepsilon_{m,n,\mathbf{k}}(\mathbf{q})$,

$$LA_\alpha(\mathbf{q}) = P(\mathbf{q})LA_\alpha(\mathbf{q}) + Q(\mathbf{q})LA_\alpha(\mathbf{q}) , \quad (\text{B.23a})$$

$$\begin{aligned} P(\mathbf{q})LA_\alpha(\mathbf{q}) &= P(\mathbf{q})L_0A_\alpha(\mathbf{q}) = \sum_{\beta} A_\beta(\mathbf{q}) (A_\beta(\mathbf{q}), L_0A_\alpha(\mathbf{q})) \\ &= \sum_{\beta} \left(\sum_{\mathbf{v}} a_{\mathbf{v}}^{(\beta)}(\mathbf{q}) \xi_{\mathbf{v}}(\mathbf{q}), \sum_{\mathbf{u}} \varepsilon_{\mathbf{u}}(\mathbf{q}) a_{\mathbf{u}}^{(\alpha)}(\mathbf{q}) \xi_{\mathbf{u}}(\mathbf{q}) \right) A_\beta(\mathbf{q}) \\ &= \sum_{\beta} \varepsilon_{\alpha,\beta}(\mathbf{q}) A_\beta(\mathbf{q}) , \end{aligned} \quad (\text{B.23b})$$

$$Q(\mathbf{q})LA_\alpha(\mathbf{q}) = L_i A_\alpha(\mathbf{q}) , \quad (\text{B.23c})$$

where we used the projector first to isolate L_0 from L when acting on $A_\alpha(\mathbf{q})$ and subsequently used its definition, Eq. (B.9), to expand $L_0A_\alpha(\mathbf{q})$ in the orthonormal basis, and we defined

$$\varepsilon_{\alpha,\beta}(\mathbf{q}) = \sum_{\mathbf{u},\mathbf{v}} \varepsilon_{\mathbf{u}}(\mathbf{q}) \left(a_{\mathbf{v}}^{(\beta)}(\mathbf{q}) \right)^* a_{\mathbf{u}}^{(\alpha)}(\mathbf{q}) (\xi_{\mathbf{v}}(\mathbf{q}), \xi_{\mathbf{u}}(\mathbf{q})) , \quad (\text{B.24})$$

which satisfies $(\varepsilon_{\alpha,\beta}(\mathbf{q}))^* = \varepsilon_{\beta,\alpha}(\mathbf{q})$ so that its matrix form is Hermitian. Once again suppressing the wavevector, we can abbreviate this result in matrix form as $\underline{LzA} = \underline{\varepsilon A} + \underline{L_i A}$. Here \underline{A} is understood as a vector while the others are matrices.

Writing Eq. (B.22) in the same way,

$$\underline{M}(z) = i \underbrace{(LA, R(z)LA)}_{(1)} - i \underbrace{(LA, R(z)A)\underline{\Phi}^{-1}(z)(A, R(z)LA)}_{(2)}, \quad (\text{B.25})$$

we notice that upon expanding using $\underline{LA} = \underline{\varepsilon}A + \underline{L}_iA$, because $\underline{\varepsilon}$ in $\underline{\varepsilon}A$ is a matrix of scalars not operators and can hence be factored out of the operator inner product, (2) in Eq. (B.22) splits into terms with factors which simplify, such as

$$(\underline{\varepsilon}A, R(z)A)\underline{\Phi}^{-1}(z) = \underline{\varepsilon}\underline{\Phi}(z)\underline{\Phi}^{-1}(z) = \underline{\varepsilon}, \quad (\text{B.26a})$$

$$\underline{\Phi}^{-1}(z)(A, R(z)A\underline{\varepsilon}) = \underline{\Phi}^{-1}(z)\underline{\Phi}(z)\underline{\varepsilon} = \underline{\varepsilon}. \quad (\text{B.26b})$$

This leads to cancellations between every term which contains $\underline{\varepsilon}A$ in the expansion of (1) and (2) of Eq. (B.22), so that only remaining terms give

$$\underline{M}(z) = i \underline{(L_iA, R(z)L_iA)} - i \underline{(L_iA, R(z)A)\underline{\Phi}^{-1}(z)(A, R(z)L_iA)}, \quad (\text{B.27})$$

or in terms of the matrix elements and with the wavevector reinstated,

$$\begin{aligned} M_{\gamma,\alpha}(\mathbf{q}, z) &= i (L_iA_\gamma(\mathbf{q}), R(z)L_iA_\alpha(\mathbf{q})) \\ &\quad - i \sum_{\beta,\eta} (L_iA_\gamma(\mathbf{q}), R(z)A_\beta(\mathbf{q})) \Phi_{\beta,\eta}^{-1}(\mathbf{q}, z) (A_\eta(\mathbf{q}), R(z)L_iA_\alpha(\mathbf{q})). \end{aligned} \quad (\text{B.28})$$

Appendix C |

Correlation functions

C.1 Density response function

C.1.1 General case

Using the time evolution in the pristine periodic system,

$$\begin{aligned}
 e^{iH_0t} \hat{\rho}(\mathbf{q}) e^{-iH_0t} &= \sum_{n',n,\mathbf{k}} M_{n',n,\mathbf{k}}(\mathbf{q}) e^{iH_0t} c_{n',\mathbf{k}-\mathbf{q}}^\dagger c_{n,\mathbf{k}} e^{-iH_0t} \\
 &= \sum_{n',n,\mathbf{k}} M_{n',n,\mathbf{k}}(\mathbf{q}) e^{i(\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}})t} c_{n',\mathbf{k}-\mathbf{q}}^\dagger c_{n,\mathbf{k}} , \tag{C.1}
 \end{aligned}$$

we find that the time-dependent density response function of the pristine system is

$$\begin{aligned}
 \chi^{(0)}(\mathbf{q}, t) &= \frac{i}{V} \left\langle \left[\hat{\rho}^\dagger(\mathbf{q}, t), \hat{\rho}(\mathbf{q}) \right] \right\rangle_0 \\
 &= \frac{i}{V} \sum_{\substack{n,n',\mathbf{k} \\ m,m',\mathbf{l}}} e^{i(\varepsilon_{n,\mathbf{k}} - \varepsilon_{n',\mathbf{k}-\mathbf{q}})t} (M_{n',n,\mathbf{k}}(\mathbf{q}))^* M_{m',m,\mathbf{l}}(\mathbf{q}) \left\langle \left[c_{n,\mathbf{k}}^\dagger c_{n',\mathbf{k}-\mathbf{q}}, c_{m',\mathbf{l}-\mathbf{q}}^\dagger c_{m,\mathbf{l}} \right] \right\rangle_0 \\
 &= \frac{i}{V} \sum_{n,n',\mathbf{k}} e^{i(\varepsilon_{n,\mathbf{k}} - \varepsilon_{n',\mathbf{k}-\mathbf{q}})t} |M_{n',n,\mathbf{k}}(\mathbf{q})|^2 (f(\varepsilon_{n,\mathbf{k}}) - f(\varepsilon_{n',\mathbf{k}-\mathbf{q}})) , \tag{C.2}
 \end{aligned}$$

where we evaluated the thermal average as

$$\begin{aligned}
 &\left\langle \left[c_{n,\mathbf{k}}^\dagger c_{n',\mathbf{k}-\mathbf{q}}, c_{m',\mathbf{l}-\mathbf{q}}^\dagger c_{m,\mathbf{l}} \right] \right\rangle_0 \\
 &= \left\langle c_{n,\mathbf{k}}^\dagger c_{n',\mathbf{k}-\mathbf{q}} c_{m',\mathbf{l}-\mathbf{q}}^\dagger c_{m,\mathbf{l}} \right\rangle_0 - \left\langle c_{m',\mathbf{l}-\mathbf{q}}^\dagger c_{m,\mathbf{l}} c_{n,\mathbf{k}}^\dagger c_{n',\mathbf{k}-\mathbf{q}} \right\rangle_0 \\
 &= \delta_{n,m} \delta_{n',m'} \delta_{\mathbf{k},\mathbf{l}} [f(\varepsilon_{n,\mathbf{k}}) (1 - f(\varepsilon_{n',\mathbf{k}-\mathbf{q}})) - f(\varepsilon_{n',\mathbf{k}-\mathbf{q}}) (1 - f(\varepsilon_{n,\mathbf{k}}))] \\
 &= \delta_{n,m} \delta_{n',m'} \delta_{\mathbf{k},\mathbf{l}} (f(\varepsilon_{n,\mathbf{k}}) - f(\varepsilon_{n',\mathbf{k}-\mathbf{q}})) . \tag{C.3}
 \end{aligned}$$

Taking the Laplace transform, we find

$$X^{(0)}(\mathbf{q}, z) = \frac{1}{V} \sum_{n, n', \mathbf{k}} \frac{f(\varepsilon_{n', \mathbf{k}-\mathbf{q}}) - f(\varepsilon_{n, \mathbf{k}})}{z + \varepsilon_{n, \mathbf{k}} - \varepsilon_{n', \mathbf{k}-\mathbf{q}}} |M_{n', n, \mathbf{k}}(\mathbf{q})|^2. \quad (\text{C.4})$$

It is mathematically clear that the factor $1/V = 1/N\Omega$ normalizes this sum to be intensive since there are N \mathbf{k} -points in the sum. To justify this definition, consider that $\chi^{(0)}(\mathbf{q}, t) = \langle [\hat{\rho}^\dagger(\mathbf{q}, t)/V, \hat{\rho}(\mathbf{q})] \rangle_0$ measures the response of the thermal average $\langle \hat{\rho}(\mathbf{q})/V \rangle$ to an external electric potential that couples to the system through the operator $\hat{\rho}(\mathbf{q})$. We are interested in measuring the response of the system per unit volume. Referring to the definition in Eq. (2.8) and dividing,

$$\frac{1}{V} \hat{\rho}(\mathbf{q}) = \frac{1}{V} \int_V d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} \hat{\rho}(\mathbf{r}), \quad (\text{C.5})$$

is the correct choice for the response per unit volume. For example, in the $\mathbf{q} \rightarrow 0$ limit, $\hat{\rho}(\mathbf{q} = 0)/V$ is the number density of electrons in the system.

C.1.2 Density response at imaginary frequencies in a time-reversal-symmetric system

The density response function of a time-reversal-symmetric system is purely real when evaluated at purely imaginary frequencies. To prove this, we show that the imaginary part of the response function vanishes in this case. The imaginary part in question is

$$\begin{aligned} \text{Im } X^{(0)}(\mathbf{q}, iM'') &= -\frac{M''}{V} \sum_{n', n, \mathbf{k}} \frac{f(\varepsilon_{n', \mathbf{k}-\mathbf{q}}) - f(\varepsilon_{n, \mathbf{k}})}{(M'')^2 + (\varepsilon_{n', \mathbf{k}-\mathbf{q}} - \varepsilon_{n, \mathbf{k}})^2} |M_{n', n, \mathbf{k}}(\mathbf{q})|^2 \\ &= -\frac{M''}{V} \left(\sum_{n', n, \mathbf{k}} \frac{f(\varepsilon_{n', \mathbf{k}-\mathbf{q}})}{(M'')^2 + (\varepsilon_{n', \mathbf{k}-\mathbf{q}} - \varepsilon_{n, \mathbf{k}})^2} |M_{n', n, \mathbf{k}}(\mathbf{q})|^2 \right. \\ &\quad \left. - \frac{f(\varepsilon_{n, \mathbf{k}})}{(M'')^2 + (\varepsilon_{n', \mathbf{k}-\mathbf{q}} - \varepsilon_{n, \mathbf{k}})^2} |M_{n', n, \mathbf{k}}(\mathbf{q})|^2 \right) \\ &= -\frac{M''}{V} \left(\sum_{n', n, \mathbf{k}} \frac{f(\varepsilon_{n, -\mathbf{k}})}{(M'')^2 + (\varepsilon_{n, -\mathbf{k}} - \varepsilon_{n', -\mathbf{k}+\mathbf{q}})^2} |M_{n, n', -\mathbf{k}+\mathbf{q}}(\mathbf{q})|^2 \right. \\ &\quad \left. - \sum_{n', n, \mathbf{k}} \frac{f(\varepsilon_{n, \mathbf{k}})}{(M'')^2 + (\varepsilon_{n', \mathbf{k}-\mathbf{q}} - \varepsilon_{n, \mathbf{k}})^2} |M_{n', n, \mathbf{k}}(\mathbf{q})|^2 \right). \quad (\text{C.6}) \end{aligned}$$

In the last line we reindexed the first term by $\mathbf{k} \rightarrow -\mathbf{k} + \mathbf{q}$, $n' \leftrightarrow n$. In a time-reversal-symmetric system, $\varepsilon_{n,-\mathbf{k}} = \varepsilon_{n,\mathbf{k}}$ and $u_{n,-\mathbf{k}}(\mathbf{s}) = u_{n,\mathbf{k}}(\mathbf{s})$. Using this and the definition of the matrix elements,

$$M_{n',n,\mathbf{k}}(\mathbf{q}) = \langle u_{n',\mathbf{k}-\mathbf{q}} | u_{n,\mathbf{k}} \rangle = \int_{\Omega} d\mathbf{s} u_{n',\mathbf{k}-\mathbf{q}}^*(\mathbf{s}) u_{n,\mathbf{k}}(\mathbf{s}), \quad (\text{C.7})$$

we have

$$\begin{aligned} M_{n,n',-\mathbf{k}+\mathbf{q}}(\mathbf{q}) &= \langle u_{n,-\mathbf{k}} | u_{n',-\mathbf{k}+\mathbf{q}} \rangle = \langle u_{n',-\mathbf{k}+\mathbf{q}} | u_{n,-\mathbf{k}} \rangle^* \\ &= \langle u_{n',\mathbf{k}-\mathbf{q}} | u_{n,\mathbf{k}} \rangle^* = (M_{n',n,\mathbf{k}}(\mathbf{q}))^*. \end{aligned} \quad (\text{C.8})$$

Using these relations on the energies and matrix elements, the two terms are identical and cancel, so that only the real part of $X^{(0)}(\mathbf{q}, iM'')$ is nonzero. It is given by

$$X^{(0)}(\mathbf{q}, iM'') = \frac{1}{V} \sum_{n',n,\mathbf{k}} \frac{(f(\varepsilon_{n,\mathbf{k}}) - f(\varepsilon_{n',\mathbf{k}-\mathbf{q}})) (\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}})}{(M'')^2 + (\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}})^2} |M_{n',n,\mathbf{k}}(\mathbf{q})|^2. \quad (\text{C.9})$$

Note that the numerator is positive because $f(\varepsilon_{n,\mathbf{k}}) - f(\varepsilon_{n',\mathbf{k}-\mathbf{q}})$ and $\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}}$ always have opposite signs, and the denominator and matrix element are clearly positive, so that $X^{(0)}(\mathbf{q}, iM'') > 0$.

This function obeys a limit related to the f -sum rule,

$$\begin{aligned} \lim_{M'' \rightarrow \infty} (M'')^2 X^{(0)}(\mathbf{q}, iM'') &= \\ &= \frac{1}{V} \sum_{n',n,\mathbf{k}} (f(\varepsilon_{n,\mathbf{k}}) - f(\varepsilon_{n',\mathbf{k}-\mathbf{q}})) (\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}}) |M_{n',n,\mathbf{k}}(\mathbf{q})|^2 \\ &= \frac{1}{V} \sum_{n,n',\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \langle u_{n,\mathbf{k}} | (\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}}) | u_{n',\mathbf{k}-\mathbf{q}} \rangle \langle u_{n',\mathbf{k}-\mathbf{q}} | u_{n,\mathbf{k}} \rangle \\ &\quad - \frac{1}{V} \sum_{n,n',\mathbf{k}} f(\varepsilon_{n',\mathbf{k}-\mathbf{q}}) \langle u_{n',\mathbf{k}-\mathbf{q}} | (\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}}) | u_{n,\mathbf{k}} \rangle \langle u_{n,\mathbf{k}} | u_{n',\mathbf{k}-\mathbf{q}} \rangle \\ &= \frac{1}{V} \sum_{n,\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \langle u_{n,\mathbf{k}} | (H_{\mathbf{k}-\mathbf{q}} - H_{\mathbf{k}}) | u_{n,\mathbf{k}} \rangle \\ &\quad - \frac{1}{V} \sum_{n',\mathbf{k}} f(\varepsilon_{n',\mathbf{k}-\mathbf{q}}) \langle u_{n',\mathbf{k}-\mathbf{q}} | (H_{\mathbf{k}-\mathbf{q}} - H_{\mathbf{k}}) | u_{n',\mathbf{k}-\mathbf{q}} \rangle \\ &= \frac{1}{V} \sum_{n,\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \langle u_{n,\mathbf{k}} | (H_{\mathbf{k}+\mathbf{q}} + H_{\mathbf{k}-\mathbf{q}} - 2H_{\mathbf{k}}) | u_{n,\mathbf{k}} \rangle \\ &= \frac{1}{V} \sum_{n,\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \langle u_{n,\mathbf{k}} | \frac{q^2}{m} | u_{n,\mathbf{k}} \rangle = \frac{n_e q^2}{m}, \end{aligned} \quad (\text{C.10})$$

where we used the completeness relation $\sum_n |u_{n,\mathbf{k}}\rangle\langle u_{n,\mathbf{k}}| = 1$ and the form and eigenvalue equation of the Bloch Hamiltonian,

$$H_{\mathbf{k}} = \frac{(\mathbf{p} + \mathbf{k})^2}{2m} + V(\mathbf{r}), \quad H_{\mathbf{k}}|u_{n,\mathbf{k}}\rangle = \varepsilon_{n,\mathbf{k}}|u_{n,\mathbf{k}}\rangle. \quad (\text{C.11})$$

The completeness relation requires a full set of bands, so that in numerical implementations, one should use a sufficiently large basis set, checking that the sum in the first line reproduces the result of the last line.

C.1.2.1 Large- M'' expansion

In the limit of large M'' , Eq. (C.9) can be expanded as

$$\begin{aligned} X^{(0)}(\mathbf{q}, iM'') &= \\ &= \frac{1}{V} \sum_{n',n,\mathbf{k}} \frac{(f(\varepsilon_{n,\mathbf{k}}) - f(\varepsilon_{n',\mathbf{k}-\mathbf{q}})) (\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}})}{(M'')^2 + (\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}})^2} |M_{n',n,\mathbf{k}}(\mathbf{q})|^2 \\ &= \frac{1}{V} \sum_{n',n,\mathbf{k}} (f(\varepsilon_{n,\mathbf{k}}) - f(\varepsilon_{n',\mathbf{k}-\mathbf{q}})) (\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}}) |M_{n',n,\mathbf{k}}(\mathbf{q})|^2 \frac{1}{(M'')^2} \sum_{j=0}^{\infty} \left(-\frac{(\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}})^2}{(M'')^2} \right)^j \\ &= \sum_{j=0}^{\infty} \frac{(-1)^j}{(M'')^{2j+2}} \left(\frac{1}{V} \sum_{n',n,\mathbf{k}} (f(\varepsilon_{n,\mathbf{k}}) - f(\varepsilon_{n',\mathbf{k}-\mathbf{q}})) (\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}})^{2j+1} |M_{n',n,\mathbf{k}}(\mathbf{q})|^2 \right) \\ &= \sum_{j=0}^{\infty} \frac{(-1)^j}{(M'')^{2j+2}} K_{2j+1}^{(0)}(\mathbf{q}), \end{aligned} \quad (\text{C.12})$$

where

$$K_j^{(0)}(\mathbf{q}) = \frac{1}{V} \sum_{n',n,\mathbf{k}} (f(\varepsilon_{n,\mathbf{k}}) - f(\varepsilon_{n',\mathbf{k}-\mathbf{q}})) (\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}})^j |M_{n',n,\mathbf{k}}(\mathbf{q})|^2. \quad (\text{C.13})$$

Note that $K_1^{(0)}(\mathbf{q}) = n_e q^2/m$ as is given by Eq. (C.10). This expansion is valid when M'' exceeds the maximum energy separation of the bands in the system. In the case of a complete set of bands, in which the maximum energy separation is infinite, this expansion is still legitimate provided we regard Eq. (C.12) as a limit of a function with finite M'' and a sum over a finite set of N bands, and we take first the limit $M'' \rightarrow \infty$ and then the limit $N \rightarrow \infty$.

We can then use the expansion of $X^{(0)}(\mathbf{q}, iM'')$ to expand the relaxation function,

$$\begin{aligned}
\frac{\Phi(\mathbf{q}, 0)}{M''} &= \frac{X^{(0)}(\mathbf{q}, 0)}{(M'')^2} \left(\frac{X^{(0)}(\mathbf{q}, 0)}{X^{(0)}(\mathbf{q}, iM'')} - 1 \right) \\
&= \frac{(X^{(0)}(\mathbf{q}, 0))^2}{K_1^{(0)}(\mathbf{q}) - \frac{1}{(M'')^2} K_3^{(0)}(\mathbf{q}) + O((M'')^{-4})} - \frac{1}{(M'')^2} X^{(0)}(\mathbf{q}, 0) \\
&= \frac{(X^{(0)}(\mathbf{q}, 0))^2}{K_1^{(0)}(\mathbf{q})} \left(1 + \frac{1}{(M'')^2} \frac{K_3^{(0)}(\mathbf{q})}{K_1^{(0)}(\mathbf{q})} + O((M'')^{-4}) \right) - \frac{1}{(M'')^2} X^{(0)}(\mathbf{q}, 0) \\
&= \frac{(X^{(0)}(\mathbf{q}, 0))^2}{K_1^{(0)}(\mathbf{q})} + \frac{1}{(M'')^2} \left(\frac{(X^{(0)}(\mathbf{q}, 0))^2 K_3^{(0)}(\mathbf{q})}{(K_1^{(0)}(\mathbf{q}))^2} - X^{(0)}(\mathbf{q}, 0) \right) + O((M'')^{-4}).
\end{aligned} \tag{C.14}$$

Inserting this into Eq. (4.15) leads to the definition of the order- $(M'')^{-2}$ term,

$$A(\mathbf{q}) = \frac{1}{n_e m} \frac{1}{V^2} \sum_{\mathbf{q}} (\hat{\mathbf{n}} \cdot \mathbf{q})^2 |F(\mathbf{q})|^2 \left(\frac{(X^{(0)}(\mathbf{q}, 0))^2 K_3^{(0)}(\mathbf{q})}{(K_1^{(0)}(\mathbf{q}))^2} - X^{(0)}(\mathbf{q}, 0) \right). \tag{C.15}$$

To see that $A(\mathbf{q})$ is positive, it suffices to show that $(K_{-1}^{(0)}(\mathbf{q})) (K_3^{(0)}(\mathbf{q})) > (K_1^{(0)}(\mathbf{q}))^2$, noting from Eq. (C.13) that we can write $X^{(0)}(\mathbf{q}, 0) = K_{-1}^{(0)}(\mathbf{q})$.

To prove this, we will reframe $K_j^{(0)}(\mathbf{q})$ in terms of a vector inner product and use the Cauchy-Schwarz inequality. The elements of the vectors $\boldsymbol{\varepsilon}_j(\mathbf{q})$ and the weight \mathbf{w} are indexed by n', n, \mathbf{k} ,

$$\begin{aligned}
\varepsilon_{n', n, \mathbf{k}; j}(\mathbf{q}) &= (\varepsilon_{n', \mathbf{k}-\mathbf{q}} - \varepsilon_{n, \mathbf{k}})^j, \\
w_{n', n, \mathbf{k}} &= \frac{1}{V} (f(\varepsilon_{n, \mathbf{k}}) - f(\varepsilon_{n', \mathbf{k}-\mathbf{q}})) (\varepsilon_{n', \mathbf{k}-\mathbf{q}} - \varepsilon_{n, \mathbf{k}}) |M_{n', n, \mathbf{k}}(\mathbf{q})|^2.
\end{aligned} \tag{C.16}$$

With this definition, $(\boldsymbol{\varepsilon}_j(\mathbf{q}), \boldsymbol{\varepsilon}_{j'}(\mathbf{q})) = K_{j+j'+1}^{(0)}(\mathbf{q})$. The Cauchy-Schwarz inequality gives

$$(\boldsymbol{\varepsilon}_j(\mathbf{q}), \boldsymbol{\varepsilon}_j(\mathbf{q})) (\boldsymbol{\varepsilon}_{j'}(\mathbf{q}), \boldsymbol{\varepsilon}_{j'}(\mathbf{q})) \geq (\boldsymbol{\varepsilon}_j(\mathbf{q}), \boldsymbol{\varepsilon}_{j'}(\mathbf{q}))^2. \tag{C.17}$$

Taking $j = -1$, $j' = 1$ and noting that the inequality is strict because the vectors are linearly independent, we have $(K_{-1}^{(0)}(\mathbf{q})) (K_3^{(0)}(\mathbf{q})) > (K_1^{(0)}(\mathbf{q}))^2$ as we set out to show.

C.2 Conductivity

The conductivity of the pristine periodic system in the time domain is

$$\begin{aligned}
\sigma^{(0)}(\mathbf{q}, t) &= \frac{1}{V} \int_0^\beta d\lambda \langle e^{\lambda H_0} \hat{\mathbf{j}}^\dagger(\mathbf{q}, t) e^{-\lambda H_0} \hat{\mathbf{j}}(\mathbf{q}) \rangle_0 \\
&= \frac{1}{V} \sum_{\substack{n, n', \mathbf{k} \\ m, m', \mathbf{l}}} (\mathbf{J}_{n', n, \mathbf{k}}(\mathbf{q}))^* \mathbf{J}_{m', m, \mathbf{l}}(\mathbf{q}) e^{i(\varepsilon_{n, \mathbf{k}} - \varepsilon_{n', \mathbf{k}-\mathbf{q}})t} \\
&\quad \times \left(\int_0^\beta d\lambda e^{\lambda(\varepsilon_{n, \mathbf{k}} - \varepsilon_{n', \mathbf{k}-\mathbf{q}})} \right) \langle c_{n, \mathbf{k}}^\dagger c_{n', \mathbf{k}-\mathbf{q}} c_{m', \mathbf{l}-\mathbf{q}}^\dagger c_{m, \mathbf{l}} \rangle_0, \tag{C.18}
\end{aligned}$$

where we used

$$\begin{aligned}
e^{\lambda H_0} \hat{\mathbf{j}}^\dagger(\mathbf{q}, t) e^{-\lambda H_0} &= e^{\lambda H_0} \left(\sum_{n, n', \mathbf{k}} \mathbf{J}_{n', n, \mathbf{k}}(\mathbf{q}) e^{i(\varepsilon_{n', \mathbf{k}-\mathbf{q}} - \varepsilon_{n, \mathbf{k}})t} c_{n', \mathbf{k}-\mathbf{q}}^\dagger c_{n, \mathbf{k}} \right)^\dagger e^{-\lambda H_0} \\
&= \sum_{n, n', \mathbf{k}} (\mathbf{J}_{n', n, \mathbf{k}}(\mathbf{q}))^* e^{\lambda(\varepsilon_{n, \mathbf{k}} - \varepsilon_{n', \mathbf{k}-\mathbf{q}})} e^{i(\varepsilon_{n, \mathbf{k}} - \varepsilon_{n', \mathbf{k}-\mathbf{q}})t} c_{n, \mathbf{k}}^\dagger c_{n', \mathbf{k}-\mathbf{q}}. \tag{C.19}
\end{aligned}$$

The thermal average is

$$\begin{aligned}
\langle c_{n, \mathbf{k}}^\dagger c_{n', \mathbf{k}-\mathbf{q}} c_{m', \mathbf{l}-\mathbf{q}}^\dagger c_{m, \mathbf{l}} \rangle_0 &= \delta_{n, m} \delta_{n' m'} \delta_{\mathbf{k}, \mathbf{l}} \langle c_{n, \mathbf{k}}^\dagger c_{n', \mathbf{k}-\mathbf{q}} c_{n', \mathbf{k}-\mathbf{q}}^\dagger c_{n, \mathbf{k}} \rangle_0 \\
&= \delta_{n, m} \delta_{n' m'} \delta_{\mathbf{k}, \mathbf{l}} f(\varepsilon_{n, \mathbf{k}}) (1 - f(\varepsilon_{n', \mathbf{k}-\mathbf{q}})). \tag{C.20}
\end{aligned}$$

Now

$$\begin{aligned}
&\left(e^{\beta(\varepsilon_{n, \mathbf{k}} - \varepsilon_{n', \mathbf{k}-\mathbf{q}})} - 1 \right) f(\varepsilon_{n, \mathbf{k}}) (1 - f(\varepsilon_{n', \mathbf{k}-\mathbf{q}})) \\
&= e^{-\beta \varepsilon_{n', \mathbf{k}-\mathbf{q}}} \left(e^{\beta \varepsilon_{n, \mathbf{k}}} - e^{\beta \varepsilon_{n', \mathbf{k}-\mathbf{q}}} \right) \frac{1}{1 + e^{\beta \varepsilon_{n, \mathbf{k}}}} \left(1 - \frac{1}{1 + e^{\beta \varepsilon_{n', \mathbf{k}-\mathbf{q}}}} \right) \\
&= \frac{\left(e^{\beta \varepsilon_{n, \mathbf{k}}} - 1 \right) - \left(e^{\beta \varepsilon_{n', \mathbf{k}-\mathbf{q}}} - 1 \right)}{\left(1 + e^{\beta \varepsilon_{n, \mathbf{k}}} \right) \left(1 + e^{\beta \varepsilon_{n', \mathbf{k}-\mathbf{q}}} \right)} = f(\varepsilon_{n', \mathbf{k}-\mathbf{q}}) - f(\varepsilon_{n, \mathbf{k}}), \tag{C.21}
\end{aligned}$$

so that the conductivity is

$$\sigma^{(0)}(\mathbf{q}, t) = \frac{1}{V} \sum_{n, n', \mathbf{k}} |\mathbf{J}_{n', n, \mathbf{k}}(\mathbf{q})|^2 e^{i(\varepsilon_{n, \mathbf{k}} - \varepsilon_{n', \mathbf{k}-\mathbf{q}})t} \frac{f(\varepsilon_{n', \mathbf{k}-\mathbf{q}}) - f(\varepsilon_{n, \mathbf{k}})}{\varepsilon_{n, \mathbf{k}} - \varepsilon_{n', \mathbf{k}-\mathbf{q}}}, \tag{C.22}$$

so that its Laplace transform is

$$\boldsymbol{\sigma}^{(0)}(\mathbf{q}, z) = \frac{i}{V} \sum_{n, n', \mathbf{k}} \frac{f(\varepsilon_{n', \mathbf{k}-\mathbf{q}}) - f(\varepsilon_{n, \mathbf{k}})}{\varepsilon_{n, \mathbf{k}} - \varepsilon_{n', \mathbf{k}-\mathbf{q}}} \frac{|\mathbf{J}_{n', n, \mathbf{k}}(\mathbf{q})|^2}{z + \varepsilon_{n, \mathbf{k}} - \varepsilon_{n', \mathbf{k}-\mathbf{q}}} . \quad (\text{C.23})$$

Now we focus on the uniform limit, $\mathbf{q} \rightarrow 0$, and specify tensor and vector components for clarity. The uniform current matrix element is the momentum matrix element given in Eq. (A.11),

$$J_{n', n, \mathbf{k}; \alpha}(0) = \langle n', \mathbf{k} | \hat{p}_\alpha / m | n, \mathbf{k} \rangle = \partial_{k_\alpha} \varepsilon_{n, \mathbf{k}} + i(\varepsilon_{n', \mathbf{k}} - \varepsilon_{n, \mathbf{k}}) X_{n', n, \mathbf{k}; \alpha} . \quad (\text{C.24})$$

Hence the uniform conductivity is

$$\begin{aligned} \sigma_{\alpha, \beta}^{(0)}(z) &= \frac{i}{V} \sum_{n, n', \mathbf{k}} \frac{1}{z + \varepsilon_{n, \mathbf{k}} - \varepsilon_{n', \mathbf{k}}} \frac{f(\varepsilon_{n', \mathbf{k}}) - f(\varepsilon_{n, \mathbf{k}})}{\varepsilon_{n, \mathbf{k}} - \varepsilon_{n', \mathbf{k}}} \\ &\quad \times \left(\delta_{n, n'} (\partial_{k_\alpha} \varepsilon_{n, \mathbf{k}}) (\partial_{k_\beta} \varepsilon_{n, \mathbf{k}}) + (\varepsilon_{n', \mathbf{k}} - \varepsilon_{n, \mathbf{k}})^2 X_{n', n, \mathbf{k}; \alpha}^* X_{n', n, \mathbf{k}; \beta} \right) \\ &= \frac{i}{zV} \sum_{n, \mathbf{k}} (-\partial_\varepsilon f(\varepsilon)) \Big|_{\varepsilon_{n, \mathbf{k}}} (\partial_{k_\alpha} \varepsilon_{n, \mathbf{k}}) (\partial_{k_\beta} \varepsilon_{n, \mathbf{k}}) \\ &\quad + \frac{i}{V} \sum_{n, n', \mathbf{k}} (f(\varepsilon_{n', \mathbf{k}}) - f(\varepsilon_{n, \mathbf{k}})) \frac{\varepsilon_{n', \mathbf{k}} - \varepsilon_{n, \mathbf{k}}}{z + \varepsilon_{n, \mathbf{k}} - \varepsilon_{n', \mathbf{k}}} X_{n', n, \mathbf{k}; \alpha}^* X_{n', n, \mathbf{k}; \beta} \\ &= \frac{i}{zV} \sum_{n, \mathbf{k}} f(\varepsilon_{n, \mathbf{k}}) \partial_{k_\alpha} \partial_{k_\beta} \varepsilon_{n, \mathbf{k}} + i \sum_{n, n', \mathbf{k}} (f(\varepsilon_{n', \mathbf{k}}) - f(\varepsilon_{n, \mathbf{k}})) X_{n', n, \mathbf{k}; \alpha}^* X_{n', n, \mathbf{k}; \beta} \\ &\quad - \frac{iz}{V} \sum_{n, n', \mathbf{k}} \frac{f(\varepsilon_{n', \mathbf{k}}) - f(\varepsilon_{n, \mathbf{k}})}{z + \varepsilon_{n, \mathbf{k}} - \varepsilon_{n', \mathbf{k}}} X_{n', n, \mathbf{k}; \alpha}^* X_{n', n, \mathbf{k}; \beta} , \end{aligned} \quad (\text{C.25})$$

where we rewrote the intraband term using

$$\begin{aligned} &\sum_{n, \mathbf{k}} (-\partial_\varepsilon f(\varepsilon)) \Big|_{\varepsilon_{n, \mathbf{k}}} (\partial_{k_\alpha} \varepsilon_{n, \mathbf{k}}) (\partial_{k_\beta} \varepsilon_{n, \mathbf{k}}) \\ &= \sum_{n, \mathbf{k}} \partial_{k_\alpha} \left(-f(\varepsilon_{n, \mathbf{k}}) (\partial_{k_\beta} \varepsilon_{n, \mathbf{k}}) \right) + \sum_{n, \mathbf{k}} f(\varepsilon_{n, \mathbf{k}}) \partial_{k_\alpha} \partial_{k_\beta} \varepsilon_{n, \mathbf{k}} \\ &= \sum_{n, \mathbf{k}} f(\varepsilon_{n, \mathbf{k}}) \partial_{k_\alpha} \partial_{k_\beta} \varepsilon_{n, \mathbf{k}} , \end{aligned} \quad (\text{C.26})$$

in which the sum of the total derivative telescopes and vanishes, and in which we divided the interband term with $\frac{\Delta\varepsilon}{z + \Delta\varepsilon} = \frac{z + \Delta\varepsilon - z}{z + \Delta\varepsilon} = 1 - \frac{z}{z + \Delta\varepsilon}$.

We can rewrite the middle term as follows,

$$\begin{aligned}
& \sum_{n,n',\mathbf{k}} (f(\varepsilon_{n',\mathbf{k}}) - f(\varepsilon_{n,\mathbf{k}})) X_{n',n,\mathbf{k};\alpha}^* X_{n',n,\mathbf{k};\beta} \\
&= \sum_{n,n',\mathbf{k}} f(\varepsilon_{n',\mathbf{k}}) \langle \partial_{k_\alpha} u_{n,\mathbf{k}} | u_{n',\mathbf{k}} \rangle \langle u_{n',\mathbf{k}} | \partial_{k_\beta} u_{n,\mathbf{k}} \rangle \\
&\quad - \sum_{n,n',\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \langle \partial_{k_\alpha} u_{n,\mathbf{k}} | u_{n',\mathbf{k}} \rangle \langle u_{n',\mathbf{k}} | \partial_{k_\beta} u_{n,\mathbf{k}} \rangle \\
&= \sum_{n,n',\mathbf{k}} f(\varepsilon_{n',\mathbf{k}}) \langle \partial_{k_\beta} u_{n',\mathbf{k}} | u_{n,\mathbf{k}} \rangle \langle u_{n,\mathbf{k}} | \partial_{k_\alpha} u_{n',\mathbf{k}} \rangle \\
&\quad - \sum_{n,n',\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \langle \partial_{k_\alpha} u_{n,\mathbf{k}} | u_{n',\mathbf{k}} \rangle \langle u_{n',\mathbf{k}} | \partial_{k_\beta} u_{n,\mathbf{k}} \rangle \\
&= \sum_{n,\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \left(\langle \partial_{k_\beta} u_{n,\mathbf{k}} | \partial_{k_\alpha} u_{n,\mathbf{k}} \rangle - \langle \partial_{k_\alpha} u_{n,\mathbf{k}} | \partial_{k_\beta} u_{n,\mathbf{k}} \rangle \right) \\
&= i \sum_{n,\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \left(\partial_{k_\alpha} X_{n,n,\mathbf{k};\beta} - \partial_{k_\beta} X_{n,n,\mathbf{k};\alpha} \right) \\
&= i \sum_{n,\mathbf{k},\gamma} f(\varepsilon_{n,\mathbf{k}}) \epsilon_{\alpha,\beta,\gamma} \Omega_{n,\mathbf{k};\gamma} , \tag{C.27}
\end{aligned}$$

where in the third line we used

$$0 = \partial_{k_\alpha} \langle u_{n',\mathbf{k}} | u_{n,\mathbf{k}} \rangle = \langle \partial_{k_\alpha} u_{n',\mathbf{k}} | u_{n,\mathbf{k}} \rangle + \langle u_{n',\mathbf{k}} | \partial_{k_\alpha} u_{n,\mathbf{k}} \rangle , \tag{C.28}$$

in the fourth line we used the resolution of the identity given in Eq. (2.5), and where $\epsilon_{\alpha,\beta,\gamma}$ is the Levi-Civita symbol and $\Omega_{n,\mathbf{k}} = \nabla \times \mathbf{X}_{n,n,\mathbf{k}}$ is the Berry curvature.

All together,

$$\begin{aligned}
\sigma_{\alpha,\beta}^{(0)}(z) &= \frac{i}{zV} \sum_{n,\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \partial_{k_\alpha} \partial_{k_\beta} \varepsilon_{n,\mathbf{k}} - \frac{1}{V} \sum_{n,\mathbf{k},\gamma} f(\varepsilon_{n,\mathbf{k}}) \epsilon_{\alpha,\beta,\gamma} \Omega_{n,\mathbf{k};\gamma} \\
&\quad - \frac{iz}{V} \sum_{n,n',\mathbf{k}} \frac{f(\varepsilon_{n',\mathbf{k}}) - f(\varepsilon_{n,\mathbf{k}})}{z + \varepsilon_{n,\mathbf{k}} - \varepsilon_{n',\mathbf{k}}} X_{n',n,\mathbf{k};\alpha}^* X_{n',n,\mathbf{k};\beta} . \tag{C.29}
\end{aligned}$$

C.2.1 Longitudinal conductivity

The longitudinal component of the conductivity is

$$\sigma_{\alpha,\alpha}^{(0)}(z) = \frac{i}{zV} \sum_{n,\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \partial_{k_\alpha}^2 \varepsilon_{n,\mathbf{k}} - \frac{iz}{V} \sum_{n,n',\mathbf{k}} \frac{f(\varepsilon_{n',\mathbf{k}}) - f(\varepsilon_{n,\mathbf{k}})}{z + \varepsilon_{n,\mathbf{k}} - \varepsilon_{n',\mathbf{k}}} |X_{n',n,\mathbf{k};\alpha}|^2 . \tag{C.30}$$

The second term can be rewritten using

$$\begin{aligned}
& \sum_{n',n,\mathbf{k}} \frac{f(\varepsilon_{n',\mathbf{k}}) - f(\varepsilon_{n,\mathbf{k}})}{z + \varepsilon_{n,\mathbf{k}} - \varepsilon_{n',\mathbf{k}}} |X_{n',n,\mathbf{k};\alpha}|^2 \\
&= \frac{1}{2} \left(\sum_{n',n,\mathbf{k}} \frac{f(\varepsilon_{n',\mathbf{k}}) - f(\varepsilon_{n,\mathbf{k}})}{z + \varepsilon_{n,\mathbf{k}} - \varepsilon_{n',\mathbf{k}}} |X_{n',n,\mathbf{k};\alpha}|^2 + \sum_{n',n,\mathbf{k}} \frac{f(\varepsilon_{n',\mathbf{k}}) - f(\varepsilon_{n,\mathbf{k}})}{z + \varepsilon_{n,\mathbf{k}} - \varepsilon_{n',\mathbf{k}}} |X_{n',n,\mathbf{k};\alpha}|^2 \right) \\
&= \frac{1}{2} \left(\sum_{n',n,\mathbf{k}} \frac{f(\varepsilon_{n',\mathbf{k}}) - f(\varepsilon_{n,\mathbf{k}})}{z + \varepsilon_{n,\mathbf{k}} - \varepsilon_{n',\mathbf{k}}} |X_{n',n,\mathbf{k};\alpha}|^2 - \sum_{n',n,\mathbf{k}} \frac{f(\varepsilon_{n',\mathbf{k}}) - f(\varepsilon_{n,\mathbf{k}})}{z - (\varepsilon_{n,\mathbf{k}} - \varepsilon_{n',\mathbf{k}})} |X_{n',n,\mathbf{k};\alpha}|^2 \right) \\
&= -\frac{1}{2} \left(\sum_{n',n',\mathbf{k}} (f(\varepsilon_{n',\mathbf{k}}) - f(\varepsilon_{n',\mathbf{k}})) \frac{2(\varepsilon_{n',\mathbf{k}} - \varepsilon_{n',\mathbf{k}})}{z^2 - (\varepsilon_{n',\mathbf{k}} - \varepsilon_{n',\mathbf{k}})^2} |X_{n',n,\mathbf{k};\alpha}|^2 \right), \tag{C.31}
\end{aligned}$$

so that

$$\begin{aligned}
\sigma_{\alpha,\alpha}^{(0)}(z) &= \tag{C.32} \\
&= \frac{i}{zV} \sum_{n,\mathbf{k}} f(\varepsilon_{n,\mathbf{k}}) \partial_{k_\alpha}^2 \varepsilon_{n,\mathbf{k}} - \frac{i}{V} \left(\sum_{n',n,\mathbf{k}} (f(\varepsilon_{n,\mathbf{k}}) - f(\varepsilon_{n',\mathbf{k}})) \frac{z(\varepsilon_{n',\mathbf{k}} - \varepsilon_{n,\mathbf{k}})}{(\varepsilon_{n',\mathbf{k}} - \varepsilon_{n,\mathbf{k}})^2 - z^2} |X_{n',n,\mathbf{k};\alpha}|^2 \right).
\end{aligned}$$

This expression makes it clear that $\lim_{|z| \rightarrow \infty} \sigma_{\alpha,\alpha}^{(0)}(z) = 0$.

C.3 Comments on implementation

The memory function formalism for scattering due to disorder has simple input, only the density response function and disorder potential, and is very general in scope, as it is capable of handling any strength of scattering, multiband systems, and zero-frequency limits of disordered systems without finite size problems. Therefore, it can be applied quite generally. However, this is not to say that one need not apply it carefully. For example, the numerical implementation must be consistent with the theory in ways that are sometimes subtle. Here we outline a few details that must be accounted for.

We used the completeness relation of Eq. (2.5) in Eqs. (4.5) and (C.10). Whereas the latter could be calculated as a numerical limit without the completeness relation, the former is a necessary step in evaluating the memory function for the case of disorder. Therefore, one must take a sufficiently large basis for the calculation. The Bloch basis only enters through the density response function, so that achieving convergence for the density response function is a sufficient criterion. This convergence should be checked in terms of whether the memory function is independent of the size of the Bloch basis

used to calculate it, as the memory function is sensitive to small changes in the response function.

There is only one physical reciprocal space lattice, and it defines both \mathbf{k} and \mathbf{q} . Therefore, to be consistent with the theory, one should take these lattices to be the same. For example, in a one-dimensional system of N unit cells with lattice constant a , the physically correct reciprocal lattice vectors are $k, q = \frac{2\pi}{Na}$ for $n \in \{0, 1, \dots, N-1\}$. Defining a grid this way guarantees that for any pair \mathbf{k}, \mathbf{q} , every $\mathbf{k} + \mathbf{q}$ is also in the \mathbf{k} -point grid. This is necessary not only physically for consistency, but also numerically, in order for the response function at imaginary frequencies to be real as in Appendix C.1.2. To simplify numerical evaluations, it is possible use a \mathbf{q} -point grid which is a proper subset of the \mathbf{k} -point grid, provided the \mathbf{q} -point grid is sufficiently fine to capture smooth variation of the density response function for the sum in Eq. (4.13).

The response function may in principle be calculated with any method provided that it fulfills the completeness criterion. Whether or not this poses a problem for tight-binding response functions is under investigation. Tight-binding response functions also are only accurate within their first Brillouin zones, as they cannot resolve details finer than the lattice length scale, which defines the first Brillouin zone boundary. Hence, one should use extra caution when studying tight-binding systems.

To use the memory function in the strong-scattering and hence large-memory-function limit, we must have a response function that is valid for large energies. This can be problematic in multiband systems whose bands extend to infinite energies, making transitions between the conduction and valence band artificially present at any energy. For example, in the Dirac cone approximation of graphene, where the cone is assumed to extend indefinitely, one finds that the interband term of the longitudinal conductivity $\sigma_{\alpha,\alpha}(0) = \sigma_{\alpha,\alpha}^{(0)}(iM'')$ in Eq. (3.15) is proportional to $\ln\left(\frac{2\mu - iM''}{2\mu + iM''}\right)$, which incorrectly tends toward a constant nonzero interband contribution in the large- M'' limit.

C.3.1 Finite supercells

As we mentioned in the context of the conductivity in Sec. 3.2.1, the memory function broadens the Lorentzians which are summed over to give correlation functions. This manifests explicitly in the intraband term of the conductivity, where the $\mathbf{q} \rightarrow 0$ limit of the excitation energy $\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}}$ is calculated analytically to produce the well-known Lorentzian that is the Drude peak. The density response function is written as a sum over Lorentzians which is evaluated for general \mathbf{q} in Eq. (C.4). For these discrete sums to be well-behaved, the Lorentzians must be sufficiently broadened. For simplicity,

here we consider the dc limit, in which the density response function is evaluated at $z + M(z) = iM''$.

Specifically, for the sum over a finite \mathbf{k} -point grid representing a finite supercell to converge to the corresponding sum in the thermodynamic limit of an infinite system, the Lorentzians in $\frac{f(\varepsilon_{n',\mathbf{k}-\mathbf{q}}) - f(\varepsilon_{n,\mathbf{k}})}{iM'' + \varepsilon_{n,\mathbf{k}} - \varepsilon_{n',\mathbf{k}-\mathbf{q}}}$ must be broadened so that for any given \mathbf{q} , the sum is not dominated by only one or a few \mathbf{k} -points. This is achieved as long as M'' is not smaller than the smallest of the excitation energies $\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}}$, the minimum of which is set by the density of the \mathbf{k} -point grid, or equivalently, the size of the supercell. This requirement is problematic when evaluating the weak-scattering limit, where M'' is small, and when evaluating the static response function, where $M'' = 0$. The problem can in principle be solved by taking a finer \mathbf{k} -point grid. As this is not always practical, a computationally simpler and physically realistic is to calculate the response functions at a finite temperature.

At finite temperature, low-energy excitations are no longer between fully occupied and unoccupied states, but instead between pairs of partially occupied states. This reduces the transition availability factor $f(\varepsilon_{n',\mathbf{k}-\mathbf{q}}) - f(\varepsilon_{n,\mathbf{k}})$ weighting the low-energy excitations that would otherwise dominate the calculation. Equivalently, a finite temperature smooths out $\frac{f(\varepsilon_{n,\mathbf{k}}) - f(\varepsilon_{n',\mathbf{k}-\mathbf{q}})}{\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}}}$, which is effectively a numerical derivative of the Fermi-Dirac distribution. The Fermi-Dirac distribution becomes smoother and more amenable to numerical differentiation as temperature is increased. At zero temperature its derivative behaves as a Dirac delta for \mathbf{k}, \mathbf{q} such that $\varepsilon_{n',\mathbf{k}-\mathbf{q}} \approx \varepsilon_{n,\mathbf{k}}$, but at a finite temperature it gives the finite slope of a smooth sigmoid. This smoothing is especially relevant for \mathbf{q} less than the diameter of the Fermi surface, $|\mathbf{q}| < 2k_F$ if the Fermi surface is circular. This range includes \mathbf{q} which are chords spanning the Fermi surface, connecting states just above the surface to states just below. As a result, these \mathbf{q} are where the smallest excitation energies $\varepsilon_{n',\mathbf{k}-\mathbf{q}} - \varepsilon_{n,\mathbf{k}}$ appear, setting the level of broadening M'' for which the density response function converges. The finite-temperature approach works in the static and broadened zero-frequency response functions, where the zero-energy excitations across the Fermi level give most sharply-peaked Lorentzians. At nonzero frequencies, where sharply-peaked Lorentzians are given by finite-energy excitations, increasing the number of \mathbf{k} -points is a more effective solution.

By thinking of the broadening and relaxation rate M'' and the minimum available excitation energy $\Delta\varepsilon$ in terms of time scales, we can understand the level of broadening necessary to achieve convergence of the density response function evaluated on a \mathbf{k} -point grid of a given density, i.e., a supercell of a given size. Here we can estimate the minimum

excitation energy to be $\Delta\varepsilon \approx \varepsilon_{n,\mathbf{k}-\Delta\mathbf{k}} - \varepsilon_{n,\mathbf{k}}$, where $|\Delta\mathbf{k}| = 2\pi/L$ is the \mathbf{k} -point spacing for a supercell with linear size L . Even if the minimum excitation energy is achieved by another \mathbf{q} , we can estimate $\varepsilon_{n',\mathbf{k}-\Delta\mathbf{k}} \approx \varepsilon_{n,\mathbf{k}-\mathbf{q}}$ since both represent energies just above the Fermi surface and hence are at roughly the same level. This reasoning generalizes to nonzero frequencies as well, where more generally the broadening is $\text{Im } M(z)$ and $\Delta\varepsilon$ is the excitation energy closest to ω . The condition that the memory function should exceed the minimum excitation energy, $M'' > \Delta\varepsilon$, can then be rewritten by using the parallel $\frac{1}{M''} \leftrightarrow \tau$ and the time for an electron to cross the system, which is $\tau_L = \frac{L}{v} = \frac{L}{\Delta\varepsilon/\Delta k} = \frac{2\pi}{\Delta\varepsilon}$, where $v = \Delta\varepsilon/\Delta k$ is the velocity. With these, $M'' > \Delta\varepsilon$ is equivalent to $\tau_L > \tau$. In other words, a finite supercell will mimic the infinite system as long as electrons scatter before they are able to cross the entire supercell and see that it is periodic, as one would expect intuitively. Note that we can always increase the range of validity for the memory function formalism by using a larger supercell, which decreases $\Delta\varepsilon$ and increases τ_L . In comparison, Boltzmann transport theory is valid when the scattering time is longer than the decoherence time, which is a property of the system and the scattering and cannot be controlled with the size of the supercell.

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Vita

Brett Green

Brett Green was born and raised in Kootenai County, Idaho, where he attended the Coeur d'Alene Charter Academy until his graduation in 2010. He then enrolled at Montana State University, earning dual Bachelors of Science with highest honors in Physics and Mathematics in 2014. In the spring of 2015, he was awarded the National Science Foundation Graduate Research Fellowship, and in the fall, he began his doctoral studies at Penn State University.

As a doctoral student, with his adviser Jorge Sofo he studied many-body ordered phases constructed from Landau levels in bilayer graphene [1], generalized a self-consistent memory function theory for the electrical conductivity to periodic systems [2,3], and defined and studied a metric of Anderson localization [4]. Outside of this research, he has been actively involved in community-building, outreach, and climate and diversity efforts at the department and college levels. While at Penn State, he received the Physics Graduate Teaching Assistant Award, the inaugural Physics Graduate Student Service Award, and the Elsbach, Downsborough, and Duncan Graduate Fellowships.

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