Non-Linear Optical response with the Kernel Polynomial Method

Simão Meneses João
Mestrado em Física
Departamento de Física e Astronomia
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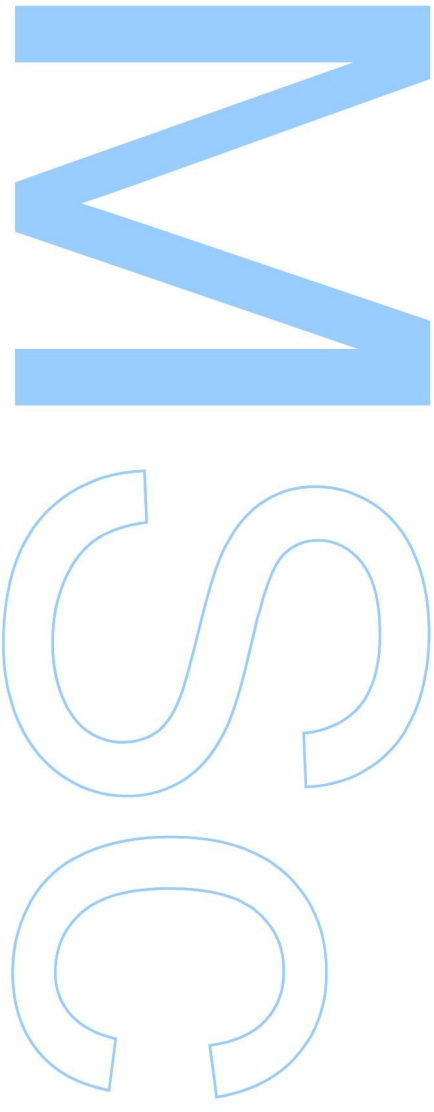
Orientador
João Manuel Viana Parente Lopes, Professor Auxiliar Convidado,
Faculdade de Ciências da Universidade do Porto

Coorientador
João Manuel Borregana Lopes dos Santos, Professor Catedrático,
Faculdade de Ciências da Universidade do Porto



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UNIVERSIDADE DO PORTO

Todas as correções determinadas pelo júri, e só essas, foram efetuadas.

O Presidente do Júri,

Acknowledgements

As the reader goes through this text, they will find that it is a reflection of my learning journey on condensed matter physics across this year. If nothing more than a modest contribution to science, this work should be understood as a set of personal notes aimed at developing my understanding of the topics at hand. This is the result of many discussions with several people who have had a profound impact in both this text and my education. First of all, I'd like to express my utmost gratitude to my supervisor, Professor João Viana Lopes, with whom I've had the pleasure to work in these last few years and whose patience and expertise have been crucial to my growth as an aspiring physicist. The countless hours spent on the weekends in the faculty teaching me how to work with KPM go largely unnoticed in this work but are implicit in the results. Secondly, I must thank my co-supervisor, Professor João Lopes dos Santos, whose profound insight and discussions helped cement the concepts in place. Thirdly, I cannot help but thank my friends António, Bruno, Maria, João Carlos and João Pedro for their invaluable company while writing this work and for the countless ideas that sprouted while discussing with them. This gratitude is extended to my colleagues Daniel, who provided results which I could use to compare to my own, and Gonçalo, who helped proofread my dissertation. A special thanks is due to all the professors and staff in the department and to Professor José Miguel for teaching me the Eraser Technique. Lastly, and most importantly, I have to thank my family José, Esmeralda and Carolina for their unconditional support over all these years by making sure I had all the necessary and sufficient conditions to study what I love, even though it meant being so far away from home.

Abstract

Built on the Keldysh formalism, this work is the link between developing a perturbation expansion for the nonlinear optical response of a quantum system and obtaining expressions amenable to numerical calculation using the Kernel Polynomial Method (KPM).

Contents

1 Introduction

Since the advent of the laser in 1960, the field of non-linear optics has received considerable interest. Previously, only weak electric fields were available. Nonlinear effects, which typically only happen due to very strong fields, went largely unnoticed. However, 1961 marked the beginning of a systematic study of this field, as P. Franken was able to demonstrate second harmonic generation (SHG) [1] experimentally. This opened the gateway to a whole new plethora of phenomena. But how strong a field is needed? For the effects to be noticeable, this external field should be comparable to the electric field inside the crystal, which is typically of the order of 10^8 V/m. All around the literature, we find many approaches to obtain the nonlinear response of a crystalline system to an external field. Some rely on generalizing Kubo's formula for higher orders [2], others on developing a perturbation expansion for the density matrix of the system and expressing the quantities of interest in terms of it [3]. Although undoubtedly useful from a theoretical point of view, the expressions aren't that useful when we want a general procedure to do numerical calculations. That is the ultimate goal of this work.

1.1 Structure of the thesis

The second chapter is a set of notes about the various tools that will be used throughout the whole work. It starts by explaining how an external field may be introduced to a quantum system, discussing the minimal coupling procedure (henceforth also called the $\boldsymbol{A}$ formalism) and the dipolar procedure ($\boldsymbol{E}$ formalism). Then, we introduce the primary object of study of this work, the electron current, as the conserved Noether current from the point of view of classical field theory. The remaining sections of this chapter include second quantization, the Schrödinger, Heisenberg and Interaction pictures of quantum mechanics and some basics about quantum statistical mechanics, including the generalization of Wick's theorem to systems at finite temperature.

Chapter three is devoted to the linear response. Starting from Kubo's formula, we obtain the current in both the $\boldsymbol{A}$ and $\boldsymbol{E}$ formalisms, showing that the two seemingly different expressions are in fact one and the same using the notation of Gonçalo [3]. Furthermore, the continuum limit is obtained, alongside with the DC limit $\omega \to 0$. The last sections provide a glimpse into what is going to be developed in the rest of the thesis, as they strive to cast the previous expressions in a basis-independent way. The Kubo-Bastin formula is re-obtained in this context.

The fourth chapter begins with a generalization of Kubo's formula, but quickly moves on to to the crux of this thesis, the Keldysh formalism. This is a very general perturbation expansion procedure which may be used for systems both interacting and time-dependent. Particularizing

to the non-interacting case, we are able to develop an expansion of the Green's functions, which are **the** fundamental piece of machinery used to obtain the conductivity.

The next chapter contains the explicit calculation of the Green's functions up to third order using the Tight Binding Hamiltonian and shows how to obtain the current and conductivity up to second order.

Chapter number six is all about the numerical method used in our calculations, the Kernel Polynomial Method (KPM). Here we show how the aforementioned Green's functions may be expressed in terms of numerical objects and how they may be used to implement the conductivity in a very efficient way [4].

At last, the seventh chapter consists of showcasing some results obtained numerically from the formulas derived in the previous chapters. We calculate the density of states and first-order conductivity of graphene and the second-order conductivity of hexagonal Boron Nitride.

2 Theoretical background

This chapter consists of a series of notes that aim to provide the basic tools which are going to be used in the subsequent chapters. We begin by explaining how to describe a quantum system in an electromagnetic field. This will allow us to identify the electron current. Then, we do a brief introduction to second quantization in order to express the current in terms of creation and annihilation operators. After that, we'll introduce the Schrödinger, Interaction and Heisenberg Pictures that will later allow us to develop perturbation expansions. Finally, we conclude with some remarks about quantum statistics, proving Wick's theorem for finite temperatures. All these are essential tools that will prove themselves useful when developing the Keldysh formalism.

2.1 Introducing an external field to a quantum system

We are interested in studying the optical conductivity of a quantum system when excited by an external electric field $\boldsymbol{E}(t)$. The case of interest will be a crystalline system, but for now we'll keep the discussion more general. Here we will discuss two distinct ways to endow a system with an electromagnetic field, starting with a classical description of the problem.

2.1.1 Classical motivation

In a classical Lagrangian description[5, 6], we know how to compute the equations of motion in a very compact and elegant way. Assuming the forces that the particle experiences are due to a potential $V(\boldsymbol{r})$, we find the Lagrangian from the kinetic and potential terms: $L = T - V$. Applying the Euler-Lagrange equation to L then yields the equations of motion. If the particle is also subject to a more general force F_i, which may depend on both the generalized coordinates and velocities, it may not be suitable for a potential description. In that case, we can still obtain the equations of motion from Lagrange's equation

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = F_i. \tag{2.1}$$

For the case at hand, it suffices to consider a system without constraints[1] in Cartesian coordinates, so the Lagrangian is $L = T - V = \frac{1}{2}m\dot{\boldsymbol{r}}^2 - V(\boldsymbol{r})$. We know that a particle of charge q experiences a Lorentz force $\boldsymbol{F} = q\left(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}\right)$ when exposed to an electromagnetic field. This

[1] From a quantum point of view, all the interactions in which we're interested are electromagnetic, so there are no constraints in the classical sense.

force then enters the equations of motion through the generalized force in the Euler-Lagrange equation. It can, however, be inserted in the Lagrangian itself if we express it in terms of the correct potential. Expressing the electric and magnetic fields in terms of the scalar and vector potentials ϕ and $\boldsymbol{A}$,

$$\boldsymbol{E} = -\frac{\partial \boldsymbol{A}}{\partial t} - \boldsymbol{\nabla}\phi \tag{2.2}$$

$$\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A} \tag{2.3}$$

we may rewrite the Lorentz force in terms of these potentials:

$$\boldsymbol{F} = q\left(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}\right) = q\left(-\frac{\partial \boldsymbol{A}}{\partial t} - \boldsymbol{\nabla}\phi + \boldsymbol{v} \times (\boldsymbol{\nabla} \times \boldsymbol{A})\right). \tag{2.4}$$

Using the identity $\boldsymbol{v} \times (\boldsymbol{\nabla} \times \boldsymbol{A}) = \boldsymbol{\nabla}(\boldsymbol{v} \cdot \boldsymbol{A}) - \frac{d\boldsymbol{A}}{dt} + \frac{\partial \boldsymbol{A}}{\partial t}$, this becomes:

$$\boldsymbol{F} = q\left(\boldsymbol{\nabla}(\boldsymbol{v} \cdot \boldsymbol{A} - \phi) - \frac{d\boldsymbol{A}}{dt}\right) = q\left[\boldsymbol{\nabla}\left(\boldsymbol{v} \cdot \boldsymbol{A} - \phi\right) - \frac{d}{dt}\boldsymbol{\nabla}_{\boldsymbol{v}}\left(\boldsymbol{v} \cdot \boldsymbol{A} - \phi\right)\right]. \tag{2.5}$$

Furthermore, eq. 2.1 may be rewritten as

$$\frac{d}{dt}\frac{\partial \tilde{L}}{\partial \dot{q}_i} - \frac{\partial \tilde{L}}{\partial q_i} = 0 \tag{2.6}$$

for a new Lagrangian $\tilde{L}$

$$\tilde{L} = \frac{1}{2}m\dot{\boldsymbol{r}}^2 - V(\boldsymbol{r}) + q\dot{\boldsymbol{r}} \cdot \boldsymbol{A} - q\phi. \tag{2.7}$$

From this we can obtain the canonical momentum $p_i = \frac{\partial \tilde{L}}{\partial \dot{r}_i} = m\dot{r}_i + qA_i$ and find the Hamiltonian by Legendre-transforming the Lagrangian:

$$H(\boldsymbol{r}, \boldsymbol{p}) = \boldsymbol{p} \cdot \dot{\boldsymbol{r}} - \tilde{L} = \frac{1}{2m}\left(\boldsymbol{p} - q\boldsymbol{A}\right)^2 + V(\boldsymbol{r}) + q\phi. \tag{2.8}$$

Note that these potentials are not uniquely determined, since $\boldsymbol{A}' = \boldsymbol{A} + \boldsymbol{\nabla}\chi$ and $\phi' = \phi - \frac{\partial \chi}{\partial t}$ yield exactly the same electric and magnetic fields and therefore the same equation of motion for the charged particle. We may use this so-called Gauge freedom to our advantage. We'll be interested in spatially homogeneous[2] time-dependent electric fields $\boldsymbol{E}(t)$, which may be obtained by two different choices of the potentials. The first choice is $\phi = 0$ and $\boldsymbol{A}(t)$ spatially uniform, so $\boldsymbol{E}(t) = -\frac{\partial \boldsymbol{A}(t)}{\partial t}$, which means that it is enough to do the replacement $\boldsymbol{p} \to \boldsymbol{p} - q\boldsymbol{A}$ in the original Hamiltonian. This procedure is called the $\boldsymbol{A}$ formalism. The second choice is $\boldsymbol{A} = \boldsymbol{0}$ and $\phi(\boldsymbol{r}) = -\boldsymbol{r} \cdot \boldsymbol{E}(t)$, which amounts to adding a dipolar term in the original Hamiltonian and is . These two procedures are completely equivalent and are merely a reflection of the Gauge freedom.

[2] In the quantum scale, the wavelength of the electric fields may be disregarded when compared to inter-atomic spacing.

2.1.2 Quantum case and Gauge invariance

Now that we know how to endow a classical system with an electromagnetic field, we can take this one step further by taking the classical Hamiltonian and quantizing it using canonical quantization. Upon replacing the variables by operators we obtain what we wanted, the Hamiltonian of a quantum system in the presence of an electric field

$$H_0(\boldsymbol{x}, \boldsymbol{p}) \to H_0(\boldsymbol{x}, \boldsymbol{p} - q\boldsymbol{A}) + q\phi. \tag{2.9}$$

If the reader is not satisfied with this justification, there is another more fundamental reason as to why the Hamiltonian should have that form. Take the Schrödinger equation in the position representation:

$$i\hbar \frac{\partial \Psi(t, \boldsymbol{x})}{\partial t} = -\frac{\hbar^2}{2m} \boldsymbol{\nabla}^2 \Psi(t, \boldsymbol{x}) + V(\boldsymbol{x}) \Psi(t, \boldsymbol{x}). \tag{2.10}$$

Performing a local Gauge transformation on the wave function, $\Psi(t, \boldsymbol{x}) \to \Psi'(t, \boldsymbol{x}) = e^{i\alpha(t, \boldsymbol{x})} \Psi(t, \boldsymbol{x})$, the Schrödinger equation becomes:

$$i\hbar \left(\frac{\partial}{\partial t} + i \frac{\partial \alpha}{\partial t} \right) \Psi = -\frac{\hbar^2}{2m} \left(\boldsymbol{\nabla} + i \boldsymbol{\nabla} \alpha \right)^2 \Psi + V\Psi. \tag{2.11}$$

This means the original equation is not Gauge invariant. To fix this, we introduce two fields $\boldsymbol{A}(t, \boldsymbol{x})$ and $\phi(t, \boldsymbol{x})$ to the equation that follow some transformation law upon being Gauge transformed. If the original Schrödinger equation is replaced by

$$i\hbar \left(\frac{\partial}{\partial t} + i \frac{q}{\hbar} \phi \right) \Psi = -\frac{\hbar^2}{2m} \left(\boldsymbol{\nabla} - i \frac{q}{\hbar} \boldsymbol{A} \right)^2 \Psi + V\Psi \tag{2.12}$$

we see that the transformation

$$\begin{aligned} \Psi(t, \boldsymbol{x}) &\to \Psi'(t, \boldsymbol{x}) = e^{i\alpha(t, \boldsymbol{x})} \Psi(t, \boldsymbol{x}) \\ \boldsymbol{A}(t, \boldsymbol{x}) &\to \boldsymbol{A}'(t, \boldsymbol{x}) = \boldsymbol{A}(t, \boldsymbol{x}) + \frac{\hbar}{q} \nabla \alpha(t, \boldsymbol{x}) \\ \phi(t, \boldsymbol{x}) &\to \phi'(t, \boldsymbol{x}) = \phi(t, \boldsymbol{x}) - \frac{\hbar}{q} \frac{\partial}{\partial t} \alpha(t, \boldsymbol{x}) \end{aligned} \tag{2.13}$$

leaves it invariant! This is equivalent to replacing the momentum operator $\boldsymbol{p} \to \boldsymbol{p} - q\boldsymbol{A}$ and adding a scalar field term $q\phi$ to the Hamiltonian, just as before. This means that the Gauge invariance of the Schrödinger equation naturally demands that the Gauge fields be added, leaving the Hamiltonian with the familiar form.

2.2 Current

We have just seen that a quantum system described by a wave function ψ satisfies Schrödinger's equation if the Hamiltonian is modified to include the Gauge fields. We may proceed further and ask if there is a Lagrangian such that the equation of motion is precisely Schrödinger's equation. If we are able to find it, we may use the tools of classical field theory to obtain the conserved currents from Noether's Theorem. This will provide a deeper insight into what we're actually calculating.

2.2.1 Lagrangian density

The assertion is that the aforementioned system, which is described by Schrödinger's equation, may be just as well described by a Lagrangian, and that the two descriptions are equivalent [7, Chapter 3]. Consider the following Lagrangian density for a field $\psi(\vec{x}, t)$:

$$\mathcal{L} = \psi^* \left(i\hbar \frac{\partial}{\partial t} \right) \psi - \frac{\hbar^2}{2m} \boldsymbol{\nabla}\psi^* \cdot \boldsymbol{\nabla}\psi - V(\boldsymbol{x}, t)\psi^*\psi \tag{2.14}$$

At first glance, one may wonder where this comes from, but upon closer inspection, we may recognize the last two terms as coming from the Hamiltonian density after an integration by parts and the first term from the Legendre transform of H. This interpretation suggests that $i\hbar\psi^*$ is the conjugate momentum of the field ψ. As we'll see, this is indeed the case. Since the field is complex, it has independent real and imaginary parts, say $\psi(\boldsymbol{x}, t) = u(\boldsymbol{x}, t) + iv(\boldsymbol{x}, t)$, which are to be considered the independent fields indexed by r, ϕ^r, in Euler-Lagrange's equation for fields:

$$\frac{\partial \mathcal{L}}{\partial \phi^r} - \frac{\partial}{\partial x^\mu} \frac{\partial \mathcal{L}}{\partial \left(\frac{\partial \phi^r}{\partial x^\mu} \right)} = 0 \tag{2.15}$$

where the index μ runs over both spatial and time coordinates. Instead of expressing the Lagrangian in terms of u and v, we use the E-L equation for one of them and use the chain rule to have derivatives with respect to the ψ.

$$0 = \frac{\partial \mathcal{L}}{\partial u} - \frac{\partial}{\partial x^\mu} \frac{\partial \mathcal{L}}{\partial \left(\frac{\partial u}{\partial x^\mu} \right)} = \frac{\partial \mathcal{L}}{\partial \psi} \frac{\partial \psi}{\partial u} - \frac{\partial}{\partial x^\mu} \left(\frac{\partial \mathcal{L}}{\partial \left(\frac{\partial \psi}{\partial x^\mu} \right)} \frac{\partial \frac{\partial \psi}{\partial x^\mu}}{\partial \frac{\partial u}{\partial x^\mu}} \right) \tag{2.16}$$

Since $\frac{\partial \psi}{\partial u} = 1$ and $\frac{\partial \frac{\partial \psi}{\partial x^\mu}}{\partial \frac{\partial u}{\partial x^\mu}} = 1$, this yields E-L equations for ψ. This can similarly be done for ψ^* and results in an equivalent equation of motion. Applying E-L's equation to ψ^*, we get

$$\frac{\partial \mathcal{L}}{\partial \psi^*} - \boldsymbol{\nabla} \cdot \frac{\partial \mathcal{L}}{\partial \left(\boldsymbol{\nabla}\psi^* \right)} - \frac{\partial}{\partial t} \frac{\partial \mathcal{L}}{\partial \left(\frac{\partial \psi^*}{\partial t} \right)} = \left(i\hbar \frac{\partial}{\partial t} \right) \psi - V(\vec{x}, t)\psi + \frac{\hbar^2}{2m} \boldsymbol{\nabla}^2 \psi = 0 \tag{2.17}$$

or, simplifying,

$$i\hbar\frac{\partial}{\partial t}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi + V(\vec{x},t)\psi. \tag{2.18}$$

This is just Schrödinger's equation for the field ψ! The Euler-Lagrange's equations for the specified Lagrangian density reduce to Schrödinger's equation, so the field has the same dynamics and the descriptions are equivalent. The other Euler-Lagrange equation gives the complex conjugate of eq. 2.18. We have thus achieved our goal of obtaining Schrödinger's equation from a Lagrangian for the field ψ. This means Noether's theorem can be used to obtain the conserved current!

2.2.2 Gauge invariant Lagrangian

As discussed before, demanding that Schrödinger's equation be Gauge invariant led to the introduction of Gauge fields through a few extra terms in the Hamiltonian. Doing this for the Lagrangian density consists of precisely the same substitutions and leads to

$$\mathcal{L} = i\hbar\psi^*\left(\frac{\partial}{\partial t} - i\frac{e}{\hbar}\phi\right)\psi - \frac{\hbar^2}{2m}\left(\boldsymbol{\nabla} - i\frac{e}{\hbar}\boldsymbol{A}\right)\psi^* \cdot \left(\boldsymbol{\nabla} + i\frac{e}{\hbar}\boldsymbol{A}\right)\psi - V(\vec{x},t)\psi^*\psi. \tag{2.19}$$

Applying Euler-Lagrange's equation as before results in

$$i\hbar\left(\frac{\partial}{\partial t} - i\frac{e}{\hbar}\phi\right)\psi = -\frac{\hbar^2}{2m}\left(\boldsymbol{\nabla} + i\frac{e}{\hbar}\boldsymbol{A}\right)^2\psi + V(\vec{x},t)\psi. \tag{2.20}$$

This is precisely the Gauge invariant Schrödinger equation (eq. 2.12), so we may use this Lagrangian density for our calculations.

2.2.3 Conserved Noether current

As we've seen before, the transformation that leaves the Lagrangian invariant is

$$\begin{aligned}
\psi(t,\boldsymbol{x}) &\rightarrow \psi'(t,\boldsymbol{x}) = e^{i\alpha(t,\boldsymbol{x})}\psi(t,\boldsymbol{x}) \\
\boldsymbol{A}(t,\boldsymbol{x}) &\rightarrow \boldsymbol{A'}(t,\boldsymbol{x}) = \boldsymbol{A}(t,\boldsymbol{x}) + \frac{\hbar}{q}\boldsymbol{\nabla}\alpha(t,\boldsymbol{x}) \\
\phi(t,\boldsymbol{x}) &\rightarrow \phi'(t,\boldsymbol{x}) = \phi(t,\boldsymbol{x}) - \frac{\hbar}{q}\frac{\partial}{\partial t}\alpha(t,\boldsymbol{x}).
\end{aligned}$$

The respective infinitesimal transformation for the field is

$$\delta\psi = i\psi\delta\alpha \tag{2.21}$$

$$\delta\psi^* = -i\psi^*\delta\alpha. \tag{2.22}$$

We can now explicitly calculate the Noether current

$$J^\mu = \sum_a \frac{\partial \mathcal{L}}{\partial(\partial_\mu \phi^a)} \frac{\delta \phi^a}{\delta \alpha} \tag{2.23}$$

where α is the infinitesimal transformation parameter and ϕ^a stands for the various fields. The spatial component of J is

$$\boldsymbol{J} = \frac{\partial \mathcal{L}}{\partial(\boldsymbol{\nabla}\psi)} \frac{\delta \psi}{\delta \alpha} + \frac{\partial \mathcal{L}}{\partial(\boldsymbol{\nabla}\psi^*)} \frac{\delta \psi^*}{\delta \alpha} = \frac{-i\hbar^2}{2m} \left[\psi \left(\boldsymbol{\nabla} - \frac{ie}{\hbar} \boldsymbol{A} \right) \psi^* - \psi^* \left(\boldsymbol{\nabla} + \frac{ie}{\hbar} \boldsymbol{A} \right) \psi \right] \tag{2.24}$$

and the temporal component is

$$J^0 = \frac{\partial \mathcal{L}}{\partial(\partial_t \psi)} \frac{\delta \psi}{\delta \alpha} + \frac{\partial \mathcal{L}}{\partial(\partial_t \psi^*)} \frac{\delta \psi^*}{\delta \alpha} = -\hbar \psi^* \psi. \tag{2.25}$$

These are, up to multiplicative factors, the electromagnetic current and the charge density, respectively. Noether's theorem tells us that J^μ follows a conservation law $\partial_\mu J^\mu = 0$, which in this case is no more than the continuity equation for the charge density $\rho = \psi^* \psi$. This current therefore represents the electrical current that passes through the material, so it is the object that we're interested in calculating. Note that if we take the derivative of the Lagrangian density with respect to the Gauge field, we get the current again

$$\frac{\partial \mathcal{L}}{\partial \left(\frac{e}{\hbar} \boldsymbol{A} \right)} = \boldsymbol{J}.$$

This may be used as a shortcut to obtaining the current. Now, we want to express the Gauge-invariant Hamiltonian in second quantization, so we can more easily perform the calculations.

2.3 Second quantization

Second quantization is a way to describe a quantum system with various particles. Instead of working with a multi-variate wave function, we exploit the statistics of the particles to introduce a set of operators that represent a particle in a certain quantum state. As we'll see, this simplifies notation greatly, while simultaneously providing a natural interpretation of the phenomena at hand. The results here presented also stand for bosons, although the derivation is slightly more complicated. As we're going to be dealing exclusively with non-interacting fermions, it seems appropriate to focus on that case. Although the calculations for the interacting case aren't done with detail, the final result which is also valid in the interacting case is still presented.

2.3.1 General many-body expansion

Consider a quantum system of one particle [8]. This particle can be in any linear combination of eigenstates of the single particle Hamiltonian H. So, if $\{|\psi_n\rangle\}$ is a complete set of eigenstates of

H, then in general $|\psi\rangle = \sum_n a_n |\psi_n\rangle$. This means that any function $\psi(x_1)$ can be expanded in terms of a complete basis of functions $\psi_n(x_1)$. The quantity x_1 is the coordinate of particle 1, which may include its spin or any other quantity needed to uniquely characterize the state of the particle.

Now consider a system of N particles, described by the wave function $\psi(x_1, \cdots, x_N)$. Since the eigenfunctions of the single particle Hamiltonian form a complete basis of functions, this function may be expanded in all its variables in terms of this basis of functions

$$\psi(x_1, \cdots, x_N) = \sum_{E'_1, \cdots, E'_2} C(E'_1, \cdots, E'_N) \psi_{E'_1}(x_1) \cdots \psi_{E'_N}(x_N). \tag{2.26}$$

The E'_i label the eigenstates of the Hamiltonian. This is a very important result that forms the basis of second quantization.

2.3.2 Constructing the fermion wave function

Now let's introduce the fermion statistics $\psi(\cdots, x_i, \cdots, x_j, \cdots) = -\psi(\cdots, x_j, \cdots, x_i, \cdots)$. Swapping $\psi_{E'_i}(x_i)$ and $\psi_{E'_j}(x_j)$ and relabeling the summation variables, we get a similar relation for the coefficients:

$$C(\cdots, E_i, \cdots, E_j, \cdots, t) = -C(\cdots, E_j, \cdots, E_i, \cdots, t). \tag{2.27}$$

We are thus summing over many configurations which have the same coefficients. If the number of particles in each state is the same, those states will have the same coefficient up to an overall sign. This interchangeability means we need only care about the number of particles in each state, not which particle is in which state. So, fix an ordering of the states and swap the entries of C until they respect that ordering. This allows us to define the coefficient $\bar{C}(n_1 n_2 \cdots n_\infty, t) = C(\cdots E_i < E_j < E_k \cdots, t)$ up to a minus sign. Let's make this explicit by summing first over all the configurations which have the same $\bar{C}$ coefficients, leaving the minus sign as a permutation coefficient $\sigma_{E'_1, \cdots, E'_2}$ in the remaining sum:

$$\psi(x_1, \cdots, x_N) = \sum_{n_1 \cdots n_\infty} \bar{C}(n_1 n_2 \cdots n_\infty, t) \sum_{\substack{E'_1, \cdots, E'_2 \\ (n_1 \cdots n_\infty)}} \sigma_{E'_1, \cdots, E'_2} \psi_{E'_1}(x_1) \cdots \psi_{E'_N}(x_N). \tag{2.28}$$

The first sum is restricted by the number of particles $N = \sum_i n_i$. The second sum is to be understood as a sum over all the states $\{E'_i\}$ compatible with the occupation numbers. This turns out to be merely permutations of the positions of the E'_i in the equation. $\sigma_{E'_1, \cdots, E'_2}$ is the sign of this permutation. As an illustrative example, take the case $N = 3$ with one particle in state 1, another in state 3 and another in state 4. The previous argument allows us to write the most general wave function compatible with the fermion statistics as the anti-symmetrized sum

of single-particle wavefunctions

$$\begin{aligned}&\bar{C}(10110\cdots 0,t)\left[\psi_1(x_1)\psi_3(x_2)\psi_4(x_3)-\psi_1(x_1)\psi_4(x_2)\psi_3(x_3)+\right.\\&-\psi_3(x_1)\psi_1(x_2)\psi_4(x_3)+\psi_3(x_1)\psi_4(x_2)\psi_1(x_3)+\\&\left.-\psi_4(x_1)\psi_3(x_2)\psi_1(x_3)+\psi_4(x_1)\psi_1(x_2)\psi_3(x_3)\right].\end{aligned} \tag{2.29}$$

This term is completely antisymmetric, as required by the statistics. The same can be done for any N if we fix the ordering of the states and define the minus sign to be the sign of the permutation. This can be neatly expressed in terms of a Slater determinant:

$$\sum_{\substack{E_1',\cdots,E_2'\\(n_1\cdots n_\infty)}} \sigma_{E_1',\cdots,E_2'}\psi_{E_1'}(x_1)\cdots\psi_{E_N'}(x_N)=\begin{vmatrix}\psi_{E_1}(x_1) & \cdots & \psi_{E_1}(x_N)\\ \vdots & \vdots & \vdots\\ \psi_{E_N}(x_1) & \cdots & \psi_{E_N}(x_N)\end{vmatrix}. \tag{2.30}$$

This will be used as the basis with which to expand fermionic wave functions, so it has to be normalized. Define

$$\Phi_{n_1,\cdots,n_\infty}(x_1,\cdots,x_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_{E_1}(x_1) & \cdots & \psi_{E_1}(x_N)\\ \vdots & \vdots & \vdots\\ \psi_{E_N}(x_1) & \cdots & \psi_{E_N}(x_N)\end{vmatrix}. \tag{2.31}$$

This introduces an extra factor in the coefficients, so define a new coefficient

$$f(n_1n_2\cdots n_\infty,t)=\sqrt{N!}\bar{C}(n_1n_2\cdots n_\infty,t). \tag{2.32}$$

We thus obtain an elegant expansion that only depends on the occupation number in each state. All the anti-symmetry is captured by the $\Phi_{n_1,\cdots,n_\infty}(x_1,\cdots,x_N)$:

$$\Psi(x_1,\cdots,x_N)=\sum_{n_1\cdots n_\infty} f(n_1n_2\cdots n_\infty,t)\Phi_{n_1,\cdots,n_\infty}(x_1,\cdots,x_N). \tag{2.33}$$

Note that the all the time dependency falls on the f coefficient.

2.3.3 Schrödinger equation

In most cases of interest (including the one in this work), the many-body Hamiltonian is described by

$$H=\sum_n^N T(x_n)+\frac{1}{2}\sum_{n\neq m}^N V(x_n,x_m). \tag{2.34}$$

Here T denotes the single-particle component of the Hamiltonian (which includes the kinetic

energy) and V takes into account the interaction between the particles. Note that the interaction between particles is symmetric, so the double sum over all the particles introduces repeated terms. These are taken into account by the $\frac{1}{2}$ term and by the restriction $n \neq m$, since $n = m$ is already considered in T. Since the coefficients C completely determine the quantum state, we want to obtain an equation of motion for them. For that matter, apply Schrödinger's equation to the general wave function 2.26, multiply on the left by $\psi^\dagger_{E_1}(x_1)\cdots\psi^\dagger_{E_N}(x_N)$ and integrate over all the coordinates. Since the basis functions are normalized, this yields the following for the kinetic term:

$$\begin{aligned}
&\int dx_1\cdots dx_N \psi^\dagger_{E_1}(x_1)\cdots\psi^\dagger_{E_N}(x_N)\sum_n^N T(x_n)\left(\sum_{E'_1,\cdots,E'_2} C(E'_1,\cdots,E'_N)\psi_{E'_1}(x_1)\cdots\psi_{E'_N}(x_N)\right)\\
&= \sum_{n=1}^N\sum_W C(E_1,\cdots,\underbrace{W}_{\text{n-th position}},\cdots,E_N)\int dx_n \psi^\dagger_{E_n}(x_n)T(x_n)\psi_W(x_n). \qquad (2.35)
\end{aligned}$$

Plugging this back into Schrödinger's equation and omitting the interaction term, we get

$$i\hbar\frac{\partial}{\partial t}C(E_1,\cdots,E_N,t) = \sum_{n=1}^N\sum_W C(E_1,\cdots,E_{n-1},W,E_{n+1},\cdots,E_N)\langle E_n|T|W\rangle + \cdots. \qquad (2.36)$$

We want to apply this to fermions. In order to do that, we first need to reorder the coefficients in each side of the equation so that they obey the fixed ordering of states. Start by treating W as if it were E_n and reorder both sides of the equation simultaneously until they're in the correct sequence. We may then assume without loss of generality that the $E_1\cdots E_N$ are already ordered according to $E_1 < E_2 < \cdots < E_N$. Now, W is out of place and has to be moved into the correct position. If $W = E_n$, the problem is solved. The remaining cases introduce a phase factor. We pick up a factor of -1 each time W is swapped.

$$(-1)^{n_{W+1}+n_{W+2}+\cdots+n_{E_n-1}} \qquad \text{if } W < E_n \qquad (2.37)$$

$$(-1)^{n_{E_n+1}+n_{E_n+2}+\cdots+n_{W-1}} \qquad \text{if } W > E_n \qquad (2.38)$$

Remember that these states have a fixed ordering, so $E+1$ should be understood as the next state in the ordering. With this factor in mind, all the coefficients become ordered and may be expressed solely in terms of the state occupation number.

$$\begin{aligned} & i\hbar\frac{\partial}{\partial t}\bar{C}(n_1 n_2 \cdots n_\infty, t) \\ = & \sum_{n=1}^{N}\sum_{W>E_n}(-1)^{n_{E_n}+n_{E_n+1}+\cdots+n_{W-1}}\bar{C}(n_1 n_2 \cdots n_{E_n}-1\cdots n_W+1\cdots n_\infty, t)\langle E_n|\,T\,|W\rangle \\ + & \sum_{n=1}^{N}\sum_{W<E_n}(-1)^{n_W+n_{W+1}+\cdots+n_{E_n-1}}\bar{C}(n_1 n_2 \cdots n_{E_n}-1\cdots n_W+1\cdots n_\infty, t)\langle E_n|\,T\,|W\rangle \\ + & \sum_{n=1}^{N}\bar{C}(n_1 n_2 \cdots n_{E_n}\cdots n_\infty, t)\langle E_n|\,T\,|E_n\rangle + \text{interaction term.} \end{aligned} \tag{2.39}$$

There is still a summation over the index of the particles. This may be replaced by a sum over states $\sum_E$ if we specify the number of times n_E that the variable E_n has the value E, since they all contribute equally to the sum:

$$\sum_E\sum_{W>E}(-1)^{n_E+n_{E+1}+\cdots+n_{W-1}}\bar{C}(n_1 n_2 \cdots n_E-1\cdots n_W+1\cdots n_\infty, t)\langle E|\,T\,|W\rangle\, n_E. \tag{2.40}$$

Multiplying both sides of the equation by $\sqrt{\frac{N!}{n_1!\cdots n_\infty!}}$ allows us to bring in the $f(n_1 n_2 \cdots n_\infty, t)$ coefficients

$$\sum_E\sum_{W>E}(-1)^{n_E+n_{E+1}+\cdots+n_{W-1}}f(n_1 n_2 \cdots n_E-1\cdots n_W+1\cdots n_\infty, t)\sqrt{n_W+1}\sqrt{n_E}\langle E|\,T\,|W\rangle\,. \tag{2.41}$$

The other kinetic terms are analogous and the interaction terms follow a similar treatment. Since this work focuses on non-interacting systems, the emphasis falls into the non-interacting terms. All the explicit dependency on the specific particles has disappeared and only the number of particles in each state remains.

2.3.4 Occupation-number base

In the previous section, we were able to describe the system with regard only to the occupation number. This has very important repercussions. Because we are no longer able to tell which particle is which if both are in the same state, the number of particles in each state becomes enough to completely characterize the system. Furthermore, the Hamiltonian preserves the number of particles, so the occupation number basis is a perfectly valid one in which to describe the states. Notice that in the fermion case, if there are two states which are the same, C is automatically zero. This means there can be no more than one particle in each state and that Pauli's exclusion principle comes naturally from the anti-commutation relations! In fact, the indistinguishability

of the particles is enough to allow for the wave function to be expanded in a basis of completely symmetric (or anti-symmetric, in the case of fermions) wave functions. For bosons, the basis wave functions are

$$\Phi_{n_1,\cdots,n_\infty}(x_1,\cdots,x_N) = \sqrt{\frac{n_1!\cdots n_\infty!}{N!}} \sum \psi_{E_1}(x_1)\cdots\psi_{E_N}(x_N) \tag{2.42}$$

where the sum is over all the $E_1,\cdots,E_N$ compatible with the number of particles in each state $n_1,\cdots,n_\infty$. This is just the permutations of the E_i. For fermions, we need to fix an ordering for the states to fix the overall sign. Therefore, assuming we have already chosen an ordering, the anti-symmetric basis wave functions are built from a Slater determinant, as we've seen before.

$$\Phi_{n_1,\cdots,n_\infty}(x_1,\cdots,x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{E_1}(x_1) & \cdots & \psi_{E_1}(x_N) \\ \vdots & \vdots & \vdots \\ \psi_{E_N}(x_1) & \cdots & \psi_{E_N}(x_N) \end{vmatrix}. \tag{2.43}$$

These explicit constructions serve to illustrate the fact that there is a way to build the basis wave functions from the original single-particle states. But the important message here is that the occupation numbers are enough to completely characterize a system of bosons or fermions. Let us now define the occupation basis $\{|n_1\cdots n_\infty\rangle\}$. This is to be understood as a state with n_1 particles in state 1, n_2 particles in state 2 and so on. Due to the orthogonality of the single-particle states, these too are orthogonal, and will be chosen to be normalized to 1. This basis is complete because the occupation number alone is enough to determine the system, so this basis, like any good basis, satisfies the orthogonality relation

$$\langle n_1' n_2' \cdots n_\infty' | \, n_1 n_2 \cdots n_\infty \rangle = \delta_{n_1' n_1}\delta_{n_2' n_2}\cdots\delta_{n_\infty' n_\infty} \tag{2.44}$$

and the closure relation

$$\sum_{n_1 n_2 \cdots n_\infty} |n_1 n_2 \cdots n_\infty\rangle \langle n_1 n_2 \cdots n_\infty| = 1. \tag{2.45}$$

As an example, we've already explicitly calculated a completely anti-symmetric wave function for the case $N = 3$ with particles in states 1, 3 and 4 (see eq. 2.29). In this new basis, it is simply expressed as $|10110\cdots0\rangle$. In fact, in the position representation,

$$\Phi_{n_1,\cdots,n_\infty}(x_1,\cdots,x_N) = \sqrt{\frac{n_1!\cdots n_\infty!}{N!}} \begin{vmatrix} \psi_{E_1}(x_1) & \cdots & \psi_{E_1}(x_N) \\ \vdots & \vdots & \vdots \\ \psi_{E_N}(x_1) & \cdots & \psi_{E_N}(x_N) \end{vmatrix} = \langle x_1 x_2 \cdots x_N | \, n_1 \cdots n_\infty \rangle . \tag{2.46}$$

Now we need a way to decrease or increase the number of particles in each state, and this will be different for bosons and fermions. Since the systems in this work consist of fermions, we'll

focus on the latter case. Define the fermion destruction and creation operators (also called ladder operators) a_i and $a_i^\dagger$, respectively, which satisfy the following anti-commutation relations:

$$\left\{a_i^\dagger, a_j\right\} = \delta_{ij} \tag{2.47}$$

$$\{a_i, a_j\} = 0 \tag{2.48}$$

$$\left\{a_i^\dagger, a_j^\dagger\right\} = 0. \tag{2.49}$$

There relations alone don't do anything. By further requiring that their product yields the number operator $\hat{n}_i = a_i^\dagger a_i$ we are able to define their action on the states. The number operator is defined by returning the number of particles in the state i when applied to a general state $|n_1 \cdots n_\infty\rangle$ as such: $\hat{n}_i |n_1 \cdots n_\infty\rangle = n_i |n_1 \cdots n_\infty\rangle$. It is perfectly well defined since we already know that the Hamiltonian preserves the number of particles. In fact, the association of the creation and destruction operators with the number operator seems fortuitous because

$$\hat{n}_i^2 = \left(a_i^\dagger a_i\right)^2 = a_i^\dagger a_i = \hat{n}_i. \tag{2.50}$$

This shows that n_i can only have eigenvalues 1 or 0, as is expected for fermions, and that is now a direct consequence of the properties of the ladder operators. Furthermore, these properties alone are enough to completely determine their action on a general state. For example, take the action of a creation operator in a state which is already filled:

$$a_i^\dagger |1_i\rangle = a_i^\dagger n_i |1_i\rangle = a_i^\dagger a_i^\dagger a_i |1_i\rangle = 0. \tag{2.51}$$

This means we cannot add a particle in state i to the system if one already exists! Similar considerations yield the action of both these operators in single particle states

$$a_i^\dagger |1_i\rangle = 0 \tag{2.52}$$

$$a_i^\dagger |0_i\rangle = |1_i\rangle \tag{2.53}$$

$$a_i |1_i\rangle = |0_i\rangle \tag{2.54}$$

$$a_i |0_i\rangle = 0. \tag{2.55}$$

This allows us to define any state only in terms of the creation and annihilation operators. Recall that a fixed order for the $a_i^\dagger$ is induced from the ordering chosen for the Slater determinant. The general state is written as

$$|n_1 n_2 \cdots n_\infty\rangle = \left(a_1^\dagger\right)^{n_1} \left(a_2^\dagger\right)^{n_2} \cdots \left(a_\infty^\dagger\right)^{n_\infty} |0\rangle \tag{2.56}$$

where $|0\rangle$ is the vacuum, a state without any particles. How do these operators act on a general state? Let's apply a_i to $|n_1 n_2 \cdots n_\infty\rangle$. This operator will anti-commute with all the a_j and $a_j^\dagger$ that appear before $a_i^\dagger$ so we pick up a phase factor $(-1)^{S_i}$ where $S_i = n_1 + \cdots + n_{i-1}$.

$$a_i \left|n_1 n_2 \cdots n_i \cdots n_\infty\right\rangle = (-1)^{S_i} \left(a_1^\dagger\right)^{n_1} \left(a_2^\dagger\right)^{n_2} \cdots a_i \left(a_i^\dagger\right)^{n_i} \cdots \left(a_\infty^\dagger\right)^{n_\infty} |0\rangle \,. \tag{2.57}$$

If $n_i = 0$, then a_i can be anti-commuted all the way to the vacuum where it gives zero, so $a_i \left|n_1 n_2 \cdots 0_i \cdots n_\infty\right\rangle = 0$. Otherwise, we get $a_i a_i^\dagger = 1 - a_i^\dagger a_i$ and we may apply the same reasoning to yield zero in the second term. The first term remains, so

$$a_i \left|n_1 n_2 \cdots 1_i \cdots n_\infty\right\rangle = (-1)^{S_i} \left(a_1^\dagger\right)^{n_1} \left(a_2^\dagger\right)^{n_2} \cdots \left(a_i^\dagger\right)^{0} \cdots \left(a_\infty^\dagger\right)^{n_\infty} |0\rangle = (-1)^{S_i} \left|n_1 n_2 \cdots 0_i \cdots n_\infty\right\rangle . \tag{2.58}$$

Similar reasoning works for $a_i^\dagger$, so in summary

$$\begin{aligned}
a_i \left|n_1 n_2 \cdots 1_i \cdots n_\infty\right\rangle &= (-1)^{S_i} \sqrt{n_i} \left|n_1 n_2 \cdots 0_i \cdots n_\infty\right\rangle && (2.59)\\
a_i \left|n_1 n_2 \cdots 0_i \cdots n_\infty\right\rangle &= 0 && (2.60)\\
a_i^\dagger \left|n_1 n_2 \cdots 0_i \cdots n_\infty\right\rangle &= (-1)^{S_i} \sqrt{n_i + 1} \left|n_1 n_2 \cdots 1_i \cdots n_\infty\right\rangle && (2.61)\\
a_i^\dagger \left|n_1 n_2 \cdots 1_i \cdots n_\infty\right\rangle &= 0. && (2.62)
\end{aligned}$$

The square root terms here are actually irrelevant, but were only placed to appeal to the similarity between the fermion and the boson cases. These relations further imply the known properties of the number operator acting on an empty state

$$\hat{n}_i \left|n_1 n_2 \cdots 0_i \cdots n_\infty\right\rangle = a_i^\dagger a_i \left|n_1 n_2 \cdots 0_i \cdots n_\infty\right\rangle = 0 \tag{2.63}$$

and on a filled state

$$\begin{aligned}
\hat{n}_i \left|n_1 n_2 \cdots 1_i \cdots n_\infty\right\rangle &= (-1)^{S_i} a_i^\dagger \left|n_1 n_2 \cdots 0_i \cdots n_\infty\right\rangle \\
&= (-1)^{2S_i} \left|n_1 n_2 \cdots 1_i \cdots n_\infty\right\rangle = \left|n_1 n_2 \cdots 1_i \cdots n_\infty\right\rangle . && (2.64)
\end{aligned}$$

This gives the expected result for the number operator for a general state

$$\hat{n}_i \left|n_1 n_2 \cdots n_i \cdots n_\infty\right\rangle = n_i \left|n_1 n_2 \cdots n_i \cdots n_\infty\right\rangle . \tag{2.65}$$

All this effort will now pay off because the second-quantized Hamiltonian will have a very simple form.

2.3.5 Back to Schrödinger's equation

Now we want to express Schrödinger's equation in terms of these vectors. As we've seen, any boson or fermion wave function can be expanded in terms of them:

$$|\psi(t)\rangle = \sum_{n_1 \cdots n_\infty} f(n_1 \cdots n_\infty, t) \left|n_1 n_2 \cdots n_\infty\right\rangle . \tag{2.66}$$

The time dependency falls into the coefficients because the single particle wave functions do

not change. Applying the Schrödinger equation to this, we get for the kinetic term

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle &= \sum_{n_1\cdots n_\infty}\sum_{E}\sum_{E<W}(-1)^{n_{E+1}+\cdots+n_{W-1}}f(n_1n_2\cdots n_E-1\cdots n_W+1\cdots n_\infty,t) \\ &\quad\times\delta_{n_E,1}\delta_{n_W,0}\sqrt{n_W+1}\sqrt{n_E}\left\langle E\right|T\left|W\right\rangle\left|n_1n_2\cdots n_\infty\right\rangle+\cdots. \end{aligned} \tag{2.67}$$

The Kronecker deltas have been introduced to assert the fact that the occupation number can only be 0 or 1. Allow for the change of notation $E=i$, $W=j$:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle &= \sum_{n_1\cdots n_\infty}\sum_{i<j}(-1)^{n_{i+1}+\cdots+n_{j-1}}f(n_1n_2\cdots n_i-1\cdots n_j+1\cdots n_\infty,t) \\ &\quad\times\delta_{n_i,1}\delta_{n_j,0}\sqrt{n_j+1}\sqrt{n_i}\left\langle i\right|T\left|j\right\rangle\left|n_1n_2\cdots n_\infty\right\rangle+\cdots. \end{aligned} \tag{2.68}$$

and relabeling $n_i'=n_i-1$, $n_j'=n_j+1$, $n_k'=n_k$:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle &= \sum_{n_1'\cdots n_\infty'}\sum_{i<j}(-1)^{n_{i+1}'+\cdots+n_{j-1}'}f(n_1'n_2'\cdots n_i'\cdots n_j'\cdots n_\infty',t) \\ &\quad\delta_{n_i',0}\delta_{n_j',1}\sqrt{n_j'}\sqrt{n_i'+1}\left\langle i\right|T\left|j\right\rangle\left|n_1'n_2'\cdots n_i'+1\cdots n_j'-1\cdots n_\infty\right\rangle+\cdots. \end{aligned} \tag{2.69}$$

In light of the calculations done in the previous section, let's express the state vector in terms of the creation and annihilation operators, assuming $j>i$:

$$\begin{aligned} a_i^\dagger a_j\left|n_1'n_2'\cdots n_i'\cdots n_j'\cdots n_\infty'\right\rangle &= (-1)^{S_i}\sqrt{n_j}a_i^\dagger\left|n_1'n_2'\cdots n_i'\cdots n_j'-1\cdots n_\infty'\right\rangle \\ &= (-1)^{S_j}\sqrt{n_j}(-1)^{S_i}\sqrt{n_i+1}\left|n_1'n_2'\cdots n_i'+1\cdots n_j'-1\cdots n_\infty'\right\rangle. \end{aligned} \tag{2.70}$$

The phase factors actually simplify, because $(-1)^{2n_i}=1$, so repeated factors in $S=S_i+S_j$ do not contribute. This means

$$(-1)^{S_i+S_j}=(-1)^{(n_1'+\cdots+n_{i-1}')+(n_1'+\cdots+n_{j-1}')}=(-1)^{n_i'+n_{i+1}'\cdots+n_{j-2}'+n_{j-1}'} \tag{2.71}$$

Furthermore if $n_i'=1$, we get no contribution from $a_i^\dagger a_j\left|n_1'n_2'\cdots n_i'\cdots n_j'\cdots n_\infty'\right\rangle=0$, so we might as well use $n_i'=0$, simplifying the phase factor to $(-1)^{n_{i+1}'\cdots+n_{j-2}'+n_{j-1}'}$. Eq. 2.70 takes the form:

$$\begin{aligned} &a_i^\dagger a_j\left|n_1'n_2'\cdots n_i'\cdots n_j'\cdots n_\infty'\right\rangle \\ &\quad=\delta_{n_i',0}\delta_{n_j',1}(-1)^{n_{i+1}'\cdots+n_{j-2}'+n_{j-1}'}\sqrt{n_j}\sqrt{n_i+1}\left|n_1'n_2'\cdots n_i'+1\cdots n_j'-1\cdots n_\infty'\right\rangle. \end{aligned} \tag{2.72}$$

This fits like a glove in Schrödinger's equation.

Rewriting 2.69 in terms of the creation and annihilation operators, we are able to factorize $|\psi(t)\rangle$ and obtain a very compact expression:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle &= \sum_{n'_1\cdots n'_\infty}\sum_{i<j} f(n'_1 n'_2\cdots n'_i\cdots n'_j\cdots n'_\infty,t)\,\langle i|\,T\,|j\rangle\, a_i^\dagger a_j\,|n'_1 n'_2\cdots n'_i\cdots n'_j\cdots n_\infty\rangle+\cdots \\ &= \sum_{i<j}\langle i|\,T\,|j\rangle\, a_i^\dagger a_j \sum_{n'_1\cdots n'_\infty} f(n'_1 n'_2\cdots n'_i\cdots n'_j\cdots n'_\infty,t)\,|n'_1 n'_2\cdots n'_i\cdots n'_j\cdots n_\infty\rangle+\cdots \\ &= \sum_{i<j}\langle i|\,T\,|j\rangle\, a_i^\dagger a_j\,|\psi(t)\rangle+\cdots. \end{aligned} \tag{2.73}$$

A similar argument holds for the remaining cases and for the interaction V so the full expression of the Hamiltonian in second quantization is

$$H=\sum_{ij}\langle i|\,T\,|j\rangle\, a_i^\dagger a_j+\frac{1}{2}\sum_{ijkl}\langle ij|\,V\,|kl\rangle\, a_i^\dagger a_j^\dagger a_l a_k. \tag{2.74}$$

The Hamiltonian has a very simple form and suggests a simple interpretation. The term $\langle i|\,T\,|j\rangle\, a_i^\dagger a_j$ may be understood as a particle in state j being destroyed while a particle in state i is created, while the coefficient is the transition probability.

2.3.6 Fermion Fields

There is another way to express the Hamiltonian in second quantization if we know the ladder operators in a particular basis. Define the field operators

$$\hat{\psi}^\dagger(\vec{x})=\sum_k \psi_k^*(\vec{x})c_k^\dagger \tag{2.75}$$

$$\hat{\psi}(\vec{x})=\sum_k \psi_k(\vec{x})c_k \tag{2.76}$$

where the ψ_k are the single particle wave functions of the states k and the c_k and $c_k^\dagger$ are their respective annihilation and creation operators. Their algebra follows from that of c_k and $c_k^\dagger$. This is valid for both bosons and fermions.

$$\begin{aligned} \left[\hat{\psi}(\vec{x}),\hat{\psi}^\dagger(\vec{x}')\right]_\mp &= \sum_{kk'}\psi_k(\vec{x})\psi_{k'}^*(\vec{x'})\left[c_k,c_{k'}^\dagger\right]_\mp=\sum_k\psi_k(\vec{x})\psi_k^*(\vec{x'})=\delta(\vec{x}-\vec{x}') \\ \left[\hat{\psi}(\vec{x}),\hat{\psi}(\vec{x}')\right]_\mp &= \sum_{kk'}\psi_k(\vec{x})\psi_{k'}^*(\vec{x'})\left[c_k,c_{k'}\right]_\mp=0. \end{aligned}$$

The lower sign refers to the anti-commutator of fermion operators and the upper sign to the commutator of boson operators. The last equality follows from the completeness of the wave functions ψ_k. These operators allow us to write the second-quantized Hamiltonian in a more

suggestive way:

$$H = \int d^3x \hat{\psi}^\dagger(\vec{x}) T(\vec{x}) \hat{\psi}(\vec{x}) + \frac{1}{2} \int \int d^3x d^3x' \hat{\psi}^\dagger(\vec{x}) \hat{\psi}^\dagger(\vec{x'}) V(\vec{x}, \vec{x}') \hat{\psi}(\vec{x}') \hat{\psi}(\vec{x}). \tag{2.77}$$

Let us verify that this is the same expression as 2.74. Unwinding the definitions,

$$\int d^3x \hat{\psi}^\dagger(\vec{x}) T(\vec{x}) \hat{\psi}(\vec{x}) = \int d^3x \sum_i \psi_i^*(\vec{x}) c_i^\dagger T(\vec{x}) \sum_j \psi_j(\vec{x}) c_j = \sum_{ij} \left(\int d^3x \psi_i^*(\vec{x}) T(\vec{x}) \psi_j(\vec{x}) \right) c_i^\dagger c_j. \tag{2.78}$$

Letting $\langle i | T | j \rangle = \int d^3x \psi_i^*(\vec{x}) T(\vec{x}) \psi_j(\vec{x})$ we obtain precisely the same kinetic term and the interaction term can also be shown to yield the expected result. We have merely re-written the Hamiltonian in the context of a field theory.

2.3.7 Current in second quantization

The primary object of study in this work is the conductivity $\sigma(t)$, which is the response coefficient of the current with respect to the electric field:

$$J^\alpha(t) = \int_{-\infty}^{\infty} dt_1 \sigma_1^{\alpha\beta}(t - t_1) E^\beta(t_1) + \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \sigma_2^{\alpha\beta\gamma}(t - t_1, t - t_2) E^\beta(t_1) E^\gamma(t_2) + O(E^3). \tag{2.79}$$

So, in order to find the conductivity we must first define the current. Consider the Hamiltonian with an electromagnetic field in second quantization in terms of fermion fields:

$$H = \int d^3\boldsymbol{x} \hat{\psi}^\dagger(\boldsymbol{x}) \left[\frac{\hbar^2}{2m} \left(\frac{\boldsymbol{\nabla}}{i} + \frac{e}{\hbar} \boldsymbol{A}(\boldsymbol{x}, t) \right)^2 + V(\boldsymbol{x}) - e\phi(\boldsymbol{x}, t) \right] \hat{\psi}(\boldsymbol{x}). \tag{2.80}$$

Expand this to unravel the powers of $\boldsymbol{A}(\boldsymbol{x}, t)$:

$$\begin{aligned} H &= \int d^3\boldsymbol{x} \hat{\psi}^\dagger(\boldsymbol{x}) \left[-\frac{\hbar^2}{2m} \boldsymbol{\nabla}^2 + V(\boldsymbol{x}) \right] \hat{\psi}(\boldsymbol{x}) + \frac{e^2}{2m} \int d^3\boldsymbol{x} \hat{\psi}^\dagger(\boldsymbol{x}) \boldsymbol{A}(\boldsymbol{x}, t)^2 \hat{\psi}(\boldsymbol{x}) \\ &+ \frac{e\hbar}{2im} \int d^3\boldsymbol{x} \left[\hat{\psi}^\dagger(\boldsymbol{x}) \left(\boldsymbol{A}(\boldsymbol{x}, t) \cdot \boldsymbol{\nabla} \hat{\psi}(\boldsymbol{x}) \right) + \hat{\psi}^\dagger(\boldsymbol{x}) \boldsymbol{\nabla} \cdot \left(\boldsymbol{A}(\boldsymbol{x}, t) \hat{\psi}(\boldsymbol{x}) \right) \right] - e \int d^3\boldsymbol{x} \phi(\boldsymbol{x}, t) \hat{\psi}^\dagger(\boldsymbol{x}) \hat{\psi}(\boldsymbol{x}). \end{aligned}$$

Now perform an integration by parts to remove the divergence operator from $\boldsymbol{A}$ and disregard the term which is a total divergence since we may consider the fields to fall off sufficiently rapidly at infinity. The Hamiltonian splits into two parts: the Hamiltonian in zero field H_0

$$H_0 = \int d^3\boldsymbol{x} \hat{\psi}^\dagger(\boldsymbol{x}) \left[-\frac{\hbar^2}{2m} \boldsymbol{\nabla}^2 + V(\boldsymbol{x}) \right] \hat{\psi}(\boldsymbol{x}) \tag{2.81}$$

and the interaction $H_{\boldsymbol{A}}$

$$H_{\boldsymbol{A}} = \frac{\hbar^2}{2m}\int d^3\boldsymbol{x}\left\{-i\left[\hat{\psi}^\dagger(\boldsymbol{x})\boldsymbol{\nabla}\hat{\psi}(\boldsymbol{x}) - \left(\boldsymbol{\nabla}\hat{\psi}^\dagger(\boldsymbol{x})\right)\hat{\psi}(\boldsymbol{x})\right]\cdot\frac{e}{\hbar}\boldsymbol{A}(\boldsymbol{x},t) + \frac{e^2}{\hbar^2}\boldsymbol{A}^2(\boldsymbol{x},t)\hat{\psi}^\dagger(\boldsymbol{x})\hat{\psi}(\boldsymbol{x})\right\} \tag{2.82}$$

We may define this to be a coupling to the zero-field Hamiltonian by introducing the current operator as a functional derivative of $H_{\boldsymbol{A}}$. Let

$$\boldsymbol{J}_{\boldsymbol{A}}(\boldsymbol{x},t) = -\frac{\delta H}{\delta \boldsymbol{A}(\boldsymbol{x},t)} \tag{2.83}$$

$$\rho(\boldsymbol{x},t) = -\frac{\delta H}{\delta \phi(\boldsymbol{x},t)}. \tag{2.84}$$

Applying this to $H_{\boldsymbol{A}}$, we get the familiar expression for the current operator

$$\boldsymbol{J}_{\boldsymbol{A}}(\boldsymbol{x},t) = -\frac{e}{V}\frac{\hbar}{2mi}\left[\hat{\psi}^\dagger(\boldsymbol{x})\vec{\nabla}\hat{\psi}(\boldsymbol{x}) - \left(\boldsymbol{\nabla}\hat{\psi}^\dagger(\boldsymbol{x})\right)\hat{\psi}(\boldsymbol{x})\right] - \frac{e^2}{mV}\boldsymbol{A}(\boldsymbol{x},t)\hat{\psi}^\dagger(\boldsymbol{x})\hat{\psi}(\boldsymbol{x}) \tag{2.85}$$

Now that we have defined the operator of interest, let's consider the case of a homogeneous electric field $\boldsymbol{E}(t)$. This can be obtained from the minimal coupling if we choose a homogeneous gauge field $\boldsymbol{A}(t)$ such that $\boldsymbol{E}(t) = -\frac{\partial \boldsymbol{A}(t)}{\partial t}$. $\boldsymbol{A}$ may therefore be removed from the integral in $\boldsymbol{x}$:

$$\begin{aligned} H &= \int d^3\boldsymbol{x}\hat{\psi}^\dagger(\boldsymbol{x})\left[-\frac{\hbar^2}{2m}\boldsymbol{x}^2 + V(\boldsymbol{x})\right]\hat{\psi}(\boldsymbol{x}) + \frac{e^2}{2m}\boldsymbol{A}(\boldsymbol{x},t)^2\int d^3\boldsymbol{x}\hat{\psi}^\dagger(\boldsymbol{x})\hat{\psi}(\boldsymbol{x}) \\ &+ \frac{e\hbar}{2im}\int d^3\boldsymbol{x}\left[\hat{\psi}^\dagger(\boldsymbol{x})\boldsymbol{\nabla}\hat{\psi}(\boldsymbol{x}) + \hat{\psi}^\dagger(\boldsymbol{x})\boldsymbol{\nabla}\hat{\psi}(\boldsymbol{x})\right]\cdot\boldsymbol{A}(t). \end{aligned}$$

The functional derivative becomes a simple derivative of H with respect to $\boldsymbol{A}$

$$\boldsymbol{J}_{\boldsymbol{A}}(\boldsymbol{x},t) = -\frac{e}{V}\frac{\hbar}{2mi}\left[\hat{\psi}^\dagger(\boldsymbol{x})\boldsymbol{\nabla}\hat{\psi}(\boldsymbol{x}) - \left(\boldsymbol{\nabla}\hat{\psi}^\dagger(\boldsymbol{x})\right)\hat{\psi}(\boldsymbol{x})\right] - \frac{e^2}{mV}\boldsymbol{A}(t)\hat{\psi}^\dagger(\boldsymbol{x})\hat{\psi}(\boldsymbol{x}). \tag{2.86}$$

Replace ψ by the creation and annihilation operators and integrate over $\boldsymbol{x}$

$$\begin{aligned} \boldsymbol{J}_{\boldsymbol{A}}(t) = \frac{1}{V}\int d^3\boldsymbol{x}\boldsymbol{J}_{\boldsymbol{A}}(\boldsymbol{x},t) &= -\frac{e}{2V}\sum_{nm}c_n^\dagger c_m\int d^3\boldsymbol{x}\left[\psi_n^*(\boldsymbol{x})\left(\frac{\hbar}{i}\frac{\boldsymbol{\nabla}}{m}\psi_m(\boldsymbol{x})\right) - \left(\frac{\hbar}{i}\frac{\boldsymbol{\nabla}}{m}\psi_n^*(\boldsymbol{x})\right)\psi_m(\boldsymbol{x})\right] \\ &\quad -\frac{e^2}{mV}\boldsymbol{A}(t)\sum_{nm}c_n^\dagger c_m\int d^3\boldsymbol{x}\psi_n^*(\boldsymbol{x})\psi_m(\boldsymbol{x}) \end{aligned}$$

Using the normalization of the wave functions and defining the velocity operator

$$\boldsymbol{v}_{nm} = \int d^3\boldsymbol{x}\left[\int\psi_n^*(\boldsymbol{x})\left(\frac{\hbar}{i}\frac{\boldsymbol{\nabla}}{m}\psi_m(\boldsymbol{x})\right) - \psi_m(\boldsymbol{x})\left(\frac{\hbar}{i}\frac{\boldsymbol{\nabla}}{m}\psi_n^*(\boldsymbol{x})\right)\right] \tag{2.87}$$

we arrive at

$$\boldsymbol{J_A}(t) = -\frac{e}{V}\sum_{nm} \boldsymbol{v}_{nm} c_n^\dagger c_m - \frac{e^2}{mV}\boldsymbol{A}(t)N \tag{2.88}$$

This is the expression of the current using the minimal coupling procedure. The current may also be obtained in the $\boldsymbol{E}$ formalism through a Gauge transformation on the current in minimal coupling [3, Chapter 2]

$$\boldsymbol{J_E}(t) = -\frac{e}{V}\sum_{nm} \boldsymbol{v}_{nm} c_n^\dagger c_m \tag{2.89}$$

It is important to note that the current operators are different, but their expected values are the same. That's to be expected because the final result cannot depend on the Gauge.

2.4 Schrödinger, Heisenberg and Interaction pictures

Here we explore the three main pictures of Quantum Mechanics, which will play a fundamental role in developing a perturbation expansion for the systems that we're studying.

2.4.1 Schrödinger Picture

In the usual description of Quantum Mechanics, we define wave functions whose time evolution is given by Schrödinger's equation:

$$i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle = H\left|\psi(t)\right\rangle. \tag{2.90}$$

We define the time evolution operator to be the relation between the wave function at a time t_0 and at a later time t:

$$\left|\psi(t)\right\rangle = U(t,t_0)\left|\psi(t_0)\right\rangle. \tag{2.91}$$

Furthermore, when we want to calculate expected values and transition probabilities, we make use of operators which act on the wave functions. These may be explicitly time-dependent, but their time evolution is not regulated by the quantum system itself, so they do not have an equation of motion. Time is just an external parameter. Usually, these are the observables of the system, such as the position or momentum. This is the so-called Schrödinger picture of Quantum Mechanics. The evolution of the system relies on the time dependency of the wave functions, while the operators are usually constant in time.

2.4.2 Interaction picture

Here we consider a different stance. We're going to assume we already know how to solve some part of the problem and try to use that to simplify the full problem. We want to achieve a separation of the solvable Hamiltonian H_0 and the perturbation $V(t)$ in the time evolution of the system. Consider a general Hamiltonian H which may depend explicitly on time and that can be written as the sum of an exactly solvable time-independent Hamiltonian H_0 and a (possibly) time-dependent perturbation $V(t)$:

$$H(t) = H_0 + V(t). \tag{2.92}$$

Its time evolution is given by Schrödinger's equation:

$$i\hbar\frac{\partial}{\partial t}\left|\psi_S(t)\right\rangle = H(t)\left|\Psi_S(t)\right\rangle = \left(H_0 + V(t)\right)\left|\psi_S(t)\right\rangle \tag{2.93}$$

where the subscript in ψ_S denotes the Schrödinger Picture. We're going to incorporate the fact that we already know how to solve H_0 by considering a set of transformations on both the wave functions and the operators. This simultaneous transformation guarantees that the expected values are unchanged:

$$\begin{aligned} \left|\psi_I(t)\right\rangle &= e^{i\frac{H_0 t}{\hbar}}\left|\psi_S(t)\right\rangle \qquad \text{wave functions} \\ A_I(t) &= e^{i\frac{H_0 t}{\hbar}} A_S e^{-i\frac{H_0 t}{\hbar}} \qquad \text{operators.} \end{aligned} \tag{2.94}$$

The subscript I in ψ_I denotes the Interaction Picture. This gives us an equation of motion for the new operators:

$$-i\hbar\frac{\partial}{\partial t}A_I(t) = e^{iH_0(t-t_0)/\hbar}\left[H_0, A_S\right]e^{-iH_0(t-t_0)/\hbar} = \left[H_0, A_I(t)\right]. \tag{2.95}$$

and for the new wave functions

$$i\hbar\frac{\partial}{\partial t}\left|\psi_I(t)\right\rangle = V_I(t)\left|\psi_I(t)\right\rangle. \tag{2.96}$$

2.4.2.1 Time evolution operator

This last expression lends itself to a formal solution by integrating both sides of the equation in time from t_0 to t:

$$i\hbar\int_{t_0}^{t}\frac{\partial}{\partial t}\left|\psi_I(t)\right\rangle dt = \int_{t_0}^{t} V_I(t)\left|\psi_I(t)\right\rangle dt. \tag{2.97}$$

Unwinding this, we get a self-consistent equation for $|\Psi_I(t)\rangle$:

$$|\psi_I(t)\rangle = |\Psi_I(t_0)\rangle + \frac{1}{i\hbar}\int_{t_0}^{t} V_I(t_1)\,|\psi_I(t_1)\rangle\,dt_1. \tag{2.98}$$

Note how $|\Psi_I(t)\rangle$ appears in the right side of the equation again. It remains valid to insert this same expression back again in the integral:

$$\begin{aligned} |\psi_I(t)\rangle &= |\psi_I(t_0)\rangle + \frac{1}{i\hbar}\int_{t_0}^{t} V_I(t_1)\left[|\psi_I(t_0)\rangle + \frac{1}{i\hbar}\int_{t_0}^{t_1} V_I(t_2)\,|\Psi_I(t_2)\rangle\,dt_2\right]dt_1 \\ &= |\psi_I(t_0)\rangle + \frac{1}{i\hbar}\int_{t_0}^{t} dt_1 V_I(t_1)\,|\psi_I(t_0)\rangle + \left(\frac{1}{i\hbar}\right)^2\int_{t_0}^{t} dt_1\int_{t_0}^{t_1} dt_2 V_I(t_1)V_I(t_2)\,|\psi_I(t_2)\rangle\,. \end{aligned} \tag{2.99}$$

If we keep doing this, we'll obtain a series in powers of V_I at different times. Assuming that this series converges if we keep doing this to infinity, we obtain an expression that only depends on the initial wave function $|\psi_I(t_0)\rangle$ and V_I:

$$\begin{aligned} |\psi_I(t)\rangle &= |\psi_I(t_0)\rangle + \frac{1}{i\hbar}\int_{t_0}^{t} dt_1 V_I(t_1)\,|\psi_I(t_0)\rangle + \left(\frac{1}{i\hbar}\right)^2\int_{t_0}^{t} dt_1\int_{t_0}^{t_1} dt_2 V_I(t_1)V_I(t_2)\,|\psi_I(t_0)\rangle \\ &\quad + \left(\frac{1}{i\hbar}\right)^3\int_{t_0}^{t} dt_1\int_{t_0}^{t_1} dt_2\int_{t_0}^{t_2} dt_3 V_I(t_1)V_I(t_2)V_I(t_3)\,|\psi_I(t_0)\rangle + \cdots. \end{aligned} \tag{2.100}$$

Let's focus our attention on the second term. We can cast it into a more symmetric form by changing the order of integration and relabeling the integration variables:

$$\int_{t_0}^{t} dt_1\int_{t_0}^{t_1} dt_2 V_I(t_1)V_I(t_2) = \int_{t_0}^{t} dt_2\int_{t_1}^{t} dt_1 V_I(t_1)V_I(t_2) = \int_{t_0}^{t} dt_1\int_{t_1}^{t} dt_2 V_I(t_2)V_I(t_1). \tag{2.101}$$

Notice that in the left expression $t_2 < t_1$ and in the right one $t_2 > t_1$ and also that the order of the operators was swapped. This can be neatly taken into account by defining the time-ordering operator, which acts on a set of operators by ordering them according to their time label:

$$T\{A(t_1)A(t_2)\} = \begin{cases} A(t_1)A(t_2) & \text{if } t_1 > t_2 \\ \pm A(t_2)A(t_1) & \text{if } t_1 < t_2. \end{cases} \tag{2.102}$$

The upper sign refers to boson operators and the lower one to fermion operators. Now, for bosons, the equation reads

$$\int_{t_0}^{t} dt_1\int_{t_0}^{t_1} dt_2 T\{V_I(t_1)V_I(t_2)\} = \int_{t_0}^{t} dt_1\int_{t_1}^{t} dt_2 T\{V_I(t_1)V_I(t_2)\}. \tag{2.103}$$

This yields no loss of generality because these interaction operators consist of an even number of creation/annihilation operators, which acts as a boson operator under time ordering. These are just integrations over different halves of the t_1t_2 plane, and they're exactly the same! Therefore,

if we sum them and divide by two, we get exactly the same result, but now the integrals run all the way from t_0 to t:

$$\begin{aligned}\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 T\{V_I(t_1)V_I(t_2)\} &= \frac{1}{2}\left[\int_{t_0}^{t} dt_1 \int_{t_1}^{t} dt_2 T\{V_I(t_1)V_I(t_2)\} + \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 T\{V_I(t_1)V_I(t_2)\}\right] \\ &= \frac{1}{2}\int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 T\{V_I(t_1)V_I(t_2)\}. \end{aligned} \tag{2.104}$$

This argument may be generalized for all the following orders of the expansion and we get the Dyson series of $V_I(t)$:

$$\begin{aligned}|\psi_I(t)\rangle &= \left[1 + \frac{-i}{\hbar}\int_{t_0}^{t} dt_1 T\left\{V_I(t_1)\right\} + \frac{1}{2!}\left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 T\left\{V_I(t_1)V_I(t_2)\right\}\right. \\ &\left. + \frac{1}{n!}\left(\frac{-i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \cdots \int_{t_0}^{t} dt_n T\left\{V_I(t_1)\cdots V_I(t_n)\right\} + \cdots\right] |\psi_I(t_0)\rangle\,. \end{aligned} \tag{2.105}$$

The time ordering operator may be factored out, which means that this series may be represented by

$$|\psi_I(t)\rangle = T\left\{\exp\left(\frac{-i}{\hbar}\int_{t_0}^{t} dt V_I(t)\right)\right\} |\psi_I(t_0)\rangle\,. \tag{2.106}$$

This is to be understood as no more than the series expansion derived previously. However, it does have one very important property. Note that for fermions or bosons

$$T\left\{[c_1(t_1), c_2(t_2)]_{\mp}\right\} = T\left\{c_1(t_1)c_2(t_2) \mp c_2(t_2)c_1(t_1)\right\} = T\left\{c_1(t_1)c_2(t_2)\right\} \mp T\left\{c_2(t_2)c_1(t_1)\right\} = 0. \tag{2.107}$$

This means that while considered inside the time ordering operator, we need not care about commutators/anticommutators for bosons and fermions respectively. Therefore, the product of exponentials reduces to the exponential of the sum. Using this formal solution, we can define the time evolution operator as

$$S(t, t_0) = T\left\{\exp\left(\frac{-i}{\hbar}\int_{t_0}^{t} dt V_I(t)\right)\right\}. \tag{2.108}$$

This expression was derived under the assumption $t > t_0$. In order to accommodate for results that will be obtained later on, we also need the case $t < t_0$. In that case, this deduction follows the exact same lines if we define the anti-time ordering operator, which does exactly what its name suggests. Therefore,

$$S(t < t_0, t_0) = \tilde{T}\left\{\exp\left(\frac{-i}{\hbar}\int_{t}^{t_0} d\tau V_I^{ext}(\tau)\right)\right\}. \tag{2.109}$$

It has the same formal expression as the regular time evolution operator, except for the limits of integration and the anti-time ordering operator instead of the time-ordering one.

2.4.2.2 Density matrix

In general, we do not know the form of the density matrix after the time-dependent interaction is turned on at $t = t_0$, because the system is no longer in equilibrium so it will no longer be $e^{-\beta H}$. However, we may find its time evolution and relate it with its expression at a time prior to the interaction since we know how the states evolve.

$$\begin{aligned} \rho_I(t) &= \sum_n p_n \left|n_I(t)\right\rangle \left\langle n_I(t)\right| = \sum_n p_n S(t,t_0) \left|n_I(t_0)\right\rangle \left\langle n_I(t_0)\right| S^\dagger(t,t_0) \\ &= S(t,t_0)\rho_I(t_0)S^\dagger(t,t_0) \end{aligned} \tag{2.110}$$

This is the density matrix in the Interaction Picture.

2.4.3 Heisenberg Picture

The Heisenberg picture takes the polar opposite stance of the Schrödinger picture. The wave functions are constant in time, while all the time dependency is left to the operators. This is used implicitly in second quantization, since each state is actually built by the creation operators acting on the vacuum, which is time independent. Take the evolution operator in the Schrödinger picture:

$$\left|\psi_S(t)\right\rangle = U(t,t_0)\left|\psi_S(t_0)\right\rangle . \tag{2.111}$$

Since $\left|\psi_S(t)\right\rangle$ satisfies the Schrödinger equation, $U(t,t_0)$ satisfies

$$i\hbar\frac{\partial}{\partial t}U(t,t_0) = H(t)U(t,t_0). \tag{2.112}$$

This equation can be integrated to yield

$$U(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} dt_1 H(t_1)U(t_1,t_0). \tag{2.113}$$

Just like in the Interaction picture, this procedure can be iterated to give a series expansion of the evolution operator.

$$U(t,t_0) = T\left\{\exp\left(\frac{-i}{\hbar}\int_{t_0}^{t} dt H(t)\right)\right\}. \tag{2.114}$$

We can use this to define the Heisenberg picture, by demanding that the expectation values be the same

$$\begin{aligned} |\psi_H(t)\rangle &= |\psi_S(t_0)\rangle && \text{wave functions} \\ A_H(t) &= U^\dagger(t,t_0)A_S U(t,t_0). && \text{operators} \end{aligned} \tag{2.115}$$

The time evolution of operators is given by

$$i\hbar\frac{\partial}{\partial t}A_H(t) = [H_H, A_H(t)]\,. \tag{2.116}$$

And the density matrix by

$$\rho_H(t) = \sum_n p_n \left|n_H(t)\right\rangle \left\langle n_H(t)\right| = \sum_n p_n \left|n_H(t_0)\right\rangle \left\langle n_H(t_0)\right| = \rho(t_0). \tag{2.117}$$

The density matrix is actually independent of time since it is built from the states themselves.

2.4.4 Relating the descriptions

We can relate all these descriptions by remembering that they all coincide at $t = t_0$. Following this guideline, we can find a relation between $S(t,t')$ and $U(t,t')$:

$$S(t,t_0)\left|\psi_S(t_0)\right\rangle = S(t,t_0)\left|\psi_I(t_0)\right\rangle = \left|\psi_I(t)\right\rangle = e^{iH_0(t-t_0)/\hbar}\left|\psi_S(t)\right\rangle = e^{iH_0(t-t_0)/\hbar}U(t,t_0)\left|\psi_S(t_0)\right\rangle. \tag{2.118}$$

Since this is valid for an arbitrary state,

$$S(t,t_0) = e^{iH_0(t-t_0)/\hbar}U(t,t_0). \tag{2.119}$$

And for operators

$$A_S(t) = U(t,t_0)A_H(t)U^\dagger(t,t_0) = e^{-iH_0(t-t_0)/\hbar}A_I(t)e^{iH_0(t-t_0)/\hbar}. \tag{2.120}$$

Which yields a relation between the Heisenberg and the Interaction pictures in terms of the evolution operator of the Interaction picture:

$$A_H(t) = U^\dagger(t,t_0)e^{-iH_0(t-t_0)/\hbar}A_I(t)e^{iH_0(t-t_0)/\hbar}U(t,t_0) = S^\dagger(t,t_0)A_I(t)S(t,t_0). \tag{2.121}$$

These results can be summarized in a table for later reference

	Schrödinger	Heisenberg	Interaction
$\|\psi\rangle$	$U(t,t_0)\|\psi_S(t_0)\rangle$	$\|\psi_H(t_0)\rangle$	$S(t,t_0)\|\psi_I(t_0)\rangle$
A	A_S	$U^\dagger(t,t_0)A_S U(t,t_0)$	$e^{iH_0(t-t_0)/\hbar}A_S e^{-iH_0(t-t_0)/\hbar}$
ρ	$U(t,t_0)\rho(t_0)U^\dagger(t,t_0)$	$\rho(t_0)$	$S(t,t_0)\rho(t_0)S^\dagger(t,t_0)$

Table 2.1: Summary of the comparison between Schrödinger, Heisenberg and Interaction pictures.

2.5 Expected value of an operator

Consider a statistical ensemble of quantum systems, each in an eigenstate of the Hamiltonian H at time t_1. Given that ensemble, the probability to find a system with energy E_n is given by the Boltzmann weight $e^{-\beta E_n}$, so the whole ensemble can be represented by the density matrix $\rho = \sum_n e^{-\beta E_n} |n\rangle \langle n|$, where the sum is over all eigenvectors $|n\rangle$ of the Hamiltonian at time t_1. From this, we can obtain the thermodynamic properties of the system. In fact, the expected value of an operator A is simply the sum of its expected value in each state multiplied by the corresponding probability to find the system in that state:

$$\langle A\rangle = \frac{\sum_n e^{-\beta E_n}\langle n|A|n\rangle}{\sum_n e^{-\beta E_n}} = \frac{\sum_n \langle n|\sum_m e^{-\beta E_m}|m\rangle\langle m|A|n\rangle}{\sum_n \langle n|\sum_m e^{-\beta E_m}|m\rangle\langle m|n\rangle} = \frac{\sum_n \langle n|\rho A|n\rangle}{\sum_n \langle n|\rho|n\rangle} = \frac{\mathrm{Tr}\,(\rho A)}{\mathrm{Tr}\,(\rho)}. \tag{2.122}$$

Here we can see the role of ρ when studying the thermodynamic properties of a system. It contains all the information about the ensemble. Also, $\mathrm{Tr}\,(\rho)$ can be identified with the partition function Z. Note that in this case, $\rho = \sum_n e^{-\beta E_n}|n\rangle\langle n| = \sum_n e^{-\beta H}|n\rangle\langle n| = e^{-\beta H}\sum_n |n\rangle\langle n| = e^{-\beta H}$. However, if the Hamiltonian depends on time, this expression is no longer true because $|n(t)\rangle$ may no longer be a state with energy E_n. This is a subtle but crucial point about thermal averages of a quantum system. If one wants to calculate $\langle A\rangle$, eq. 2.122 seems to suggest that the way to do it is by tracing over all the eigenstates of the system with the Boltzmann weight. That is, every time we wanted to calculate the average value at a fixed time t, we would take the Hamiltonian at that time H_t with eigenstates $|n\rangle$ of energy E_n, each of which appearing with a probability $e^{-\beta E_n}$. This would indeed make the previous expression take the form $\langle A\rangle = \frac{\mathrm{Tr}(e^{-\beta H}A)}{\mathrm{Tr}(e^{-\beta H})}$. However, that is the wrong interpretation. What we're actually doing is starting with a given ensemble of systems and allowing them to evolve in time with the Hamiltonian H. Each system evolves independently of the others. The Boltzmann weight is simply the probability to find that particular system, so it remains unchanged. In particular, the partition function used to evaluate this average also remains unchanged.

2.6 Wick's Theorem at finite temperature

Consider a typical term in a perturbation expansion, where the α may be creation or destruction operators in second quantization. Begin commuting (or anti-commuting if it's a fermion operator) α_1 through:

$$\begin{aligned}\mathrm{Tr}\left[\rho\alpha_1\alpha_2\cdots\alpha_n\right] &= \mathrm{Tr}\left[\rho\left[\alpha_1,\alpha_2\right]_{\mp}\cdots\alpha_n\right] \pm \mathrm{Tr}\left[\rho\alpha_2\alpha_1\cdots\alpha_n\right] = \\ &= \mathrm{Tr}\left[\rho\left[\alpha_1,\alpha_2\right]_{\mp}\cdots\alpha_n\right] \pm \mathrm{Tr}\left[\rho\alpha_2\left[\alpha_1,\alpha_3\right]_{\mp}\cdots\alpha_n\right] + \cdots \pm \mathrm{Tr}\left[\rho\alpha_2\cdots\alpha_n\alpha_1\right] \\ &= \mathrm{Tr}\left[\rho\left[\alpha_1,\alpha_2\right]_{\mp}\cdots\alpha_n\right] \pm \mathrm{Tr}\left[\rho\alpha_2\left[\alpha_1,\alpha_3\right]_{\mp}\cdots\alpha_n\right] + \cdots \pm \mathrm{Tr}\left[\alpha_1\rho\alpha_2\cdots\alpha_n\right]. \quad (2.123)\end{aligned}$$

It would be very convenient if we were able to commute α_1 and ρ. To do that, we employ a trick similar to determining an operator in the interaction picture:

$$\frac{d}{d\beta}\left(e^{\beta H_0}\alpha_1 e^{-\beta H_0}\right) = e^{\beta H_0}\left[H_0,\alpha_1\right]e^{-\beta H_0}. \quad (2.124)$$

Since $H_0 = \sum_n \epsilon_n \alpha_n^+ \alpha_n^-$ (the plus sign denotes a creation operator and the minus an annihilation operator), the commutator can be explicitly calculated, and yields $[H_0, \alpha_m^{\pm}] = \pm\epsilon_m \alpha_m^{\pm}$, from which:

$$\frac{d}{d\beta}\left(e^{\beta H_0}\alpha_1^{\pm} e^{-\beta H_0}\right) = \pm\epsilon_1 e^{\beta H_0}\alpha_1^{\pm} e^{-\beta H_0}. \quad (2.125)$$

This is a differential equation that is readily solved with the initial condition $\left(e^{\beta H_0}\alpha_1^{\pm}e^{-\beta H_0}\right)_{\beta=0} = \alpha_1^{\pm}$:

$$e^{\beta H_0}\alpha_1^{\pm}e^{-\beta H_0} = e^{\pm\beta\epsilon_1}\alpha_1^{\pm}. \quad (2.126)$$

Multiplying both sides on the left by $e^{-\beta H_0}$, we get the desired commutation:

$$\alpha_1^{\pm}\rho_o = e^{\pm\beta\epsilon_1}\rho_o\alpha_1^{\pm}. \quad (2.127)$$

Let $\lambda_1 = 1$ if α_1 is a creation operator and -1 if it's a destruction operator. Then,

$$\mathrm{Tr}\left[\rho_o\alpha_1\alpha_2\cdots\alpha_n\right] = \mathrm{Tr}\left[\rho_0\left[\alpha_1,\alpha_2\right]_{\mp}\cdots\alpha_n\right] \pm \mathrm{Tr}\left[\rho_0\alpha_2\left[\alpha_1,\alpha_3\right]_{\mp}\cdots\alpha_n\right] + \cdots \pm e^{\lambda_1\beta\epsilon_1}\mathrm{Tr}\left[\rho_0\alpha_1\alpha_2\cdots\alpha_n\right]. \quad (2.128)$$

The last term is identical to the left-hand side of the equation so they may be joined and their coefficient divided through:

$$\mathrm{Tr}\left[\rho_0\alpha_1\alpha_2\cdots\alpha_n\right] = \mathrm{Tr}\left[\rho_0\frac{\left[\alpha_1,\alpha_2\right]_{\mp}}{1\mp e^{\lambda_1\beta\epsilon_1}}\alpha_3\cdots\alpha_n\right] \pm \mathrm{Tr}\left[\rho_0\frac{\left[\alpha_1,\alpha_3\right]_{\mp}}{1\mp e^{\lambda_1\beta\epsilon_1}}\alpha_2\cdots\alpha_n\right] + \cdots. \quad (2.129)$$

Dividing through by $\mathrm{Tr}\left(\rho_0\right)$, this can be expressed in terms of an average over non-interacting

states:

$$\langle \alpha_1 \alpha_2 \cdots \alpha_n \rangle_0 = \left\langle \frac{[\alpha_1, \alpha_2]_\mp}{1 \mp e^{\lambda_1 \beta \epsilon_1}} \alpha_3 \cdots \alpha_n \right\rangle_0 \pm \left\langle \frac{[\alpha_1, \alpha_3]_\mp}{1 \mp e^{\lambda_1 \beta \epsilon_1}} \alpha_2 \cdots \alpha_n \right\rangle_0 + \cdots . \tag{2.130}$$

These commutators (or anti-commutators) are merely c-numbers, but are kept inside the average symbol for reasons that will soon become clear. If there were only two operators, the previous result would allow us to find their average directly.

$$\langle \alpha_1 \alpha_2 \rangle_0 = \frac{[\alpha_1, \alpha_2]_\mp}{1 \mp e^{\lambda_1 \beta \epsilon_1}}. \tag{2.131}$$

Use this to define the Wick contraction between two operators:

$$\overbrace{\alpha_1 \alpha_2} = \langle \alpha_1 \alpha_2 \rangle_0 = \frac{[\alpha_1, \alpha_2]_\mp}{1 \mp e^{\lambda_1 \beta \epsilon_1}}. \tag{2.132}$$

This notation turns the previous expression into

$$\langle \alpha_1 \alpha_2 \cdots \alpha_n \rangle_0 = \left\langle \overbrace{\alpha_1 \alpha_2} \alpha_3 \cdots \alpha_n \right\rangle_0 \pm \left\langle \overbrace{\alpha_1 \alpha_3} \alpha_2 \cdots \alpha_n \right\rangle_0 + \cdots . \tag{2.133}$$

Wick's contraction only makes sense when two operators are adjacent, for then it can be simply interpreted as a c-number that may be taken outside of the average. Now we're going to give the Wick contraction a new property that simplifies the notation. When you contract any two operators, wherever they may be, you commute (or anti-commute for fermions) the contracted operators with the operators in the middle (even if these are already contracted with something else themselves), until you can join them. For example:

$$\overbrace{\alpha_1 \alpha_2 \alpha_3} = \pm \overbrace{\alpha_1 \alpha_3} \alpha_2 \tag{2.134}$$

and

$$\overbrace{\alpha_1 \overbrace{\alpha_3 \alpha_2} \alpha_4} = \pm \overbrace{\alpha_1 \alpha_2} \overbrace{\alpha_3 \alpha_4}. \tag{2.135}$$

This allows for the averages to be cast in a very elegant way because it takes care of the awkward minus signs

$$\langle \alpha_1 \alpha_2 \cdots \alpha_n \rangle_0 = \left\langle \overbrace{\alpha_1 \alpha_2} \alpha_3 \alpha_4 \cdots \alpha_n \right\rangle_0 + \left\langle \overbrace{\alpha_1 \alpha_2 \alpha_3} \alpha_4 \cdots \alpha_n \right\rangle_0 + \left\langle \overbrace{\alpha_1 \alpha_2 \alpha_3 \alpha_4} \cdots \alpha_n \right\rangle_0 + \cdots . \tag{2.136}$$

We can thus see that the first iteration of our result corresponds to contracting the first operator with all other operators, one at a time, resulting in $n - 1$ terms.

Iterating this process means that the average is the sum over all possible contractions of all the operators:

$$\langle \alpha_1 \alpha_2 \cdots \alpha_n \rangle_0 = \left\langle \overbrace{\alpha_1 \alpha_2} \overbrace{\alpha_3 \alpha_4} \cdots \overbrace{\alpha_n} \right\rangle_0 + \left\langle \overbrace{\alpha_1 \overbrace{\alpha_2 \alpha_3} \alpha_4} \cdots \overbrace{\alpha_n +} \right\rangle_0 + \cdots . \tag{2.137}$$

This is Wick's Theorem for finite temperatures. As an explicit example, for four operators, this is

$$\begin{aligned} \langle \alpha_1 \alpha_2 \alpha_3 \alpha_4 \rangle_0 &= \left\langle \overbrace{\alpha_1 \alpha_2} \alpha_3 \alpha_4 \right\rangle_0 + \left\langle \overbrace{\alpha_1 \alpha_2 \alpha_3} \alpha_4 \right\rangle_0 + \left\langle \overbrace{\alpha_1 \alpha_2 \alpha_3 \alpha_4} \right\rangle_0 \\ &= \left\langle \overbrace{\alpha_1 \alpha_2} \overbrace{\alpha_3 \alpha_4} \right\rangle_0 + \left\langle \overbrace{\alpha_1 \overbrace{\alpha_2 \alpha_3} \alpha_4} \right\rangle_0 + \left\langle \overbrace{\alpha_1 \overbrace{\alpha_2 \alpha_3 \alpha_4}} \right\rangle_0 \\ &= \left\langle \overbrace{\alpha_1 \alpha_2} \overbrace{\alpha_3 \alpha_4} \right\rangle_0 \pm \left\langle \overbrace{\alpha_1 \alpha_3} \overbrace{\alpha_2 \alpha_4} \right\rangle_0 + \left\langle \overbrace{\alpha_1 \alpha_4} \overbrace{\alpha_2 \alpha_3} \right\rangle_0 . \end{aligned} \tag{2.138}$$

Since the contractions are averages themselves, this is also:

$$\langle \alpha_1 \alpha_2 \alpha_3 \alpha_4 \rangle_0 = \langle \alpha_1 \alpha_2 \rangle_0 \langle \alpha_3 \alpha_4 \rangle_0 \pm \langle \alpha_1 \alpha_3 \rangle_0 \langle \alpha_2 \alpha_4 \rangle_0 + \langle \alpha_1 \alpha_4 \rangle_0 \langle \alpha_2 \alpha_3 \rangle_0 . \tag{2.139}$$

This is a remarkable result. An average over non-interacting states of any number of operators may be simply calculated using averages of two operators!

2.6.1 Wick's theorem and time-ordering

Suppose that instead we wanted to calculate an average over time-ordered operators $\langle T \alpha_1 \alpha_2 \cdots \alpha_n \rangle_0$. Taking as an example eq. 2.139, under time-ordering, we may simultaneously reorder the terms on both sides of the equation without any additional minus signs. After reordering, we are still summing over all the possible contractions, which are precisely the same contractions as before reordering, although the order of each contraction may be inverted. That is, we may find $\overbrace{\alpha_1 \alpha_2}$ instead of $\overbrace{\alpha_2 \alpha_1}$. Bearing this in mind and knowing that after time-ordering, all the contractions are necessarily time-ordered, we might as well do the contractions before time-ordering and then order each contraction. The final result is the same. Let us then redefine the Wick contraction to take this into account:

$$\overbrace{\alpha_1 \alpha_2} = \langle T \alpha_1 \alpha_2 \rangle_0 . \tag{2.140}$$

Wick's theorem now also holds with time ordering

$$\langle T \alpha_1 \alpha_2 \cdots \alpha_n \rangle_0 = \left\langle \overbrace{\alpha_1 \alpha_2} \overbrace{\alpha_3 \alpha_4} \cdots \overbrace{\alpha_n} \right\rangle_0 + \left\langle \overbrace{\alpha_1 \overbrace{\alpha_2 \alpha_3} \alpha_4} \cdots \overbrace{\alpha_n +} \right\rangle_0 \cdots . \tag{2.141}$$

This result will very considerably simplify our perturbative calculations.

2.6.2 Examples - Fermions

This short section is to be used as a reference point, because these expressions will be used copiously in the next chapter.

Averages of two operators

The first result is very straightforward and has already been considered while deriving Wick's theorem:

$$\left\langle a_1^\dagger a_2 \right\rangle_0 = \frac{\left\{ a_1^\dagger, a_2 \right\}}{1 + e^{\beta\epsilon_1}} = \delta_{12} f(\epsilon_1). \tag{2.142}$$

The second one is easy if we consider the anti-commutation relations:

$$\left\langle a_1 a_2^\dagger \right\rangle_0 = \left\langle \left\{ a_1^\dagger, a_2 \right\} - a_1^\dagger a_2 \right\rangle_0 = \delta_{12} \left[1 - f(\epsilon_1) \right] \tag{2.143}$$

Averages of four operators

This too has already been calculated using Wick's theorem:

$$\begin{aligned} \left\langle a_1^\dagger a_2^\dagger a_3 a_4 \right\rangle_0 &= - \left\langle a_1^\dagger a_3 \right\rangle_0 \left\langle a_2^\dagger a_4 \right\rangle_0 + \left\langle a_1^\dagger a_4 \right\rangle_0 \left\langle a_2^\dagger a_3 \right\rangle_0 . \\ &= f(\epsilon_1) f(\epsilon_2) \left[\delta_{14}\delta_{23} - \delta_{24}\delta_{13} \right] \end{aligned} \tag{2.144}$$

This concludes the theoretical background needed to understand the following chapters.

3 Linear order response

In most of Physics, it becomes hopeless to expect an exact solution for a given problem. In the quantum case, for example, this requires diagonalizing the Hamiltonian matrix, which is a strenuous task and indeed hopeless if it doesn't have some obvious symmetries. It's this difficulty that led to Perturbation Theory. We may not get an exact result, but we may obtain an arbitrarily good approximation by considering a series expansion (assuming it converges) in the coupling between the exact (solvable) Hamiltonian and the perturbation. Even so, the expressions obtained in this way become very cumbersome very quickly. That's why most of the times, we stick to the first order. One of the fundamental tools to study the linear response of a quantum system to a coupling is Kubo's formula, which we prove in the first section. The next sections are dedicated to the study of the current in first order. We'll do it with both the $\boldsymbol{A}$ and the $\boldsymbol{E}$ formalisms, obtain basis-independent descriptions and finally obtain some interesting limiting cases that allow us to recover some results in the literature.

3.1 Linear Response Theory - Kubo's formula

Consider an ensemble of systems just like the one in the previous sections. Allow for the ensemble to evolve in time according to the Hamiltonian H. While the perturbation isn't turned on ($t < t_0$), ρ remains unchanged because $H = H_0$ is time independent. For $t > t_0$, the Hamiltonian may depend on time due to the perturbation $V(t)$. The original eigenstates at time t_0 will evolve and may no longer be eigenstates at later times. The evolution of the ensemble is again captured by ρ, since $\rho(t) = \sum_n e^{-\beta E_n} |n(t)\rangle \langle n(t)|$. We do not know how to calculate the time evolution of these states exactly, but we do know how to do it order by order. To do this, it's more useful to work in the interaction picture. Tracing over the Schrödinger picture or the Interaction Picture is the same since

$$\begin{aligned}\mathrm{Tr}\,(\rho A) = &\mathrm{Tr}\left(e^{-i\frac{H_0 t}{\hbar}} e^{i\frac{H_0 t}{\hbar}} \rho(t) e^{-i\frac{H_0 t}{\hbar}} e^{i\frac{H_0 t}{\hbar}} A(t)\right) \\ =&\mathrm{Tr}\left(e^{i\frac{H_0 t}{\hbar}} \rho(t) e^{-i\frac{H_0 t}{\hbar}} e^{i\frac{H_0 t}{\hbar}} A(t) e^{-i\frac{H_0 t}{\hbar}}\right) = \mathrm{Tr}\,(\rho_I(t) A_I(t))\end{aligned} \tag{3.1}$$

where we have made explicit use of the cyclic property of the trace.

We may now expand this in powers of V. To do so, let $|n\rangle = |n_I(t_0)\rangle$ be the eigenstate of H_0 before the perturbation and consider the expansion of the density matrix in the interaction picture:

$$\begin{aligned}\rho_I(t) &= \frac{1}{Z_0}\sum_n e^{-\beta E_n}\,|n_I(t)\rangle\,\langle n_I(t)| \\ &= \frac{1}{Z_0}\sum_n e^{-\beta E_n}\left(1+\frac{1}{i\hbar}\int_{t_0}^{t} V_I(t')dt'\right)|n\rangle\,\langle n|\left(1-\frac{1}{i\hbar}\int_{t_0}^{t} V_I(t')dt'\right)+O(V^2). \qquad (3.2)\end{aligned}$$

Retaining terms only up to linear order,

$$\begin{aligned}\rho_I(t) &= \frac{1}{Z_0}\sum_n e^{-\beta E_n}\,|n\rangle\,\langle n| + \frac{1}{i\hbar}\int_{t_0}^{t} dt'\,\frac{1}{Z_0}\left(V_I(t')\sum_n e^{-\beta E_n}\,|n\rangle\,\langle n| - \sum_n e^{-\beta E_n}\,|n\rangle\,\langle n|\,V_I(t')\right) \\ &= \rho_0 + \frac{1}{i\hbar}\int_{t_0}^{t} dt'\left(V_I(t')\rho_0 - \rho_0 V_I(t')\right) \qquad (3.3)\end{aligned}$$

We want to calculate the expected value of a given operator A for each time t only retaining terms up to first order. Using eq. 2.122, plug the expansion of $\rho_I(t)$

$$\begin{aligned}\langle A\rangle(t) &= \mathrm{Tr}\left(\rho_0 A_I(t) + \frac{1}{i\hbar}\int_{t_0}^{t} dt'\left(V_I(t')\rho_0 - \rho_0 V_I(t')\right)A_I(t)\right) \\ &= \mathrm{Tr}\left(\rho_0 A_I(t)\right) + \frac{1}{i\hbar}\int_{t_0}^{t} dt'\mathrm{Tr}\left(\left(V_I(t')\rho_0 - \rho_0 V_I(t')\right)A_I(t)\right).\end{aligned}$$

The first term is just the average of $A_I(t)$ calculated with respect to the unperturbed Hamiltonian, $\langle A_I(t)\rangle_0$. By the same argument as before, since the trace is the same in the Schrödinger picture and the interaction picture, this is just $\langle A\rangle_0$. The second term is just the ensemble average of the commutator

$$\mathrm{Tr}\left(V_I(t')\rho_0 A_I(t) - \rho_0 V_I(t')A_I(t)\right) = \mathrm{Tr}\left(\rho_0\left[A_I(t), V_I(t')\right]\right) = \left\langle\left[A_I(t), V_I(t')\right]\right\rangle_0 \qquad (3.4)$$

Putting this back together, we obtain the famous Kubo's Formula:

$$\boxed{\langle A\rangle(t) = \langle A\rangle_0 + \frac{1}{i\hbar}\int_{t_0}^{t} dt'\left\langle\left[A_I(t), V_I(t')\right]\right\rangle_0} \qquad (3.5)$$

This will be our primary tool in the first section of this work.

3.2 Calculation of $\langle J^\alpha_\omega \rangle$ to first order - A formalism

We are now in conditions to apply Kubo's formula to our case in study. As discussed in the Introduction, one of the ways to endow our quantum system with an electric field is through the minimal coupling $\boldsymbol{p} \to \boldsymbol{p} + e\boldsymbol{A}(t)$. Start with the unperturbed (solvable) Hamiltonian:

$$H_0 = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r}). \tag{3.6}$$

After minimal coupling, we get some extra terms:

$$H = \frac{1}{2m}\left(\boldsymbol{p} + e\boldsymbol{A}(t)\right)^2 + V(\boldsymbol{r}) = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r}) + \frac{1}{2m}\left(e^2\boldsymbol{A}(t)^2 + 2e\boldsymbol{p}\cdot\boldsymbol{A}(t)\right). \tag{3.7}$$

And so our Hamiltonian splits into H_0 and a time-dependent contribution $V(t)$:

$$V(t) = \frac{e}{m}\boldsymbol{p}\cdot\boldsymbol{A}(t) + \frac{e^2}{2m}\boldsymbol{A}(t)^2. \tag{3.8}$$

In second quantization, these operators are:

$$H_0 = \sum_n \epsilon_n c_n^\dagger c_n \tag{3.9}$$

$$V(t) = e\boldsymbol{A}\cdot\sum_{nm}\boldsymbol{v}_{nm}c_n^\dagger c_m + \frac{e^2}{2m}\boldsymbol{A}^2. \tag{3.10}$$

The operator we want to calculate is the current

$$\boldsymbol{J}_{\boldsymbol{A}}(t) = -\frac{e}{V}\sum_{pq}\boldsymbol{v}_{pq}c_p^\dagger c_q - \frac{e^2}{mV}N_e\boldsymbol{A}(t). \tag{3.11}$$

First, we're going to need to express the creation and destruction operators in the interaction picture. The interaction picture label of these operators will be dropped because the time dependency alone is enough to tell them apart. We have to solve

$$c_n(t) = e^{i\frac{H_0 t}{\hbar}}c_n e^{-i\frac{H_0 t}{\hbar}}. \tag{3.12}$$

This can be done by finding an equation of motion for $c_n(t)$. For this purpose, differentiate both sides with respect to time:

$$\begin{aligned}\frac{d}{dt}c_n(t) &= \frac{d}{dt}\left(e^{i\frac{H_0 t}{\hbar}}c_n e^{-i\frac{H_0 t}{\hbar}}\right) = \left(\frac{d}{dt}e^{i\frac{H_0 t}{\hbar}}\right)c_n e^{-i\frac{H_0 t}{\hbar}} + e^{i\frac{H_0 t}{\hbar}}c_n\left(\frac{d}{dt}e^{-i\frac{H_0 t}{\hbar}}\right)\\ &= \frac{iH_0}{\hbar}e^{i\frac{H_0 t}{\hbar}}c_n e^{-i\frac{H_0 t}{\hbar}} + e^{i\frac{H_0 t}{\hbar}}c_n\frac{-iH_0}{\hbar}e^{-i\frac{H_0 t}{\hbar}}.\end{aligned}$$

Since any operator commutes with any function of itself, this is expressed in terms of a com-

mutator, which is already known:

$$\frac{d}{dt}c_n(t) = \frac{i}{\hbar}e^{i\frac{H_0 t}{\hbar}}\left[H_0, c_n\right]e^{-i\frac{H_0 t}{\hbar}} = -\frac{i\epsilon_n}{\hbar}e^{i\frac{H_0 t}{\hbar}}c_n e^{-i\frac{H_0 t}{\hbar}} = -\frac{i\epsilon_n}{\hbar}c_n(t). \tag{3.13}$$

Upon solving this differential equation for $c_n(t)$ using the initial condition $c_n(0) = c_n$, we find:

$$c_n(t) = c_n e^{-\frac{i\epsilon_n}{\hbar}t}. \tag{3.14}$$

The process is entirely analogous for the creation operator:

$$c_n^\dagger(t) = c_n^\dagger e^{\frac{i\epsilon_n}{\hbar}t}. \tag{3.15}$$

This allows us to express the previous operators in the Interaction Picture.

$$V_I(t') = e\boldsymbol{A}\cdot\sum_{nm}\boldsymbol{v}_{nm}c_n^\dagger c_m e^{\frac{i}{\hbar}(\epsilon_n-\epsilon_m)t'} + \frac{e^2}{2m}\boldsymbol{A}^2 \tag{3.16}$$

$$\boldsymbol{J}_I(t) = -\frac{e}{V}\sum_{pq}\boldsymbol{v}_{pq}c_p^\dagger c_q e^{\frac{i}{\hbar}(\epsilon_p-\epsilon_q)t} - \frac{e^2}{mV}N_e\boldsymbol{A}. \tag{3.17}$$

Note that each of these operators contains different orders of $\boldsymbol{A}$. The first term in Kubo's formula already includes one linear factor.

$$\begin{aligned}\langle \boldsymbol{J}_{\boldsymbol{A}}\rangle_0 &= \left\langle \frac{e}{V}\sum_{pq}\boldsymbol{v}_{pq}c_p^\dagger c_q - \frac{e^2}{mV}N_e\boldsymbol{A}(t)\right\rangle_0 = \frac{e}{V}\sum_{pq}\boldsymbol{v}_{pq}\left\langle c_p^\dagger c_q\right\rangle_0 - \frac{e^2}{mV}N_e\boldsymbol{A}(t)\\ &= \frac{e}{V}\sum_{p}\boldsymbol{v}_{pp}f(\epsilon_p) - \frac{e^2}{mV}N_e\boldsymbol{A}(t) = -\frac{e^2}{mV}N_e\boldsymbol{A}(t)\end{aligned}$$

Here we have used $\left\langle c_p^\dagger c_q\right\rangle_0 = \delta_{pq}f(\epsilon_p)$ and the fact that the zeroth order term is zero[1]. The second term requires the calculation of $\langle [J_I^\alpha(t), V_I(t')]\rangle_0$:

$$\left\langle \left[J_I^\alpha(t), V_I(t')\right]\right\rangle_0 = \left\langle \left[-\frac{e}{V}\sum_{pq}v^\alpha_{pq}c_p^\dagger c_q e^{\frac{i}{\hbar}(\epsilon_p-\epsilon_q)t} - \frac{e^2}{mV}N_e A^\alpha, eA^\beta\sum_{nm}v^\beta_{nm}c_n^\dagger c_m e^{\frac{i}{\hbar}(\epsilon_n-\epsilon_m)t'} + \frac{e^2}{2m}\boldsymbol{A}^2\right]\right\rangle_0. \tag{3.18}$$

Commuting the c-numbers and ignoring the higher order terms in $\boldsymbol{A}$:

$$\left\langle \left[J_I^\alpha(t), V_I(t')\right]\right\rangle_0 = -\frac{e^2A^\beta}{V}\sum_{pqnm}v^\alpha_{pq}v^\beta_{nm}\left\langle\left[c_p^\dagger c_q, c_n^\dagger c_m\right]\right\rangle_0 e^{\frac{i}{\hbar}(\epsilon_p-\epsilon_q)t}e^{\frac{i}{\hbar}(\epsilon_n-\epsilon_m)t'}. \tag{3.19}$$

[1] In fact, the zeroth order term is zero because $\boldsymbol{v} = \frac{1}{i\hbar}[\boldsymbol{r}, H]$. The trace of $\boldsymbol{v}$ with $f(\epsilon_p)$ may be written as $\sum_p \boldsymbol{v}_{pp}f(\epsilon_p) = \int_{-\infty}^{\infty}d\epsilon f(\epsilon)\mathrm{Tr}\left[\boldsymbol{v}\delta(\epsilon - H)\right]$. Therefore, the cyclic property of the trace coupled with the fact that operators commute with any function of themselves, $\mathrm{Tr}\left[\boldsymbol{v}\delta(\epsilon-H)\right] = \mathrm{Tr}\left[\frac{1}{i\hbar}[\boldsymbol{r}, H]\delta(\epsilon-H)\right] = 0$.

This average of the commutator is calculated in the appendix 8.13 and evaluates to

$$\left\langle \left[c_p^\dagger c_q, c_n^\dagger c_m\right]\right\rangle_0 = \left\{c_q, c_n^\dagger\right\}\left\langle c_p^\dagger c_m\right\rangle_0 - \left\{c_m, c_p^\dagger\right\}\left\langle c_n^\dagger c_q\right\rangle_0 = \delta_{qn}\delta_{pm}\left(f(\epsilon_p) - f(\epsilon_q)\right). \tag{3.20}$$

Plugging this back into eq. 3.19 and integrating in time from t_0 to t gives us the second term in Kubo's formula:

$$\begin{aligned}
&\frac{1}{i\hbar}\int_{t_0}^{t} dt' \left\langle \left[J_I^\alpha(t), V_I(t')\right]\right\rangle_0 \\
&= -\frac{e^2}{V}\sum_{pqnm} v_{pq}^\alpha v_{nm}^\beta \delta_{qn}\delta_{pm}\left(f(\epsilon_p) - f(\epsilon_q)\right)\frac{1}{i\hbar}\int_{t_0}^{t} dt' e^{\frac{i}{\hbar}(\epsilon_p-\epsilon_q)t} e^{\frac{i}{\hbar}(\epsilon_n-\epsilon_m)t'} A^\beta(t') \\
&= \frac{ie^2}{\hbar V}\sum_{pq} v_{pq}^\alpha v_{qp}^\beta \left(f(\epsilon_p) - f(\epsilon_q)\right)\int_{t_0}^{t} dt' e^{\frac{i}{\hbar}(\epsilon_p-\epsilon_q)(t-t')} A^\beta(t').
\end{aligned} \tag{3.21}$$

We have thus found the full expression of the current in first order:

$$\left\langle J^\alpha\right\rangle(t) = \frac{ie^2}{\hbar V}\sum_{pq} v_{pq}^\alpha v_{qp}^\beta \left(f(\epsilon_p) - f(\epsilon_q)\right)\int_{t_0}^{t} dt' e^{\frac{i}{\hbar}(\epsilon_p-\epsilon_q)(t-t')} A^\beta(t') + \frac{-e^2}{mV} N A^\alpha(t). \tag{3.22}$$

In principle, we are done because this expression gives us everything we need, but we can obtain a friendlier expression if we go to Fourier space. Introducing the Fourier transform of $A^\beta(t)$ and the shorthand notation $\omega_{pq} = \left(\epsilon_p - \epsilon_q\right)/\hbar$, the Fourier transform of $\left\langle J^\alpha\right\rangle(t)$ is:

$$\begin{aligned}
\left\langle J_\omega^\alpha\right\rangle &= \frac{ie^2}{\hbar V}\sum_{pq} v_{pq}^\alpha v_{qp}^\beta \left(f(\epsilon_p) - f(\epsilon_q)\right)\int_{-\infty}^{\infty} dt e^{i\omega t}\int_{-\infty}^{t} dt' \\
&\quad\times\left(\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi} A_{\omega'}^\beta e^{-i\omega' t'}\right) e^{i\omega_{pq}(t-t')} + \frac{-e^2}{mV} N A_\omega^\alpha.
\end{aligned} \tag{3.23}$$

Reordering the terms, we obtain a double time integral of imaginary exponentials. This integral is calculated in the appendix (eq. 8.9) and yields the following result:

$$\int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt' e^{i(\omega+\omega_{pq})t} e^{-i(\omega'+\omega_{pq})t'} = \frac{2\pi i\delta(\omega'-\omega)}{\omega + \omega_{pq} + i0^+} \tag{3.24}$$

This puts the current into a much nicer form:

$$\left\langle J_\omega^\alpha\right\rangle = \frac{ie^2}{\hbar V}\sum_{pq}\left[f(\epsilon_p) - f(\epsilon_q)\right] v_{pq'}^\alpha v_{qp}^\beta \int_{-\infty}^{\infty}\frac{d\omega'}{2\pi} A_{\omega'}^\beta \frac{2\pi i\delta(\omega'-\omega)}{\omega + \omega_{pq} + i\epsilon} + \frac{-e^2}{mV} N A_\omega^\alpha. \tag{3.25}$$

Integrating over ω', we arrive at

$$\boxed{\left\langle J_\omega^\alpha\right\rangle = \frac{-e^2}{V}\sum_{pq}\frac{\left[f(\epsilon_p) - f(\epsilon_q)\right] v_{pq}^\alpha v_{qp}^\beta}{\hbar\omega + \epsilon_p - \epsilon_q + i\epsilon} A_\omega^\beta + \frac{-e^2}{mV} N A_\omega^\alpha} \tag{3.26}$$

This shall be taken as the fundamental result from which to obtain the consequences, since it's relatively simple to obtain and it's easier to manipulate than its basis-independent counterpart.

3.3 Calculation of $\langle J^\alpha_\omega \rangle$ to first order - scalar potential

We have obtained a formula for the current in Fourier space using $\boldsymbol{A}$ as the source of electromagnetic interaction. Now, for completeness, we shall do the same but with a scalar potential coupling. The non-perturbed Hamiltonian in its eigenbasis is:

$$H_0 = \sum_n \epsilon_n c_n^\dagger c_n. \tag{3.27}$$

Recall that the external perturbation is now due to the dipolar interaction $e\boldsymbol{E}\cdot\boldsymbol{r}$, which in second quantization is

$$H^{ext}(t) = e\boldsymbol{E}(t)\cdot\sum_{nm}\boldsymbol{r}_{nm}c_n^\dagger c_m. \tag{3.28}$$

The current in the $\boldsymbol{E}$ formalism is

$$\boldsymbol{J}_{\boldsymbol{E}} = \frac{-e}{V}\sum_{nm}\boldsymbol{v}_{nm}c_n^\dagger c_m. \tag{3.29}$$

These form all the ingredients necessary to compute the expected value of $\boldsymbol{J}$. Since we have an expression for the eigen energies, the description of these operators in the interaction picture becomes $c_n^\dagger \to c_n^\dagger(t) = e^{i\epsilon_n t/\hbar}c_n^\dagger$. Thus, for the first order term, Kubo's formula yields:

$$\begin{aligned}
\langle J_S^\alpha\rangle(t) &= -\frac{i}{h}\int_{t_0}^t dt' \left\langle\left[J_I^\alpha(t), H_I^{ext}(t')\right]\right\rangle_0 \\
&= -\frac{i}{h}\int_{t_0}^t dt' \left\langle\left[\frac{-e}{V}\sum_{ab} v_{ab}^\alpha c_a^\dagger(t)c_b(t), eE^\beta(t')\sum_{cd} r_{cd}^\beta c_c^\dagger(t')c_d(t')\right]\right\rangle_0 \\
&= \frac{ie^2}{\hbar V}\sum_{abcd} r_{cd}^\beta v_{ab}^\alpha \int_{t_0}^t dt' E^\beta(t')\left\langle\left[c_a^\dagger(t)c_b(t), c_c^\dagger(t')c_d(t')\right]\right\rangle_0 .
\end{aligned} \tag{3.30}$$

This commutator has already been evaluated (eq. 8.13) and turns the current into

$$\begin{aligned}
\langle J_S^\alpha\rangle(t) &= \frac{ie^2}{\hbar V}\sum_{abcd} r_{cd}^\beta v_{ab}^\alpha \int_{t_0}^t dt' E^\beta(t')\left\langle\left[c_a^\dagger(t)c_b(t), c_c^\dagger(t')c_d(t')\right]\right\rangle_0 \qquad (3.31)\\
&= \frac{ie^2}{\hbar V}\sum_{abcd} r_{cd}^\beta v_{ab}^\alpha \int_{t_0}^t dt' E^\beta(t')\left[\left\{c_b(t), c_c^\dagger(t')\right\}\left\langle c_a^\dagger(t)c_d(t')\right\rangle_0 - \left\{c_d(t'), c_a^\dagger(t)\right\}\left\langle c_c^\dagger(t')c_b(t)\right\rangle_0\right].
\end{aligned}$$

Introducing the Fourier transform of the electric field $\boldsymbol{E}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \boldsymbol{E}_\omega e^{-i\omega t}$ and adopting the simpler notation $\omega_{ab} = (\epsilon_a - \epsilon_b)/\hbar$, we get:

$$\langle J_S^\alpha \rangle (t) = \frac{ie^2}{\hbar V} \sum_{ab} r_{ba}^\beta v_{ab}^\alpha \left[f(\epsilon_a) - f(\epsilon_b) \right] \int_{t_0}^{t} dt' \left[\int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} E_{\omega'}^\beta e^{-i\omega' t'} \right] e^{i\omega_{ab}(t-t')}. \tag{3.32}$$

Now we assume the perturbation is turned on at $t_0 \to -\infty$. Taking the Fourier Transform of the whole expression:

$$\begin{aligned} \langle J_\omega^\alpha \rangle &= \frac{ie^2}{\hbar V} \sum_{ab} r_{ba}^\beta v_{ab}^\alpha \left[f(\epsilon_a) - f(\epsilon_b) \right] \int_{-\infty}^{\infty} dt e^{i\omega t} \int_{-\infty}^{t} dt' \left[\int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} E_{\omega'}^\beta e^{-i\omega' t'} \right] e^{i\omega_{ab}(t-t')} \\ &= \frac{-e^2}{\hbar V} \sum_{ab} r_{ba}^\beta v_{ab}^\alpha \frac{f(\epsilon_a) - f(\epsilon_b)}{\omega_{ab} + \omega + i\epsilon} E_\omega^\beta. \end{aligned} \tag{3.33}$$

We are left with the simple expression for the current:

$$\boxed{\langle J_\omega^\alpha \rangle = \frac{-e^2}{\hbar V} \sum_{ab} r_{ba}^\beta v_{ab}^\alpha \frac{f(\epsilon_a) - f(\epsilon_b)}{\omega_{ab} + \omega + i\epsilon} E_\omega^\beta.} \tag{3.34}$$

3.4 Periodic limit

So far, what we've calculated is valid for a general quantum system. The goal of this section is to take eq. 3.34 and see what it looks like when it's periodic, so as to be able to compare it with the expressions in [3]. For a detailed discussion of the origin of all the terms, the reader is directed to that text. Here we merely apply the definitions to our formula and see if it coincides with those results. First of all, let's assume that the system has translational symmetry, which allows us to use Bloch's theorem. Now we know that the eigenstates may be specified in terms of a momentum $\boldsymbol{p}$ and an index s which contains the remaining degrees of freedom unrelated to the translational symmetry, such as the band. Therefore, split each state n into $\boldsymbol{p}, s$

$$\langle J_\omega^\alpha \rangle = \frac{-e^2}{V} \sum_{psp's'} r_{p's'ps}^\beta v_{psp's'}^\alpha \frac{f(\epsilon_{ps}) - f(\epsilon_{p's'})}{\epsilon_{ps} - \epsilon_{p's'} + \hbar\omega + i\epsilon} E_\omega^\beta. \tag{3.35}$$

If the system is taken to be infinite, we may take the continuum limit $\sum_p \to V \int \frac{d^3p}{(2\pi)^3}$, but we need to be careful when using the position and velocity operators. The definition of $\boldsymbol{r}$ in this basis is [3, 3rd chapter]

$$\boldsymbol{r}_{psp's'} = -i(2\pi)^3 \delta_{ss'} \boldsymbol{\nabla}_{\boldsymbol{p}} \delta(\boldsymbol{p} - \boldsymbol{p}') + (2\pi)^3 \delta(\boldsymbol{p} - \boldsymbol{p}') \boldsymbol{\xi}_{\boldsymbol{p}ss'}. \tag{3.36}$$

Where $\boldsymbol{\xi}_{\boldsymbol{p}ss'}$ is the Berry connection defined by $\boldsymbol{\xi}_{\boldsymbol{p}ss'} = i \langle u_{\boldsymbol{k}s'} | \boldsymbol{\nabla}_{\boldsymbol{k}} u_{\boldsymbol{k}s} \rangle$ and $u_{\boldsymbol{k}s}$ is the component of the Bloch waves with the periodicity of the lattice. The derivative of the Dirac delta is

understood as being inside an integral and by acting through an integration by parts, as follows:

$$\int \frac{d^3\boldsymbol{p}}{(2\pi)^3} f(\epsilon_{\boldsymbol{p}s})(2\pi)^3 \boldsymbol{\nabla}^\beta_{\boldsymbol{p}} \delta(\boldsymbol{p}-\boldsymbol{p}') = -\int d^3\boldsymbol{p}\delta(\boldsymbol{p}-\boldsymbol{p}')\boldsymbol{\nabla}^\beta_{\boldsymbol{p}} f(\epsilon_{\boldsymbol{p}s}) = \boldsymbol{\nabla}^\beta_{\boldsymbol{p}'} f(\epsilon_{\boldsymbol{p}'s}). \tag{3.37}$$

Replacing in 3.35, we obtain

$$\begin{aligned}
\langle J^\alpha_\omega \rangle &= -Ve^2 \sum_{ss'} \int \frac{d^3\boldsymbol{p}}{(2\pi)^3} \int \frac{d^3\boldsymbol{p}'}{(2\pi)^3} \left[-i(2\pi)^3 \delta_{ss'} \boldsymbol{\nabla}^\beta_{\boldsymbol{p}} \delta(\boldsymbol{p}-\boldsymbol{p}') + (2\pi)^3 \delta(\boldsymbol{p}-\boldsymbol{p}') \xi^\beta_{\boldsymbol{p}ss'} \right] \\
&\quad \times v^\alpha_{\boldsymbol{p}s\boldsymbol{p}'s'} \frac{f(\epsilon_{\boldsymbol{p}s}) - f(\epsilon_{\boldsymbol{p}'s'})}{\epsilon_{\boldsymbol{p}s} - \epsilon_{\boldsymbol{p}'s'} + \hbar\omega + i\epsilon} E^\beta_\omega \\
&= ie^2 V \sum_{ss'} \int \frac{d^3\boldsymbol{p}}{(2\pi)^3} \int \frac{d^3\boldsymbol{p}'}{(2\pi)^3} (2\pi)^3 \delta_{ss'} \boldsymbol{\nabla}^\beta_{\boldsymbol{p}} \delta(\boldsymbol{p}-\boldsymbol{p}') v^\alpha_{\boldsymbol{p}s\boldsymbol{p}'s'} \frac{f(\epsilon_{\boldsymbol{p}s}) - f(\epsilon_{\boldsymbol{p}'s'})}{\epsilon_{\boldsymbol{p}s} - \epsilon_{\boldsymbol{p}'s'} + \hbar\omega + i\epsilon} E^\beta_\omega \\
&\quad -e^2 V \sum_{ss'} \int \frac{d^3\boldsymbol{p}}{(2\pi)^3} \xi^\beta_{\boldsymbol{p}ss'} v^\alpha_{\boldsymbol{p}s\boldsymbol{p}s'} \frac{f(\epsilon_{\boldsymbol{p}s}) - f(\epsilon_{\boldsymbol{p}s'})}{\epsilon_{\boldsymbol{p}s} - \epsilon_{\boldsymbol{p}s'} + \hbar\omega + i\epsilon} E^\beta_\omega.
\end{aligned} \tag{3.38}$$

The first term in this expression has to be treated carefully because many terms will cancel. Moving the derivative from the Dirac delta to the rest of the expression through an integration by parts we get two terms:

$$\begin{aligned}
& ie^2 V \sum_{ss'} \int \frac{d^3\boldsymbol{p}}{(2\pi)^3} \int \frac{d^3\boldsymbol{p}'}{(2\pi)^3} (2\pi)^3 \delta_{ss'} \nabla^\beta_p \delta(\boldsymbol{p}-\boldsymbol{p}') v^\alpha_{psp's'} \frac{f(\epsilon_{\boldsymbol{p}s}) - f(\epsilon_{\boldsymbol{p}'s'})}{\epsilon_{\boldsymbol{p}s} - \epsilon_{\boldsymbol{p}'s'} + \hbar\omega + i\epsilon} E^\beta_\omega \qquad (3.39) \\
= \; & -ie^2 V \sum_{ss'} \int \frac{d^3\boldsymbol{p}}{(2\pi)^3} \int \frac{d^3\boldsymbol{p}'}{(2\pi)^3} (2\pi)^3 \delta_{ss'} \delta(\boldsymbol{p}-\boldsymbol{p}') \left(\boldsymbol{\nabla}^\beta_{\boldsymbol{p}} v^\alpha_{\boldsymbol{p}s\boldsymbol{p}'s'} \right) \frac{f(\epsilon_{\boldsymbol{p}s}) - f(\epsilon_{\boldsymbol{p}'s'})}{\epsilon_{\boldsymbol{p}s} - \epsilon_{\boldsymbol{p}'s'} + \hbar\omega + i\epsilon} E^\beta_\omega \\
+ \; & -ie^2 V \sum_{ss'} \int \frac{d^3\boldsymbol{p}}{(2\pi)^3} \int \frac{d^3\boldsymbol{p}'}{(2\pi)^3} (2\pi)^3 \delta_{ss'} \delta(\boldsymbol{p}-\boldsymbol{p}') v^\alpha_{\boldsymbol{p}s\boldsymbol{p}'s'} \boldsymbol{\nabla}^\beta_{\boldsymbol{p}} \left[\frac{f(\epsilon_{\boldsymbol{p}s}) - f(\epsilon_{\boldsymbol{p}'s'})}{\epsilon_{\boldsymbol{p}s} - \epsilon_{\boldsymbol{p}'s'} + \hbar\omega + i\epsilon} \right] E^\beta_\omega.
\end{aligned}$$

In virtue of the Dirac delta and the Kronecker delta, the first term with the difference of Fermi functions disappears and all that remains is the derivative of the quotient. The same argument can be repeated while acting with the derivative through the quotient, leading to

$$-ie^2 V \sum_{ss'} \int \frac{d^3\boldsymbol{p}}{(2\pi)^3} \int \frac{d^3\boldsymbol{p}'}{(2\pi)^3} (2\pi)^3 \delta_{ss'} \delta(\boldsymbol{p}-\boldsymbol{p}') v^\alpha_{\boldsymbol{p}s\boldsymbol{p}'s'} \frac{\boldsymbol{\nabla}^\beta_{\boldsymbol{p}} f(\epsilon_{\boldsymbol{p}s})}{\epsilon_{\boldsymbol{p}s} - \epsilon_{\boldsymbol{p}'s'} + \hbar\omega + i\epsilon} E^\beta_\omega \tag{3.40}$$

which, after simplifying the deltas is

$$-ie^2 V \sum_{s} \int \frac{d^3\boldsymbol{p}}{(2\pi)^3} v^\alpha_{\boldsymbol{p}s\boldsymbol{p}s} \frac{\boldsymbol{\nabla}^\beta_{\boldsymbol{p}} f(\epsilon_{\boldsymbol{p}s})}{\hbar\omega + i\epsilon} E^\beta_\omega. \tag{3.41}$$

Putting it all back together,

$$\langle J^\alpha_\omega \rangle = -e^2 V E^\beta_\omega \sum_{ss'} \int \frac{d^3\boldsymbol{p}}{(2\pi)^3} \frac{i\delta_{ss'} v^\alpha_{\boldsymbol{p}s\boldsymbol{p}s'} \boldsymbol{\nabla}^\beta_{\boldsymbol{p}} f(\epsilon_{\boldsymbol{p}s}) + \xi^\beta_{\boldsymbol{p}ss'} v^\alpha_{\boldsymbol{p}s\boldsymbol{p}s'} \left(f(\epsilon_{\boldsymbol{p}s}) - f(\epsilon_{\boldsymbol{p}s'}) \right)}{\epsilon_{\boldsymbol{p}s} - \epsilon_{\boldsymbol{p}s'} + \hbar\omega + i\epsilon}. \tag{3.42}$$

Here, we'll be able to extract two components of the current: one which only considers transi-

tions between states in the same band $s \to s$ and one which only considers transitions between different bands $s \to s'$.

3.4.1 Intra-band term

Being diagonal in the band space, this first term is:

$$\begin{aligned}\langle J^\alpha_\omega\rangle_{\text{intra}} &= \frac{-e^2V}{\hbar}E^\beta_\omega\sum_{ss'}\int\frac{d^3\boldsymbol{q}}{(2\pi)^3}\delta_{ss'}v^\alpha_{\boldsymbol{q}s's}i\boldsymbol{\nabla}^\beta_{\boldsymbol{q}}f(\epsilon_{\boldsymbol{q}s})\frac{1}{\omega+\omega_{\boldsymbol{q}s's}+i\epsilon}\\ &= \frac{-e^2V}{\hbar}E^\beta_\omega\sum_{s}\int\frac{d^3\boldsymbol{q}}{(2\pi)^3}v^\alpha_{\boldsymbol{q}ss}i\boldsymbol{\nabla}^\beta_{\boldsymbol{q}}f(\epsilon_{\boldsymbol{q}s})\frac{1}{\omega+i\epsilon}.\end{aligned} \tag{3.43}$$

Now note that the velocity matrix elements may be written as $v^\alpha_{\boldsymbol{q}ss'} = \frac{1}{\hbar}\left[\delta_{ss'}\boldsymbol{\nabla}^\alpha_{\boldsymbol{q}}\epsilon_{\boldsymbol{q}s} + i\xi^\alpha_{\boldsymbol{q}ss'}\left(\epsilon_{\boldsymbol{q}s}-\epsilon_{\boldsymbol{q}s'}\right)\right]$ (see eq. 3.2.7 in [3]) and that $\nabla^\beta_{\boldsymbol{q}}f(\epsilon_{\boldsymbol{q}s}) = \nabla^\beta_{\boldsymbol{q}}\epsilon_{\boldsymbol{q}s}\frac{\partial f(\epsilon_{\boldsymbol{q}s})}{\partial\epsilon_{\boldsymbol{q}s}}$ so we get:

$$\langle J^\alpha_\omega\rangle_{\text{intra}} = \frac{-ie^2V}{\hbar^2}\frac{E^\beta_\omega}{\omega+i\epsilon}\sum_s\int\frac{d^3\boldsymbol{q}}{(2\pi)^3}\nabla^\beta_{\boldsymbol{q}}\epsilon_{\boldsymbol{q}s}\frac{\partial f(\epsilon_{\boldsymbol{q}s})}{\partial\epsilon_{\boldsymbol{q}s}}\nabla^\alpha_{\boldsymbol{q}}\epsilon_{\boldsymbol{q}s}. \tag{3.44}$$

Allowing for a change of notation for the derivatives and allowing for the notation $V\int\frac{d^3\boldsymbol{q}}{(2\pi)^3}\to\sum_{\boldsymbol{q}}$:

$$\langle J^\alpha_\omega\rangle_{\text{intra}} = \frac{-e^2}{\hbar^2}\sum_{\boldsymbol{q}s}\frac{\partial\epsilon_{qs}}{\partial q_\alpha}\frac{\partial\epsilon_{qs}}{\partial q_\beta}\left[-\frac{\partial f(\epsilon_{\boldsymbol{q}s})}{\partial\epsilon_{\boldsymbol{q}s}}\right]\frac{-iE^\beta_\omega}{\omega+i\epsilon}. \tag{3.45}$$

This is the intra-band component of the first-order current. By analyzing the expression, we see two interesting features. First of all, this term has the frequency in the denominator with only an infinitesimal factor to balance it out, so it diverges as $\omega \to 0$. Secondly, this intra-band contribution is multiplied by the derivative of the Fermi function, which approaches a Dirac delta centered at the chemical potential as the temperature goes to zero. The majority of the contribution to this term therefore comes from energies close to the chemical potential. For this term to contribute, there need to be states with that energy. This means that if the density of states has a gap and the chemical potential falls inside that gap, this term will be zero and the divergence will be gone.

3.4.2 Inter-band term

The second term is off-diagonal in band space. Letting $V\int\frac{d^3\boldsymbol{q}}{(2\pi)^3}\to\sum_{\boldsymbol{q}}$

$$\begin{aligned}\langle J^\alpha_\omega\rangle_{\text{inter}} &= \frac{-e^2}{\hbar}\sum_{ss'}\sum_{\boldsymbol{q}}v^\alpha_{\boldsymbol{q}s's}\xi^\beta_{\boldsymbol{q}ss'}\frac{f(\epsilon_{\boldsymbol{q}s'})-f(\epsilon_{\boldsymbol{q}s})}{\omega+\omega_{\boldsymbol{q}s's}+i\epsilon}E^\beta_\omega\\ &= -e^2\sum_{ss'}\sum_{\boldsymbol{q}}v^\alpha_{\boldsymbol{q}s's}\xi^\beta_{\boldsymbol{q}ss'}\frac{f(\epsilon_{\boldsymbol{q}s'})-f(\epsilon_{\boldsymbol{q}s})}{\hbar\omega+\epsilon_{\boldsymbol{q}s'}-\epsilon_{\boldsymbol{q}s}+i\epsilon}E^\beta_\omega\end{aligned}$$

This is the inter-band component. So, to first order, the current is

$$\boxed{\langle J^\alpha_\omega\rangle = \frac{-e^2}{\hbar^2}\sum_{\boldsymbol{q}s}\frac{\partial\epsilon_{\boldsymbol{q}s}}{\partial q_\alpha}\frac{\partial\epsilon_{\boldsymbol{q}s}}{\partial q_\beta}\left[-\frac{\partial f(\epsilon_{\boldsymbol{q}s})}{\partial\epsilon_{\boldsymbol{q}s}}\right]\frac{-iE^\beta_\omega}{\omega+i\epsilon} - e^2\sum_{\boldsymbol{q}ss'}v^\alpha_{\boldsymbol{q}s's}\xi^\beta_{\boldsymbol{q}ss'}\frac{f(\epsilon_{\boldsymbol{q}s'})-f(\epsilon_{\boldsymbol{q}s})}{\hbar\omega+\epsilon_{\boldsymbol{q}s'}-\epsilon_{\boldsymbol{q}s}+i\epsilon}E^\beta_\omega} \quad (3.46)$$

This is the result obtained in [3] but with an added convergence factor $i\epsilon$.

3.5 Equivalence of the two descriptions

So far we've obtained two seemingly different expressions for the current that should express the same thing. As we'll see, this is indeed the case. Start with the first formula we obtained, eq. 3.26:

$$\langle J^\alpha_\omega\rangle = \frac{-e^2}{V}A^\beta_\omega\sum_{nm}v^\alpha_{nm}v^\beta_{mn}\frac{f(\epsilon_n)-f(\epsilon_m)}{\hbar\omega+\epsilon_n-\epsilon_m+i\epsilon}+\frac{-e^2}{mV}NA^\alpha_\omega \quad (3.47)$$

Using the definition of $\boldsymbol{v}=\frac{1}{i\hbar}[\boldsymbol{r},H]$ in the energy basis, we find $\boldsymbol{v}_{mn}=\frac{\boldsymbol{r}_{mn}(\epsilon_n-\epsilon_m)}{i\hbar}$, which may be applied in the above formula to remove the second velocity operator:

$$\begin{aligned}
\langle J^\alpha_\omega\rangle &= \frac{-e^2}{V}A^\beta_\omega\sum_{nm}v^\alpha_{nm}\frac{r^\beta_{mn}(\epsilon_n-\epsilon_m)}{i\hbar}\frac{f(\epsilon_n)-f(\epsilon_m)}{\hbar\omega+\epsilon_n-\epsilon_m+i\epsilon}+\frac{-e^2}{mV}NA^\alpha_\omega \quad (3.48)\\
&= \frac{-e^2}{i\hbar V}A^\beta_\omega\sum_{nm}v^\alpha_{nm}r^\beta_{mn}\frac{\hbar\omega+(\epsilon_n-\epsilon_m)+i\epsilon-\hbar\omega-i\epsilon}{\hbar\omega+\epsilon_n-\epsilon_m+i\epsilon}\left(f(\epsilon_n)-f(\epsilon_m)\right)+\frac{-e^2}{mV}NA^\alpha_\omega\\
&= \frac{-e^2}{i\hbar V}A^\beta_\omega\sum_{nm}v^\alpha_{nm}r^\beta_{mn}\left(f(\epsilon_n)-f(\epsilon_m)\right)+\frac{-e^2}{mV}NA^\alpha_\omega\\
&\quad+\frac{e^2}{i^2\hbar V}i\left(\hbar\omega+i\epsilon\right)A^\beta_\omega\sum_{nm}v^\alpha_{nm}r^\beta_{mn}\frac{f(\epsilon_n)-f(\epsilon_m)}{\hbar\omega+\epsilon_n-\epsilon_m+i\epsilon}.
\end{aligned}$$

Now, the first term can be re-expressed in terms of $\left[v^\alpha,r^\beta\right]$, which is simply related to the canonical commutation relation $\left[v^\alpha,r^\beta\right]_{ab}=\frac{1}{m}\left[p^\alpha,r^\beta\right]_{ab}=-\frac{1}{m}i\hbar\delta_{ab}\delta^{\alpha\beta}$.

$$\frac{-e^2}{i\hbar V}A^\beta_\omega\sum_{nm}v^\alpha_{nm}r^\beta_{mn}\left(f(\epsilon_n)-f(\epsilon_m)\right)=\frac{-e^2}{i\hbar V}A^\beta_\omega\sum_n f(\epsilon_n)\sum_m\left(v^\alpha_{nm}r^\beta_{mn}-v^\alpha_{mn}r^\beta_{nm}\right)=\frac{e^2}{mV}NA^\alpha_\omega. \quad (3.49)$$

This is valid when the Hamiltonian H_0 is of the form $\boldsymbol{p}^2/2m+V(\boldsymbol{r})$. This term precisely cancels the previous $\frac{e^2}{mV}NA^\alpha_\omega$ term, so we are left with

$$\langle J^\alpha_\omega\rangle = \frac{-e^2}{\hbar V}i\left(\hbar\omega+i\epsilon\right)A^\beta_\omega\sum_{nm}v^\alpha_{nm}r^\beta_{mn}\frac{f(\epsilon_n)-f(\epsilon_m)}{\hbar\omega+\epsilon_n-\epsilon_m+i\epsilon}. \quad (3.50)$$

Finally, we may replace $i(\hbar\omega + i\epsilon) A^\beta_\omega = E^\beta_\omega$:

$$\langle J^\alpha_\omega \rangle = \frac{-e^2}{\hbar V} E^\beta_\omega \sum_{nm} v^\alpha_{nm} r^\beta_{mn} \frac{f(\epsilon_n) - f(\epsilon_m)}{\hbar\omega + \epsilon_n - \epsilon_m + i\epsilon}. \tag{3.51}$$

We thus re-obtain eq. 3.34 calculated with the dipolar interaction, showing that the two descriptions indeed reproduce the same results.

3.6 Basis-independent description - vector potential

This current has been calculated in an explicit basis of the non-interacting Hamiltonian. We seek a result that can be calculated in any basis because this will allow us to choose the most convenient one when doing calculations. The goal then is to express this in terms of a trace of operators. Start with equation 3.26:

$$\langle J^\alpha_\omega \rangle = \frac{-e^2}{V} \sum_{nm} \left[f(\epsilon_n) - f(\epsilon_m) \right] v^\alpha_{nm} v^\beta_{mn} \frac{A^\beta_\omega}{\hbar\omega + \epsilon_m - \epsilon_m + i\epsilon} + \frac{-e^2}{mV} N A^\alpha_\omega. \tag{3.52}$$

Start by swapping the summation labels in order to factor out the Fermi functions:

$$\begin{aligned} & \frac{-e^2}{V} \sum_{nm} \left[f(\epsilon_n) - f(\epsilon_m) \right] v^\alpha_{nm} v^\beta_{mn} \frac{A^\beta_\omega}{\hbar\omega + \epsilon_n - \epsilon_m + i\epsilon} \qquad (3.53) \\ = & \frac{-e^2}{V} A^\beta_\omega \sum_{nm} f(\epsilon_n) \left[\frac{v^\alpha_{nm} v^\beta_{mn}}{\hbar\omega + \epsilon_n - \epsilon_m + i\epsilon} - \frac{v^\alpha_{mn} v^\beta_{nm}}{\hbar\omega + \epsilon_m - \epsilon_n + i\epsilon} \right] \\ = & \frac{-e^2}{V} A^\beta_\omega \sum_{nm} f(\epsilon_n) \left[\frac{v^\alpha_{nm} v^\beta_{mn}}{\hbar\omega + \epsilon_n - \epsilon_m + i\epsilon} + \frac{v^\beta_{nm} v^\alpha_{mn}}{-\hbar\omega + \epsilon_n - \epsilon_m - i\epsilon} \right]. \end{aligned}$$

Define the Green operator[2] $G^\pm(\epsilon) = \frac{1}{\epsilon - \hat{H} \pm i0^+}$ and note that

$$\begin{aligned} \frac{f(\epsilon_n)}{\hbar\omega + \epsilon_n - \epsilon_m + i0^+} &= \langle m| G^+(\hbar\omega + \epsilon_n) |m\rangle f(\epsilon_n) = \int_{-\infty}^{\infty} d\epsilon f(\epsilon) \delta(\epsilon - \epsilon_n) \langle m| G^+(\hbar\omega + \epsilon) |m\rangle \\ &= \int_{-\infty}^{\infty} d\epsilon f(\epsilon) \langle n| \delta(\epsilon - \hat{H}) |n\rangle \langle m| G^+(\hbar\omega + \epsilon) |m\rangle . \end{aligned} \tag{3.54}$$

Since $v^\alpha_{nm} = \langle n| \hat{v}^\alpha |m\rangle$, the first term of the previous expression reads

$$\sum_{nm} f(\epsilon_n) \frac{v^\alpha_{nm} v^\beta_{mn}}{\hbar\omega + \epsilon_n - \epsilon_m + i\epsilon} = \sum_{nm} \int_{-\infty}^{\infty} d\epsilon f(\epsilon_n) \langle n| \delta(\epsilon - \hat{H}) |n\rangle \langle m| G^+(\epsilon + \hbar\omega) |m\rangle \langle n| \hat{v}^\alpha |m\rangle \langle m| \hat{v}^\beta |n\rangle . \tag{3.55}$$

[2] G^+ corresponds to the retarded Green's function and G^- to the advanced Green's function.

Now compare this with the following trace:

$$\begin{aligned}&\mathrm{Tr}\left[\delta(\epsilon-\hat{H})\hat{v}^{\alpha}G^{+}(\epsilon+\hbar\omega)\hat{v}^{\beta}\right] \\ &\quad=\sum_{mnab}\langle n|\,\delta(\epsilon-\hat{H})\,|a\rangle\,\langle a|\,\hat{v}^{\alpha}\,|b\rangle\,\langle b|\,G^{+}(\epsilon+\hbar\omega)\,|m\rangle\,\langle m|\,\hat{v}^{\beta}\,|n\rangle \\ &\quad=\sum_{mn}\langle n|\,\delta(\epsilon-\hat{H})\,|n\rangle\,\langle n|\,\hat{v}^{\alpha}\,|m\rangle\,\langle m|\,G^{+}(\epsilon+\hbar\omega)\,|m\rangle\,\langle m|\,\hat{v}^{\beta}\,|n\rangle\,.\end{aligned} \tag{3.56}$$

These are precisely the matrix elements in eq. 3.55. Therefore

$$\begin{aligned}&\frac{-e^2}{V}\sum_{nm}\frac{\left[f(\epsilon_n)-f(\epsilon_m)\right]v^{\alpha}_{nm}v^{\beta}_{mn}}{\hbar\omega+\epsilon_n-\epsilon_m+i\epsilon}A^{\beta}_{\omega} \\ =\;&\frac{-e^2}{V}\int_{-\infty}^{\infty}d\epsilon f(\epsilon)\mathrm{Tr}\left[\delta(\epsilon-\hat{H})\hat{v}^{\alpha}G^{+}(\epsilon+\hbar\omega)\hat{v}^{\beta}+\delta(\epsilon-\hat{H})\hat{v}^{\beta}G^{-}(\epsilon-\hbar\omega)\hat{v}^{\alpha}\right]A^{\beta}_{\omega}\end{aligned} \tag{3.57}$$

and finally, replacing $\boldsymbol{A}_{\omega}=\frac{\boldsymbol{E}_{\omega}}{i\omega}$ we obtain

$$\boxed{\langle J^{\alpha}_{\omega}\rangle=\frac{-e^2}{Vi\omega}\left[\int_{-\infty}^{\infty}d\epsilon f(\epsilon)\mathrm{Tr}\left[\delta(\epsilon-\hat{H})\hat{v}^{\alpha}G^{+}(\epsilon+\hbar\omega)\hat{v}^{\beta}+\delta(\epsilon-\hat{H})\hat{v}^{\beta}G^{-}(\epsilon-\hbar\omega)\hat{v}^{\alpha}\right]+\frac{N}{m}\right]E^{\beta}_{\omega}} \tag{3.58}$$

This expression makes no reference to any basis and so we have reached our first goal.

3.7 Basis-independent description - scalar potential

The same may be achieved with the $\boldsymbol{E}$ formalism. Starting with eq. 3.34,

$$\langle J^{\alpha}_{\omega}\rangle=\frac{-e^2}{\hbar V}\sum_{ab}r^{\beta}_{ba}v^{\alpha}_{ab}\frac{f(\epsilon_a)-f(\epsilon_b)}{\omega_{ab}+\omega+i\epsilon}E^{\beta}_{\omega} \tag{3.59}$$

the procedure is very similar and gives the following result:

$$\boxed{\langle J^{\alpha}_{\omega}\rangle=\frac{-e^2}{V}\sum_{ab}\int_{-\infty}^{\infty}d\epsilon f(\epsilon)\mathrm{Tr}\left[v^{\alpha}G^{+}(\epsilon+\hbar\omega)r^{\beta}\delta(\epsilon-H)+v^{\alpha}\delta(\epsilon-H)r^{\beta}G^{-}(\epsilon-\hbar\omega)\right]E^{\beta}_{\omega}.} \tag{3.60}$$

Compared with the one obtained through the $\boldsymbol{A}$ formalism, this expression is almost identical. The difference resides in replacing one of the $\hat{\boldsymbol{v}}$ operators by $\hat{\boldsymbol{r}}$, which eliminates the last term. Here is a good place to discuss the applicability of both expressions. While eq. 3.60 seems simpler it suffers from a very serious problem. Usually, we want to use periodic boundary conditions in our calculations. This is a simple way to reproduce translation invariance of an infinite system in a finite one. The Hamiltonian operator isn't problematic because it only makes reference to hoppings between two sites, which is translation invariant. The position itself is not translation invariant so it cannot be implemented with periodic boundary conditions. What about the velocity operator? In all the applications considered in this text, we will be working in the position basis,

so we may calculate the matrix elements of $\boldsymbol{v}$ from $\frac{1}{i\hbar}[\boldsymbol{r}, H]$. In fact, $i\hbar \boldsymbol{v}_{ij} = H_{ij}(\boldsymbol{r}_i - \boldsymbol{r}_j)$. It depends on the difference of positions, so it is translation invariant if H is too. As long as we only use H and $\boldsymbol{v}$, there is no problem. That's why the preferred expression is actually 3.58.

3.8 DC limit $\omega \to 0$

The presence of the frequency in the denominator of eq. 3.58 may suggest that $\omega = 0$ makes the whole expression diverge. This section is devoted to exploring this limit. In order to obtain the zero frequency limit, start with eq. 3.53

$$\langle J^\alpha_\omega \rangle = \frac{-e^2}{V} \sum_{n \neq m} \left[f(\epsilon_n) - f(\epsilon_m) \right] v^\alpha_{nm} v^\beta_{mn} \frac{A^\beta_\omega}{\hbar\omega + \epsilon_n - \epsilon_m + i\epsilon} + \frac{-e^2}{mV} N A^\alpha_\omega \tag{3.61}$$

and expand the denominator in a harmonic series:

$$\frac{1}{\omega + \omega_{nm} + i\epsilon} = \frac{1}{\omega_{nm} + i\epsilon} \left(\frac{1}{1 + \frac{\omega}{\omega_{nm} + i\epsilon}} \right) = \frac{1}{\omega_{nm} + i\epsilon} \left(1 - \frac{\omega}{\omega_{nm} + i\epsilon} + O(\omega^2) \right). \tag{3.62}$$

From the definition of Green's function, we may identify this as its Taylor expansion, which will be useful later.

$$\frac{1}{\hbar\omega + \epsilon_n - \epsilon_m \pm i\epsilon} = \langle m | G^\pm(\hbar\omega + \epsilon_n) | m \rangle = \langle m | G^\pm(\epsilon_n) | m \rangle + \omega \langle m | \frac{dG^\pm}{d\epsilon}(\epsilon_n) | m \rangle + O(\omega^2). \tag{3.63}$$

The current becomes:

$$\langle J^\alpha_\omega \rangle = \frac{-e^2}{V\hbar} A^\beta_\omega \sum_{nm} \left[f(\epsilon_n) - f(\epsilon_m) \right] v^\alpha_{nm} v^\beta_{mn} \left[\frac{1}{\omega_{nm} + i\epsilon} - \frac{\omega}{(\omega_{nm} + i\epsilon)^2} + O(\omega^2) \right] + \frac{-e^2}{mV} N A^\alpha_\omega. \tag{3.64}$$

There is no ω in the first term, so the imaginary infinitesimal becomes irrelevant and we may drop it. This term turns out to cancel the $\frac{-e^2}{mV} N A^\alpha_\omega$ term exactly!

$$\begin{aligned}
& \frac{-e^2}{V} A^\beta_\omega \sum_{n \neq m} \left[f(\epsilon_n) - f(\epsilon_m) \right] v^\alpha_{nm} v^\beta_{mn} \frac{1}{\epsilon_n - \epsilon_m} = \frac{-e^2}{V} A^\beta_\omega \sum_{nm} \left[f(\epsilon_n) - f(\epsilon_m) \right] \frac{r^\alpha_{nm}}{i\hbar} v^\beta_{mn} \\
= & \frac{-e^2}{Vi\hbar} A^\beta_\omega \sum_n f(\epsilon_n) \sum_m \left[r^\alpha_{nm} v^\beta_{mn} - r^\alpha_{mn} v^\beta_{nm} \right] = \frac{-e^2}{Vi\hbar} A^\beta_\omega \sum_n f(\epsilon_n) \left[r^\alpha, v^\beta \right]_{nn} \\
= & \frac{-e^2}{V} A^\beta_\omega \sum_n f(\epsilon_n) \frac{1}{m} \delta_{\alpha\beta} (-1_{nn}) = -\frac{-e^2}{V} A^\alpha_\omega \sum_n f(\epsilon_n) = -\frac{-e^2}{Vm} A^\alpha_\omega N.
\end{aligned} \tag{3.65}$$

So we are left with:

$$\begin{aligned}\langle J^\alpha_\omega\rangle &= \frac{-\hbar e^2}{iV}\sum_{nm}\left[f(\epsilon_n)-f(\epsilon_m)\right]v^\alpha_{nm}v^\beta_{mn}\frac{-i\omega A^\beta_\omega}{(\epsilon_n-\epsilon_m+i\epsilon)^2} \\ &= \frac{-\hbar e^2}{iV}\sum_{nm}f(\epsilon_n)\left[v^\alpha_{nm}v^\beta_{mn}\frac{-1}{(\epsilon_n-\epsilon_m+i\epsilon)^2}-v^\beta_{nm}v^\alpha_{mn}\frac{-1}{(\epsilon_m-\epsilon_n+i\epsilon)^2}\right]E^\beta_\omega \\ &= \frac{-\hbar e^2}{iV}\sum_{nm}f(\epsilon_n)\left[v^\alpha_{nm}v^\beta_{mn}\frac{-1}{(\epsilon_n-\epsilon_m+i\epsilon)^2}-v^\beta_{nm}v^\alpha_{mn}\frac{-1}{(\epsilon_n-\epsilon_m-i\epsilon)^2}\right]E^\beta_\omega.\end{aligned} \tag{3.66}$$

This calculation is identical to the one performed in Section 3.6, with the replacement $G^\pm \to \frac{dG^\pm}{d\epsilon}$ and $\omega \to 0$, which yields

$$\boxed{\langle J^\alpha_0\rangle = \frac{-e^2}{V}\int_{-\infty}^{\infty}d\epsilon f(\epsilon)\mathrm{Tr}\left[\delta(\epsilon-\hat{H})\hat{v}^\alpha\frac{dG^+}{d\epsilon}(\epsilon)\hat{v}^\beta-\delta(\epsilon-\hat{H})\hat{v}^\beta\frac{dG^-}{d\epsilon}(\epsilon)\hat{v}^\alpha\right]E^\beta_0.} \tag{3.67}$$

This is the Kubo-Bastin formula.

3.9 Real part of the conductivity

Most of the times, what is calculated numerically is just the real part of the conductivity. This section aims to study this case and to reproduce the result of [9]. Start again with eq. 3.26.

$$\langle J^\alpha_\omega\rangle = \frac{-e^2}{V}\sum_{nm}\left[f(\epsilon_n)-f(\epsilon_m)\right]v^\alpha_{nm}v^\beta_{mn}\frac{A^\beta_\omega}{\hbar\omega+\epsilon_n-\epsilon_m+i\eta}+\frac{-e^2}{mV}NA^\alpha_\omega. \tag{3.68}$$

This can be separated into its real and imaginary parts by using the Sokhotski-Plemelj theorem[3]

$$\langle J^\alpha_\omega\rangle = \frac{-e^2}{V}\sum_{nm}\left[f(\epsilon_n)-f(\epsilon_m)\right]v^\alpha_{nm}v^\beta_{mn}\left[P\left(\frac{1}{\hbar\omega+\epsilon_n-\epsilon_m}\right)-i\pi\delta\left(\hbar\omega+\epsilon_n-\epsilon_m\right)\right]\frac{E^\beta_\omega}{i\omega}+\frac{-e^2}{mV}N\frac{E^\beta_\omega}{i\omega}. \tag{3.71}$$

[3] A simple proof of the result used here is as follows. Given an integral defined between $a<0<b$,

$$\lim_{\epsilon\to0^+}\int_a^b\frac{f(x)}{x\pm i\epsilon}dx = \mp i\pi\lim_{\epsilon\to0^+}\int_a^b\frac{\epsilon}{\pi\left(x^2+\epsilon^2\right)}f(x)dx+\lim_{\epsilon\to0^+}\int_a^b\frac{x^2}{x^2+\epsilon^2}\frac{f(x)}{x}dx \tag{3.69}$$

The first term $\frac{\epsilon}{\pi\left(x^2+\epsilon^2\right)}$ approaches a Dirac delta function when $\epsilon\to0^+$. The second term $\frac{x^2}{x^2+\epsilon^2}$ approaches 1 for $|x|\gg\epsilon$, 0 for $|x|\ll\epsilon$ and is symmetric about 0, so it turns the integral into a Cauchy principal value integral. We thus obtain the famous Sokhotski-Plemelj theorem for the real line:

$$\lim_{\epsilon\to0^+}\int_a^b\frac{f(x)}{x\pm i\epsilon}dx = \mp i\pi f(0)+P\int_a^b\frac{f(x)}{x}dx \tag{3.70}$$

Since this is valid for any (well behaved) test function and integral, we may think of this as an identity on $\lim_{\epsilon\to0^+}\frac{1}{x\pm i\epsilon}$.

Isolating the electric field, we obtain the conductivity

$$\sigma_\omega^{\alpha\beta} = \frac{-e^2}{V}\sum_{nm}\left[f(\epsilon_n) - f(\epsilon_m)\right] v_{nm}^\alpha v_{mn}^\beta \left[P\left(\frac{1}{\hbar\omega + \epsilon_n - \epsilon_m}\right) - i\pi\delta\left(\hbar\omega + \epsilon_n - \epsilon_m\right)\right]\frac{1}{i\omega} + \frac{-e^2}{mV}N\frac{1}{i\omega}. \tag{3.72}$$

Its real part is

$$\Re\left\langle\sigma_\omega^{\alpha\beta}\right\rangle = \frac{\pi e^2}{V\omega}\sum_{nm}\left[f(\epsilon_n) - f(\epsilon_m)\right] v_{nm}^\alpha v_{mn}^\beta \delta\left(\hbar\omega + \epsilon_n - \epsilon_m\right). \tag{3.73}$$

Now we want to obtain a basis-independent description of the longitudinal conductivity $\alpha\alpha$ at zero temperature and finite frequency, so we employ the same procedure as before. The result is

$$\Re\left\langle\sigma_\omega^{\alpha\alpha}\right\rangle = \frac{\pi e^2}{V\omega}\int_{-\infty}^{\infty} d\epsilon f(\epsilon)\mathrm{Tr}\left[\delta(\epsilon - H)v^\alpha\delta\left(\hbar\omega + \epsilon - H\right)v^\alpha - \delta(\epsilon - H)v^\alpha\delta\left(\hbar\omega - \epsilon + H\right)v^\alpha\right]. \tag{3.74}$$

For the second term in this expression, apply the change of variables $\epsilon = \epsilon' + \hbar\omega$ and use the cyclic property of the trace to swap the order of the two Dirac deltas:

$$\int_{-\infty}^{\infty} d\epsilon f(\epsilon)\mathrm{Tr}\left[\delta(\epsilon - H)v^\alpha\delta\left(\hbar\omega - \epsilon + H\right)v^\alpha\right] = \int_{-\infty}^{\infty} d\epsilon' f(\epsilon'+\hbar\omega)\mathrm{Tr}\left[\delta\left(\epsilon' - H\right)v^\alpha\delta(\hbar\omega + \epsilon' - H)v^\alpha\right]. \tag{3.75}$$

Dropping the primes and putting it all together, we arrive at

$$\Re\left\langle\sigma_\omega^{\alpha\alpha}\right\rangle = \frac{\pi e^2}{V\omega}\int_{-\infty}^{\infty} d\epsilon\left[f(\epsilon) - f(\epsilon + \hbar\omega)\right]\mathrm{Tr}\left[\delta(\epsilon - H)v^\alpha\delta\left(\hbar\omega + \epsilon - H\right)v^\alpha\right]. \tag{3.76}$$

Finally, note that at zero temperature, $f(\epsilon) - f(\epsilon + \hbar\omega)$ is zero unless $\mu - \hbar\omega < \epsilon < \mu$. Then,

$$\Re\left\langle\sigma_\omega^{\alpha\alpha}\right\rangle = \frac{\pi e^2}{V\omega}\int_{\mu-\hbar\omega}^{\mu} d\epsilon\mathrm{Tr}\left[\delta(\epsilon - H)v^\alpha\delta\left(\hbar\omega + \epsilon - H\right)v^\alpha\right]. \tag{3.77}$$

This is precisely the result used in [9].

3.10 Finishing remarks

By now we see that the result obtained from Kubo's formula yields results consistent with the ones found in the literature. Furthermore, it allows us to compute both the real and the imaginary parts of the conductivity. However, the most important part of this chapter was obtaining a basis-independent formula for the current resorting only to the Hamiltonian and the velocity operator, which allows us to use periodic boundary conditions. This is crucial for numerical implementations.

4 Higher order perturbation expansions

So far, we've obtained the first term of the expansion using Kubo's formula, which is a fairly simple formula. However, if we proceed to higher orders, the formula becomes very cumbersome and it becomes hard to put it to good use. In the first section we will nevertheless provide a derivation just to see what it looks like. The following sections will then be used to develop a different approach of obtaining a perturbation expansion of the current - the Keldysh formalism.

4.1 Second order Kubo's formula

Start from the formal solution of the interacting Hamiltonian, $|\Psi_I(t)\rangle$

$$|\Psi_I(t)\rangle = T\left\{\exp\left(\frac{-i}{\hbar}\int_{t_0}^{t} dt V_I(t)\right)\right\}|\Psi_I(t_0)\rangle\,. \tag{4.1}$$

Up to second order, this reads

$$|\Psi_I(t)\rangle = \left[1+\frac{-i}{\hbar}\int_{t_0}^{t} dt_1 V_I(t_1) + \frac{1}{2!}\left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t} dt_1\int_{t_0}^{t} dt_2 T\left\{V_I(t_1)V_I(t_2)\right\}\right]|\Psi_I(t_0)\rangle\,. \tag{4.2}$$

Or, unfolding the time ordering

$$|\Psi_I(t)\rangle = \left[1+\frac{-i}{\hbar}\int_{t_0}^{t} dt_1 V_I(t_1) + \left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t} dt_1\int_{t_0}^{t_1} dt_2 V_I(t_1)V_I(t_2)\right]|\Psi_I(t_0)\rangle\,. \tag{4.3}$$

We may now use this to calculate $\rho_I(t)$ up to second order. To do so, let $|n\rangle = |n_I(t_0)\rangle$ be an eigenstate of H_0 before the perturbation.

$$\begin{aligned}
\rho_I(t) &= \frac{1}{Z_0}\sum_n e^{-\beta E_n}|n_I(t)\rangle\langle n_I(t)| \\
&= \frac{1}{Z_0}\sum_n e^{-\beta E_n}\left(1+\frac{-i}{\hbar}\int_{t_0}^{t} dt_1 V_I(t_1) + \left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t} dt_1\int_{t_0}^{t_1} dt_2 V_I(t_1)V_I(t_2)\right)|n\rangle\langle n| \\
&\quad\times\left(1+\frac{i}{\hbar}\int_{t_0}^{t} dt_1 V_I(t_1) + \left(\frac{i}{\hbar}\right)^2\int_{t_0}^{t} dt_1\int_{t_0}^{t_1} dt_2 V_I(t_2)V_I(t_1)\right) + O(V^3).
\end{aligned} \tag{4.4}$$

The factor $\sum_n e^{-\beta E_n}$ can pass through the operators (since all the n dependency is now on $|n\rangle\langle n|$) and retrieve the original density matrix ρ_0.

Collecting the second order terms,

$$\rho_I(t) = \frac{1}{\hbar^2}\left\{-\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \left[V_I(t_1)V_I(t_2)\rho_0 + \rho_0 V_I(t_2)V_I(t_1)\right] + \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 V_I(t_1)\rho_0 V_I(t_2)\right\}. \tag{4.5}$$

To join terms, we need to take the last integral and separate it into two integrals, one from t_0 to t_1 and another from t_1 to t. Then, change the order of integration and swap the time labels to get

$$\begin{aligned}
\rho_I(t) &= \frac{1}{\hbar^2}\left\{-\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \left(V_I(t_1)V_I(t_2)\rho_0 + \rho_0 V_I(t_2)V_I(t_1)\right)\right\} \\
&+ \frac{1}{\hbar^2}\left\{\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 V_I(t_1)\rho_0 V_I(t_2) + \int_{t_0}^{t} dt_1 \int_{t_1}^{t} dt_2 V_I(t_1)\rho_0 V_I(t_2)\right\} \qquad (4.6) \\
&= \frac{1}{\hbar^2}\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \left[-V_I(t_1)V_I(t_2)\rho_0 - \rho_0 V_I(t_2)V_I(t_1) + V_I(t_1)\rho_0 V_I(t_2) + V_I(t_2)\rho_0 V_I(t_1)\right].
\end{aligned}$$

The averages are calculated with respect to the system in equilibrium, so the partition function Z_0 is unaltered. These tools allow us to finally calculate the expected value of an operator in second order. Using $\langle A\rangle(t) = \mathrm{Tr}(\rho A)$, we arrive at

$$\begin{aligned}
\langle A\rangle(t) &= \frac{1}{\hbar^2}\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \mathrm{Tr}\left[-V_I(t_1)V_I(t_2)\rho_0 A_I - \rho_0 V_I(t_2)V_I(t_1)A_I + \right. \\
&\quad \left. + V_I(t_1)\rho_0 V_I(t_2)A_I + V_I(t_2)\rho_0 V_I(t_1)A_I\right] \\
&= \frac{1}{\hbar^2}\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \mathrm{Tr}\left(\rho_0\left[V_I(t_2),\left[A_I, V_I(t_1)\right]\right]\right). \qquad (4.7)
\end{aligned}$$

Combining this with Kubo's formula (eq. 3.5) we obtain the desired generalization.

$$\boxed{\langle A\rangle(t) = \langle A\rangle_0 + \left(\frac{-i}{\hbar}\right)\int_{t_0}^{t} dt' \left\langle\left[A_I(t), V_I(t')\right]\right\rangle_0 + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \left\langle\left[V_I(t_2),\left[V_I(t_1), A_I\right]\right]\right\rangle_0.} \tag{4.8}$$

This expansion is starting to reveal a nested commutator structure, so one might expect this pattern to continue. Although this may be proven, it will not be used. As we arrive at higher and higher orders, we'll have to compute more and more commutators, which may become rather cumbersome. Even if we decide to go through that, the resulting expressions will be written in the energy basis of the solvable Hamiltonian, and if we want to express them in a basis-independent way, we'll have to go through case by case. This is the reason that leads us to abandon Kubo's formalism in virtue of a more elegant one, the Keldysh formalism[10]. This will allow us to use the familiar Feynman diagram techniques, which simplify the calculations immensely, with the added bonus of being expressed precisely in terms of the numerical objects that we need.

4.2 Green's functions out of equilibrium - Keldysh Formalism

Suppose we have a system that is described by a time-dependent Hamiltonian

$$H(t) = H_0 + V + H_{ext}(t) = H_0 + V_{ext}(t) \tag{4.9}$$

where H_0 is the Hamiltonian that we can solve exactly, V is the interaction term and $H_{ext}(t)$ is the time-dependent non-interacting external perturbation. In terms of the creation and destruction operators of second quantization, we may write

$$H_0 = \sum_n \epsilon_n c_n^\dagger c_n. \tag{4.10}$$

We want to develop a perturbation theory that neatly takes into account the fact that the system has a finite temperature. For reasons that will soon become clear, the object that we need to calculate is the finite-temperature Green's function [10].

4.2.1 Green's functions

We want to calculate the following Green's function:

$$G(1,1') = -i \left\langle T\left[c_H(1) c_H^\dagger(1')\right]\right\rangle. \tag{4.11}$$

The subscript H denotes the Heisenberg picture and the labels 1 and $1'$ are a shorthand for the time, space, energy or any coordinates needed to completely describe the particle's state. For example for a particle with spin in the position representation, $c(1) = c_{\boldsymbol{x},\sigma}(t)$. The average $\langle\cdots\rangle$ stands for $\frac{\mathrm{Tr}[\rho(t_0)\cdots]}{\mathrm{Tr}[\rho(t_0)]}$ in the grand canonical ensemble. We now express this in the interaction picture, recalling that the time-ordering operator can be written out explicitly using a Heaviside function $\Theta(t)$. We also make use of the evolution operator in the Interaction Picture $S(t,t')$ to transform the creation operators in the Heisenberg Picture to their correspondence in the Interaction Picture (eq. 2.121):

$$\begin{aligned} T\left[c_H(1)c_H(1')\right] &= \Theta(t-t')c_H(1)\psi_H(1') \pm \Theta(t'-t)c_H^\dagger(1')c_H(1) \\ &= \Theta(t-t')S(t_0,t)c_I(1)S(t,t')c_I^\dagger(1')S(t',t_0) \\ &\pm \Theta(t'-t)S(t_0,t')c_I^\dagger(1')S(t',t)c_I(1)S(t,t_0) \end{aligned} \tag{4.12}$$

which can be written in a neat compact form by defining $t_m = \max(t,t')$:

$$T\left[c_H(1)c_H(1')\right] = S(t_0,t_m)T\left[S(t_m,t_0)c_I(1)c_I^\dagger(1')\right]. \tag{4.13}$$

Write explicitly the formal expressions for the evolution operators.

$$\begin{aligned} iG(1,1') &= \left\langle S(t_0,t_m)T\left[S(t_m,t_0)c_I(1)c_I^\dagger(1')\right]\right\rangle \\ &= \left\langle \tilde{T}\exp\left(\frac{-i}{\hbar}\int_{t_m}^{t_0}d\tau V_I^{ext}(\tau)\right)T\left[\exp\left(\frac{-i}{\hbar}\int_{t_0}^{t_m}d\tau V_I^{ext}(\tau)\right)c_I(1)c_I^\dagger(1')\right]\right\rangle. \end{aligned} \tag{4.14}$$

Note that the time integration runs from t_0 to t_m and then back from t_m to t_0. We may imagine that as a contour followed by the the time integration (fig. 4.1). With that in mind, define the contour ordering operator T_C in analogy to the regular time-ordering operator:

$$T_C\left[A(t_1)B(t_2)\right] = \begin{cases} A(t_1)B(t_2) & t_1 \overset{c}{>} t_2 \\ \pm B(t_2)A(t_1) & t_2 \overset{c}{<} t_1 \end{cases}. \tag{4.15}$$

We say $t_1 \overset{c}{>} t_2$ if t_1 is further along the contour than t_2. Ordering along $\overrightarrow{C}$ corresponds to the regular time ordering and ordering along $\overleftarrow{C}$ to anti-time ordering.

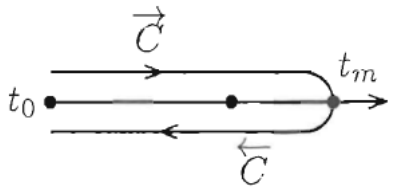


Figure 4.1: The time contour.

Now the Green's function takes the form:

$$iG(1,1') = \left\langle T_C\exp\left(\frac{-i}{\hbar}\int_{\overleftarrow{C}}d\tau V_I^{ext}(\tau)\right)T_C\left[\exp\left(\frac{-i}{\hbar}\int_{\overrightarrow{C}}d\tau V_I^{ext}(\tau)\right)c_I(1)c_I^\dagger(1')\right]\right\rangle. \tag{4.16}$$

Since the left-most term is entirely further along the contour than the right-most term, they may be joined inside the same contour ordering operator.

$$iG(1,1') = \left\langle T_C\left[\exp\left(\frac{-i}{\hbar}\int_C d\tau V_I^{ext}(\tau)\right)c_I(1)c_I^\dagger(1')\right]\right\rangle \tag{4.17}$$

We have assumed t and t' lie along the forward part of the contour, but this need not be the case. In fact, there are four possible ways to place t and t'. Define the contour-ordered Green's function as:

$$iG_C(r\sigma t, r'\sigma' t') = \left\langle T_C\left[c_H(1)c_H^\dagger(1')\right]\right\rangle. \tag{4.18}$$

Depending on how we place t and t' along the contour, we will obtain several other known Green's functions as particular cases of this more general one.

4.2.2 Particular Green's functions

Here we'll see how the contour-ordered Green's function encapsulates the other known Green's functions.

1. $t, t' \in \overrightarrow{C}$:
   This is the case we have just seen and corresponds to the regular time-ordered Green's function:
   $$iG_C(1,1') = \left\langle T\left[c_H(1)c_H^\dagger(1')\right]\right\rangle = iG^T(1,1'). \tag{4.19}$$

2. $t \in \overrightarrow{C}$ and $t' \in \overleftarrow{C}$
   This case yields the lesser Green's function. Remember that swapping $c_I(1)$ and $c_I^\dagger(1')$ inside the ordering operator produces a minus sign if they're fermions. Swapping the evolution operator with any of them will not produce a minus sign because V_I always consists of an even number of fermion or boson operators.
   $$\begin{aligned} iG_C(1,1') &= \left\langle T_C\left[\exp\left(\int_C d\tau V_I^{ext}(\tau)\right) c_I(1)c_I^\dagger(1')\right]\right\rangle \\ &= \pm\left\langle S(t',t_0)c_I^\dagger(1')S(t,t')c_I(1)S(t_0,t)\right\rangle \\ &= \pm\left\langle c_H^\dagger(1')c_H(1)\right\rangle \\ &= iG^<(1,1'). \end{aligned} \tag{4.20}$$

The other two ways are analogous and are summarized as follows:

$$iG_C(1,1') = \begin{cases} iG^T(1,1') = \left\langle T\left[c_H(1)c_H^\dagger(1')\right]\right\rangle & t,t' \in \overrightarrow{C} \\ iG^<(1,1') = \pm\left\langle c_H^\dagger(1')c_H(1)\right\rangle & t \in \overrightarrow{C} \text{ and } t' \in \overleftarrow{C} \\ iG^>(1,1') = \left\langle c_H(1)c_H^\dagger(1')\right\rangle & t' \in \overrightarrow{C} \text{ and } t \in \overleftarrow{C} \\ iG^{\tilde{T}}(1,1') = \left\langle \widetilde{T}\left[c_H(1)c_H^\dagger(1')\right]\right\rangle & t,t' \in \overleftarrow{C} \end{cases}. \tag{4.21}$$

Unfolding the definitions, we can check that

$$G^T + G^{\tilde{T}} = G^< + G^>. \tag{4.22}$$

Furthermore, the retarded Green's function can be obtained from these

$$iG^R = \Theta(t-t')\left\langle\left[c_H(1), c_H(1')\right]_\mp\right\rangle = i\Theta(t-t')\left[G^>(1,1') - G^<(1,1')\right]. \tag{4.23}$$

Similarly, for the advanced Green's function

$$iG^a = -\Theta(t'-t)\left\langle\left[c_H(1), c_H(1')\right]_\mp\right\rangle = i\Theta(t'-t)\left[-G^>(1,1') + G^<(1,1')\right]. \tag{4.24}$$

Some more useful relations can be obtained for the retarded and advanced Green's functions, which can be checked directly

$$G^R = G^T - G^< \tag{4.25}$$
$$G^a = -G^{\tilde{T}} + G^<. \tag{4.26}$$

These are the relations that will be used extensively while doing the calculations. Their expressions are calculated in the Appendix (eq. 8.43) to be used as a reference.

4.2.3 Perturbation expansion

So far we've only restated our initial problem in terms of a fancy language. Now we need to re-express all these operators in terms of something we can calculate: averages over non-interacting time-independent states. Under time ordering, boson operators commute, so we can replace the exponential of $V_I(t) = H_I^{ext}(t) + V_I$ by the exponential of the product

$$iG(1,1') = \left\langle T_C\left[e^{\frac{-i}{\hbar}\int_C d\tau V_I^{ext}(\tau)} c_I(1) c_I^\dagger(1')\right]\right\rangle = \left\langle T_C\left[e^{\frac{-i}{\hbar}\int_C d\tau V_I(\tau)} e^{\frac{-i}{\hbar}\int_C d\tau H_I^{ext}(\tau)} c_I(1) c_I^\dagger(1')\right]\right\rangle. \tag{4.27}$$

Taking into account this separation, define the operators

$$S_C^V = e^{\frac{-i}{\hbar}\int_C d\tau V_I(\tau)} \tag{4.28}$$
$$S_C^{ext} = e^{\frac{-i}{\hbar}\int_C d\tau H_I^{ext}(\tau)}. \tag{4.29}$$

Allowing us to rewrite the Green's function

$$iG(1,1') = \left\langle T_C\left[S_C^V S_C^{ext} c_I(1) c_I^\dagger(1')\right]\right\rangle = \frac{\mathrm{Tr}\left(\rho_H T_C\left[S_C^V S_C^{ext} c_I(1) c_I^\dagger(1')\right]\right)}{\mathrm{Tr}\left(\rho_H T_C\left[S_C^V S_C^{ext}\right]\right)}. \tag{4.30}$$

It still remains to expand the density matrix. Recall that

$$iG(1,1') = \frac{\mathrm{Tr}\left(\rho_H T_C\left[c_H(1) c_H^\dagger(1')\right]\right)}{\mathrm{Tr}\left(\rho_H\right)}. \tag{4.31}$$

The density matrix remains the same even after the interaction has been switched on, so $\rho_H(t) = \rho(t_0)$. This means we can still treat it as an exponential. Now we employ a trick that allows us to write ρ in terms of S^V. In the grand canonical ensemble, since the Hamiltonian preserves the number of particles, N commutes with H as well as H_0:

$$\rho(t_0) = e^{-\beta(H-\mu N)} = e^{-\beta H} e^{\beta\mu N} = e^{-\beta(H_0-\mu N)} e^{\beta H_0} e^{-\beta H} = \rho_0 e^{\beta H_0} e^{-\beta H}. \tag{4.32}$$

Before the interaction is turned on ($t < t_0$), the Hamiltonian has no time dependency so

the time evolution operator takes the simple form $U(t,t_0) = e^{-iH(t-t_0)/\hbar}$. Likewise, in the Interaction picture, the relation between $U(t,t')$ and $S(t,t')$ (eq. 2.119) reduces to $S(t,t_0) = e^{iH_0(t-t_0)/\hbar}e^{-iH(t-t_0)/\hbar}$. This has precisely the same form as the factor $e^{\beta H_0}e^{-\beta H}$ in the previous expression. Making the identification $t = t' - i\beta\hbar$ and $t_0 = t'$, the density matrix becomes

$$\rho(t_0) = \rho_0 S^V(t' - i\beta\hbar, t'). \tag{4.33}$$

So far, the real part is arbitrary, but we want to incorporate it in the time contour, so we take $t' = t_0$. Insert this back into the Green's function

$$iG(1,1') = \frac{\mathrm{Tr}\left[\rho_0 S^V(t_0 - i\beta\hbar, t_0) T_C\left[S_C^V S_C^{ext} c_I(1) c_I^\dagger(1')\right]\right]}{\mathrm{Tr}\left[\rho_0 S^V(t_0 - i\beta\hbar, t_0) T_C\left[S_C^V S_C^{ext}\right]\right]}. \tag{4.34}$$

Now note that S^V occurs to the left of T_C. Therefore, if we want to include it inside the time ordering, it must correspond to a time later than all the others. Define a new contour C' as in Figure 4.2.

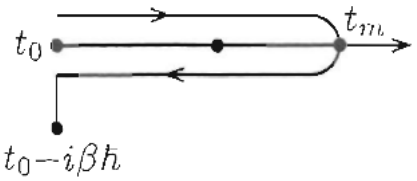


Figure 4.2: Kadanoff-Baym three-branch contour.

We may finally express this Green's function in terms of non-interacting averages:

$$iG(1,1') = \frac{\mathrm{Tr}\left[\rho_0 T_{C'}\left[S_{C'}^V S_C^{ext} c_I(1) c_I^\dagger(1')\right]\right]}{\mathrm{Tr}\left[\rho_0 T_{C'}\left[S_{C'}^V S_C^{ext}\right]\right]} = \frac{\left\langle T_{C'}\left[S_{C'}^V S_C^{ext} c_I(1) c_I^\dagger(1')\right]\right\rangle_0}{\left\langle T_{C'}\left[S_{C'}^V S_C^{ext}\right]\right\rangle_0}. \tag{4.35}$$

Expanding $S_{C'}^V$ and S_C^{ext} order by order, we obtain a perturbation series for $G(1,1')$ valid for all times t and t'. Since the ensemble average is over the non-interacting system, Wick's theorem applies.

4.2.4 Keldysh contour

Usually, we're interested in studying the system long after the interactions have been turned on, that is $t, t' \gg t_0$. In this regime, assuming a steady state develops, we should expect no dependency on t_0. Alternatively, we may assume that the interactions are turned on adiabatically,

so $\rho_H(t_0 = -\infty) = \rho_0$. Consequently, the contour from t_0 to $t_0 - i\beta\hbar$ may be disregarded altogether. The contour is now the original C contour and extends from $-\infty$ to t_m. The time integration might as well be taken all the way to $+\infty$ because integrating from t_m to $+\infty$ and back will yield exactly zero because in that interval the integrand remains unchanged under the time ordering operator. We thus finally arrive at the Keldysh contour, which is depicted in Fig. 4.3 and a simpler expression for the expansion of the Green's function, which is the one that will be used thoroughly through the next chapter.

$$iG(1,1') = \frac{\left\langle T_{C'}\left[S_C^V S_C^{ext} c_I(1) c_I^\dagger(1')\right]\right\rangle_0}{\left\langle T_C\left[S_C^V S_C^{ext}\right]\right\rangle_0}. \tag{4.36}$$

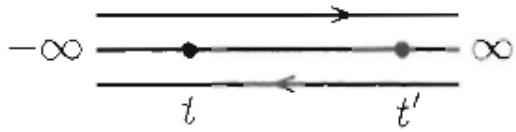


Figure 4.3: Keldysh contour.

We have obtained the expression of Green's function in terms of averages in the non-interacting system, so in principle our goal has been achieved. There are still some simplifications to be had and the next sections of this chapter are devoted to developing some techniques to simplify the use of this expansion. The first simplification arises from the type of problem we're analyzing. In our case, the perturbation does not involve interaction between the particles, so $S_C^V = 1$ and we need only care about the time-dependent part. Unless stated otherwise, this will be used implicitly in the following sections.

4.2.5 Feynman Diagrams

Consider the numerator in eq. 4.36. Upon expanding the exponentials, a typical term of the expansion is

$$\frac{1}{2}\left\langle T_C\left[\frac{-i}{\hbar}\int_C d\tau_1 H^{ext}(\tau_1)\int_C d\tau_2 \frac{-i}{\hbar} H^{ext}(\tau_2) c_n(t) c_m^\dagger(t')\right]\right\rangle_0. \tag{4.37}$$

These operators are in the Interaction Picture, but for simplicity of notation, that label has been dropped. Henceforth, we shall use that notation. Defining $V(t) = \frac{-i}{\hbar} H^{ext}(t) = \sum_{ab} V_{ab}(\tau_1) c_a^\dagger(\tau_1) c_b(\tau_1)$ and using Einstein's summation convention,

$$\frac{1}{2}\int_C d\tau_1 \int_C d\tau_2 V_{ab}(\tau_1) V_{cd}(\tau_2)\left\langle T_C\left[c_a^\dagger(\tau_1) c_b(\tau_1) c_c^\dagger(\tau_2) c_d(\tau_2) c_n(t) c_m^\dagger(t')\right]\right\rangle_0. \tag{4.38}$$

This is a rather unwieldy expression that can be tamed using Wick's theorem (eq. 2.141). To

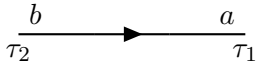
simplify our notation for now, let's drop the time-dependency of the operators. Wick's theorem then provides all the six possible (non-zero) contractions:

$$\begin{aligned}\left\langle T_C\left[c_a^\dagger c_b c_c^\dagger c_d c_n c_m^\dagger\right]\right\rangle_0 &= \left\langle \overbrace{c_a^\dagger c_b}\, \overbrace{c_c^\dagger c_d}\, \overbrace{c_n c_m^\dagger}\right\rangle_0 + \left\langle \overbrace{c_a^\dagger c_b \overbrace{c_c^\dagger c_d}\, c_n c_m^\dagger}\right\rangle_0 + \left\langle \overbrace{c_a^\dagger c_b \overbrace{c_c^\dagger c_d c_n c_m^\dagger}}\right\rangle_0 \\ &+ \left\langle \overbrace{c_a^\dagger c_b}\, \overbrace{c_c^\dagger c_d \overbrace{c_n c_m^\dagger}}\right\rangle_0 + \left\langle \overbrace{c_a^\dagger c_b \overbrace{c_c^\dagger c_d c_n c_m^\dagger}}\right\rangle_0 + \left\langle \overbrace{c_a^\dagger c_b \overbrace{c_c^\dagger c_d c_n c_m^\dagger}}\right\rangle_0 \end{aligned} \tag{4.39}$$

Now denoting the non-interacting green's function by a lowercase $g_{ab}^C(t_1,t_2) = i\left\langle T_C\left[c_a(t_1)c_b^\dagger(t_2)\right]\right\rangle_0$, the previous result is

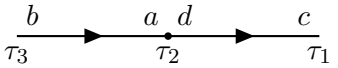
$$\begin{aligned}&\left\langle T_C\left[c_a^\dagger c_b c_c^\dagger c_d c_n c_m^\dagger\right]\right\rangle_0 \\ &= \left(-ig_{ba}^C(\tau_1,\tau_1)\right)\left(-ig_{dc}^C(\tau_2,\tau_2)\right) ig_{nm}^C(t,t') + \left(-ig_{da}^C(\tau_2,\tau_1)\right) ig_{bc}^C(\tau_1,\tau_2) g_{nm}^C(t,t') + \\ &- \left(-ig_{na}^C(t,\tau_1)\right) ig_{bc}^C(\tau_1,\tau_2) ig_{dm}^C(\tau_2,t') - \left(-ig_{ba}^C(\tau_1,\tau_1)\right)\left(-ig_{nc}^C(t,\tau_2)\right) ig_{dm}^C(\tau_2,t') + \\ &+ \left(-ig_{da}^C(\tau_2,\tau_1)\right)\left(-ig_{nc}^C(t,\tau_2)\right) ig_{bm}^C(\tau_1,t') - \left(-ig_{na}^C(t,\tau_1)\right)\left(-ig_{dc}^C(\tau_2,\tau_2)\right) ig_{bm}^C(\tau_1,t').\end{aligned} \tag{4.40}$$

The minus signs inside the parenthesis are due to the definition of the Green's function: the annihilation operator must appear first inside the time-ordering, which may require an anti-commutation. The other minus signs appear due to anti-commutations of Wick contractions. In order to deal with this kind of expressions, we adopt a diagrammatic notation. We may think about the Green's function $g_{ab}^C(t_1,t_2)$ as a particle being created at time t_2 with energy ϵ_b and destroyed at time t_1 with energy ϵ_a. We thus represent the Green's function by a directed line from the second time argument to the first:



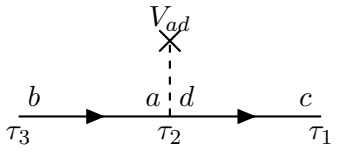
$$= ig_{ab}^C(\tau_1,\tau_2). \tag{4.41}$$

A product of Green's functions that share a time argument integrated over is depicted by connecting two diagrams like the previous one. In fact, each time label is a vertex on the diagram, to which multiple objects may be connected. Vertices with more than one edge are to be understood as being integrated over time:



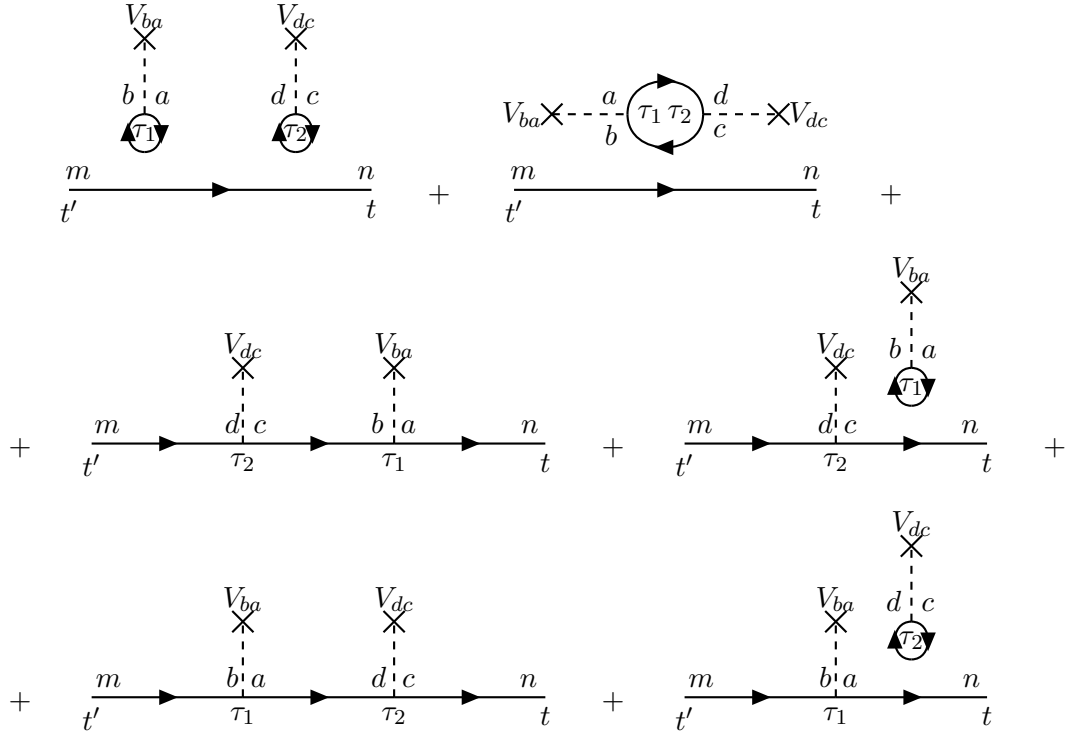
$$= \int_C d\tau_2 ig_{cd}^C(\tau_1,\tau_2) ig_{ab}^C(\tau_2,\tau_3). \tag{4.42}$$

The interaction is represented by a dotted line with a cross in the end:



$$= \int_C d\tau_2 i g^C_{cd}(\tau_1, \tau_2) V_{da}(\tau_2) i g^C_{ab}(\tau_2, \tau_3). \tag{4.43}$$

Using these rules, we may represent schematically eq. 4.38



These are all the possible ways to arrange three fermion lines and two interactions and they represent all the non-zero Wick contractions in eq. 4.39. Next, we state without proof some properties of these diagrams that will simplify the calculations considerably [10].

4.2.5.1 Cancellation of disconnected diagrams, overall minus sign and symmetry factors

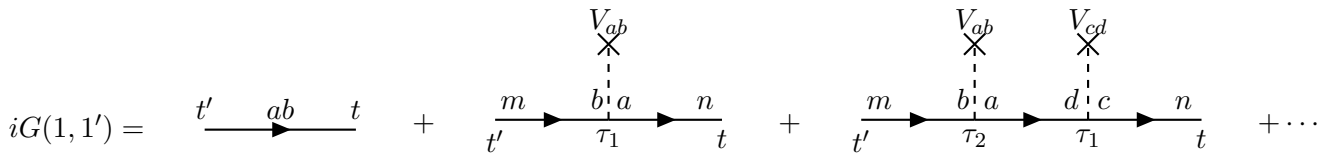
1. We haven't taken into account the minus signs that come from the definition of the Green's functions and the anti-commutation due to Wick's contractions. The overall sign of the diagram is $(-1)^{n_\ell}$ where n_ℓ is the number of closed fermion loops.

2. The effect of the denominator in eq. 4.36 is to cancel out all the diagrams which are not fully connected. The only surviving diagrams are the third and the fifth.

3. Topologically identical diagrams have the exact same contribution to the expansion. The 3rd and 5th diagrams are actually identical because they only differ by dummy variables. So we only need to draw one diagram and multiply by its multiplicity, that is, the number

of ways to swap labels and obtain the same result. That number is $n!$ where n is the order of the expansion. This cancels precisely the factorial coming from the expansion of the exponential.

This means we only need to consider the third diagram in the previous expression. The expansion of $G(1,1')$ is therefore very simple since there is only one diagram in each order:

$iG(1,1') =$ 

Up to second order,

$$\begin{aligned} iG^C_{nm}(t,t') &= ig^C_{nm}(t,t') + \int_C d\tau i g^C_{na}(t,\tau) V_{ab}(\tau) i g^C_{bm}(\tau,t') \\ &+ \int_C d\tau_1 \int_C d\tau_2 i g^C_{na}(t,\tau_1) V_{ab}(\tau_1) i g^C_{bc}(\tau_1,\tau_2) V_{cd}(\tau_2) i g^C_{dm}(\tau_2,t'). \end{aligned}$$

Or, more compactly in matrix notation:

$$\begin{aligned} iG^C(t,t') &= ig^C(t,t') + \int_C d\tau i g^C(t,\tau) V(\tau) i g^C(\tau,t') \\ &+ \int_C d\tau_1 \int_C d\tau_2 i g^C(t,\tau_1) V(\tau_1) i g^C(\tau_1,\tau_2) V(\tau_2) i g^C(\tau_2,t'). \end{aligned} \tag{4.44}$$

4.2.6 Langreth Rules

Despite the previous sections allowing us to obtain a perturbation expansion of the full Green's function in terms of contour integrals, these are not the quantities we want. Our goal is to express everything in terms of real Green's functions like the ones in section 4.2.2. Langreth's rules are a prescription to do just that. A typical term in the expansion is of the form

$$C(\tau,\tau') = \int_C A(\tau,\tau_1) B(\tau_1,\tau') d\tau. \tag{4.45}$$

where both A and B are contour-ordered functions. Just like Green's functions, they have a real-time counterpart

$$A(\tau,\tau') = \begin{cases} A^T(t,t') & \tau,\tau' \in \overrightarrow{C} \\ A^<(t,t') & \tau \in \overrightarrow{C} \text{ and } \tau' \in \overleftarrow{C} \\ A^>(t,t') & \tau' \in \overrightarrow{C} \text{ and } \tau \in \overleftarrow{C} \\ A^{\tilde{T}}(t,t') & \tau,\tau' \in \overleftarrow{C} \end{cases}. \tag{4.46}$$

And the retarded and advanced functions are defined just like before

$$A^R(t,t') = \theta(t-t')\left[A^>(t,t') - A^<(t,t')\right] \tag{4.47}$$

$$A^a(t,t') = \theta(t'-t)\left[A^<(t,t') - A^>(t,t')\right]. \tag{4.48}$$

We'll focus on the case where $\tau \in \overrightarrow{C}$ and $\tau' \in \overleftarrow{C}$ since that's the one we'll use the most. Now it's just a matter of dividing the contour into its two parts:

$$C^<(t,t') = \int_C A(\overrightarrow{t},\tau_1)B(\tau_1,\overleftarrow{t'})d\tau = \int_{-\infty}^{\infty} A(\overrightarrow{t},\overrightarrow{t_1})B(\overrightarrow{t_1},\overleftarrow{t'})dt_1 + \int_{\infty}^{-\infty} A(\overrightarrow{t},\overleftarrow{t_1})B(\overleftarrow{t_1},\overleftarrow{t'})dt_1.$$

The arrows over the time labels refer to the branch in the contour to which they belong. The forward (backward) arrow refers to the forward (backward) part of the contour. Swap the limits of the second integral to yield a minus sign and note that the functions now reduce to their real-time counterparts:

$$\begin{aligned} C^<(t,t') &= \int_{-\infty}^{\infty} A(\overrightarrow{t},\overrightarrow{t_1})B(\overrightarrow{t_1},\overleftarrow{t'})dt_1 - \int_{-\infty}^{\infty} A(\overrightarrow{t},\overleftarrow{t_1})B(\overleftarrow{t_1},\overleftarrow{t'})dt_1 \\ &= \int_{-\infty}^{\infty} \left(A^T(t,t_1)B^<(t_1,t')dt_1 - A^<(t,t_1)B^{\tilde{T}}(t_1,t')\right)dt_1. \end{aligned}$$

Time-ordered quantities are not the most useful to calculate, but we can relate them to other more useful quantities using eqs. 4.25 and 4.26. In terms of these, the previous expression takes on its final form:

$$C^<(t,t') = \int_{-\infty}^{\infty} \left[A^R(t,t_1)B^<(t_1,t') + A^<(t,t_1)B^a(t_1,t')\right]dt_1. \tag{4.49}$$

The other cases follow an identical derivation and can be checked by the diligent reader. The results are summarized using a simplified matrix notation [11] where $C = AB$ means $C(\tau,\tau') = \int_C A(\tau,\tau_1)B(\tau_1,\tau')d\tau$.

$$\begin{aligned} C^< &= A^RB^< + A^<B^a \\ C^> &= A^RB^> + A^>B^a \\ C^R &= A^RB^R \\ C^a &= A^aB^a \end{aligned}$$

This notation reveals something very interesting. The Langreth rules actually form a closed space of $>$, $<$, R and a operators, the so-called Keldysh space. If we use T and $\widetilde{T}$ instead of R and a, the rules are slightly different but still follow a pattern:

$$\begin{aligned} C^{>} &= A^{>}B^{T} - A^{\tilde{T}}B^{>} \\ C^{<} &= A^{T}B^{<} - A^{<}B^{\tilde{T}} \\ C^{T} &= A^{T}B^{T} - A^{<}B^{>} \\ C^{\tilde{T}} &= A^{>}B^{<} - A^{\tilde{T}}B^{\tilde{T}}. \end{aligned}$$

We may further increase the level of abstraction by putting these in a matrix

$$C = \begin{bmatrix} C^{T} & C^{<} \\ -C^{>} & -C^{\tilde{T}} \end{bmatrix}. \tag{4.50}$$

And the the rules are simply $C = AB$ in this matrix form, that is

$$\begin{bmatrix} C^{T} & C^{<} \\ -C^{>} & -C^{\tilde{T}} \end{bmatrix} = \begin{bmatrix} A^{T} & A^{<} \\ -A^{>} & -A^{\tilde{T}} \end{bmatrix} \begin{bmatrix} B^{T} & B^{<} \\ -B^{>} & -B^{\tilde{T}} \end{bmatrix}. \tag{4.51}$$

The other set of rules may be obtained from defining a different matrix

$$C' = \begin{bmatrix} C^{R} & C^{<} \\ 0 & C^{a} \end{bmatrix} \tag{4.52}$$

which can be confirmed from $C' = A'B'$:

$$\begin{bmatrix} C^{R} & C^{<} \\ 0 & C^{a} \end{bmatrix} = \begin{bmatrix} A^{R} & A^{<} \\ 0 & A^{a} \end{bmatrix} \begin{bmatrix} B^{R} & B^{<} \\ 0 & B^{a} \end{bmatrix}. \tag{4.53}$$

Higher order expansions such as

$$D(\tau, \tau') = \int_{C} d\tau_1 \int_{C} d\tau_2 A(\tau, \tau_1) B(\tau_1, \tau_2) C(\tau_2, \tau') \tag{4.54}$$

can be seen as

$$D(\tau, \tau') = \int_{C} d\tau_1 A(\tau, \tau_1) \int_{C} d\tau_2 B(\tau_1, \tau_2) C(\tau_2, \tau') = \int_{C} d\tau_1 A(\tau, \tau_1) BC(\tau_1, \tau') \tag{4.55}$$

and thus follow the exact same procedure considering BC as the new object. In matrix notation, $D = ABC$, which allows us to calculate $D^{<}$:

$$D^{<} = A^{R}\left(BC\right)^{<} + A^{<}\left(BC\right)^{a} = A^{R}B^{R}C^{<} + A^{R}B^{<}C^{a} + A^{<}B^{a}C^{a}. \tag{4.56}$$

The other relations follow the same derivation and all this may be summarized as follows:

$$\begin{aligned} D^{<} &= A^R B^R C^{<} + A^R B^{<} C^a + A^{<} B^a C^a \\ D^{>} &= A^R B^R C^{>} + A^R B^{>} C^a + A^{>} B^a C^a \\ D^{R} &= A^R B^R C^R \\ D^{a} &= A^a B^a C^a. \end{aligned}$$

This concludes the discussion about the Keldysh formalism and we are now ready to begin the calculations.

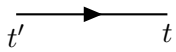
5 Higher order expansions - explicit calculation

The previous chapter was devoted to developing the tools needed to do perturbation theory. Now all our effort will pay off because obtaining the expressions in each order will be easier. This next section is devoted to obtaining the explicit expression of the primary object of study, the Green's function, up to third order.

5.1 Green's functions

5.1.1 Zeroth order

This order is trivial but nonetheless very important. The system we will be studying, the Tight Binding Hamiltonian, has a perturbation $H^{\text{ext}}(t)$ with terms of all orders, so there will be couplings with the zeroth order term. Its Feynman diagram is



This is, by definition,

$$iG^C(t,t') = ig^C(t,t'). \tag{5.1}$$

In most of its applications, this zeroth order term will be evaluated at $t' = t$, so we should pay special attention to that case. In the Appendix (eq. 8.32) we may find the expression for the lesser Green's function in the energy basis:

$$ig^<_{nm}(t,t') = -\delta_{nm} f(\epsilon_n) e^{i\epsilon_m(t'-t)}. \tag{5.2}$$

Taking the case $t' = t$, the time dependency is gone

$$ig^<_{nm}(t,t) = -\delta_{nm} f(\epsilon_n) = -\int_{-\infty}^{\infty} d\epsilon f(\epsilon)\delta(\epsilon - H)_{mn}. \tag{5.3}$$

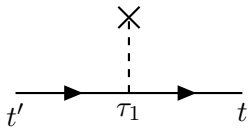
In frequency space, it has a very simple expression

$$ig^<(\omega) = -2\pi \int_{-\infty}^{\infty} d\epsilon f(\epsilon)\delta(\epsilon - H)\delta(\omega). \tag{5.4}$$

This is the term that will be responsible for the Fermi functions.

5.1.2 First order

The diagram that represents the first order contribution to the perturbation expansion is



Using Feynman's rules, this translates to

$$iG^C(t,t') = \int_C d\tau i g^C(t,\tau)V(\tau)ig^C(\tau,t'). \tag{5.5}$$

Using Langreth's rules, this integral is promptly converted into a real-time integral in terms of known Green's functions. Let $t' = t$:

$$iG^<(t,t) = \int_{-\infty}^{\infty} dt_1 \left(ig^R(t,t_1)V(t_1)ig^<(t_1,t) + ig^<(t,t_1)V(t_1)ig^a(t_1,t)\right). \tag{5.6}$$

The Green's function only depends on t, so we may express it in frequency space. In order to keep track of the minus signs inside the Dirac deltas, we'll use the negative frequency $-\omega$ instead of ω.

$$\begin{aligned} iG^<(-\omega) &= \int \frac{d\omega_1}{2\pi}\int \frac{d\omega_2}{2\pi}\int \frac{d\omega_3}{2\pi} 2\pi\delta(\omega_1+\omega_2-\omega_3)2\pi\delta(\omega+\omega_3-\omega_1) \\ &\quad \times \left(ig^R(\omega_1)V(\omega_2)ig^<(\omega_3) + ig^<(\omega_1)V(\omega_2)ig^a(\omega_3)\right) \end{aligned} \tag{5.7}$$

In the first term, we replace $\omega_1 = \omega + \omega_3$ and in the second $\omega_3 = \omega_1 - \omega$, eliminating the second delta. The first delta becomes $\delta(\omega+\omega_2)$ and may be used to eliminate ω_2. Now we relabel the remaining variables, that is $\omega' = \omega_3$ in the first term and $\omega' = \omega_1$ in the second. These replacements yield a much simpler expression for the first order Green's function:

$$iG^<(\omega) = \int \frac{d\omega'}{2\pi}\left(ig^R(\omega'-\omega)V(\omega)ig^<(\omega') + ig^<(\omega')V(\omega)ig^a(\omega'+\omega)\right). \tag{5.8}$$

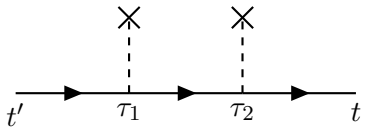
The final step is to replace $ig^<(\omega')$ by its definition (eq. 8.43) in terms of the Fermi function

$$\begin{aligned} iG^<(\omega) &= -\int_{-\infty}^{\infty} d\epsilon f(\epsilon)\left(ig^R(-\epsilon/\hbar-\omega)V(\omega)\delta(\epsilon-H) + \right. \\ &\quad \left. + \delta(\epsilon-H)V(\omega)ig^a(-\epsilon/\hbar+\omega)\right). \end{aligned} \tag{5.9}$$

This is the expression of Green's function in first order.

5.1.3 Second order

The diagram that represents this order is



which in algebraic terms is

$$iG^{C(2)}(t,t) = \int_C d\tau_1 \int_C d\tau_2 ig^C(t,\tau_1)V(\tau_1)ig^C(\tau_1,\tau_2)V(\tau_2)ig^C(\tau_2,t) \tag{5.10}$$

Using Langreth's rules we get three contributions

$$\begin{aligned} iG^{<(2)}(t,t) &= \int dt_1 \int dt_2 \left\{ ig^R(t,t_1)V(t_1)ig^R(t_1,t_2)V(t_2)ig^<(t_2,t) \right. \\ &+ \left. ig^R(t,t_1)V(t_1)ig^<(t_1,t_2)V(t_2)ig^a(t_2,t) + ig^<(t,\tau_1)V(\tau_1)ig^a(\tau_1,\tau_2)V(\tau_2)ig^a(\tau_2,t) \right\} \end{aligned} \tag{5.11}$$

In frequency space

$$\begin{aligned} iG^{<(2)}(-\omega) &= \int \frac{d\omega_1}{2\pi} \int \frac{d\omega_2}{2\pi} \int \frac{d\omega_3}{2\pi} \int \frac{d\omega_4}{2\pi} \int \frac{d\omega_5}{2\pi} (2\pi)^3 \delta(\omega_5 + \omega - \omega_1)\delta(\omega_1 + \omega_2 - \omega_3)\delta(\omega_3 + \omega_4 - \omega_5) \\ &\times \left\{ ig^R(\omega_1)V(\omega_2)ig^R(\omega_3)V(\omega_4)ig^<(\omega_5) + ig^R(\omega_1)V(\omega_2)ig^<(\omega_3)V(\omega_4)ig^a(\omega_5) \right. \\ &+ \left. ig^<(\omega_1)V(\omega_2)ig^a(\omega_3)V(\omega_4)ig^a(\omega_5) \right\} \end{aligned} \tag{5.12}$$

There are many options as to which variables to eliminate using the Dirac deltas, so we'll choose the most convenient one. The lesser Green's functions will give us the Fermi function, so we'll want to keep the variable inside $g^<$ in each term. This means we'll keep ω_5 in the first term, ω_3 in the second and ω_1 in the third. The frequencies in which the perturbation V depends (ω_2 and ω_4) will also be kept because we'll use them to define the higher order conductivity. All other frequencies may be eliminated. The remaining Dirac delta shall be $\delta(\omega + \omega_2 + \omega_4)$, which will fit nicely with the definition of the conductivity. After some relabeling, these considerations turn the previous expression into

$$\begin{aligned} iG^{<(2)}(\omega) &= \int \frac{d\omega_1}{2\pi} \int \frac{d\omega_2}{2\pi} 2\pi\delta(\omega_1 + \omega_2 - \omega) \int \frac{d\omega'}{2\pi} \\ &\times \left\{ ig^R(\omega' - \omega_1 - \omega_2)V(\omega_1)ig^R(\omega' - \omega_2)V(\omega_2)ig^<(\omega') + \right. \\ &+ ig^R(\omega' - \omega_1)V(\omega_1)ig^<(\omega')V(\omega_2)ig^a(\omega' + \omega_2) + \\ &+ \left. ig^<(\omega')V(\omega_1)ig^a(\omega' + \omega_1)V(\omega_2)ig^a(\omega' + \omega_1 + \omega_2) \right\}. \end{aligned} \tag{5.13}$$

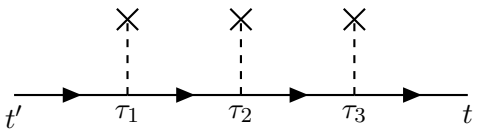
Again, replacing $ig^<(\omega)$ we get

$$\begin{aligned} iG^{<(2)}(\omega) &= -\int \frac{d\omega_1}{2\pi}\int \frac{d\omega_2}{2\pi} 2\pi\delta(\omega_1+\omega_2-\omega)\int_{-\infty}^{\infty} d\epsilon f(\epsilon) \\ &\times \left\{ ig^R(-\epsilon/\hbar-\omega_1-\omega_2)V(\omega_1)ig^R(-\epsilon/\hbar-\omega_2)V(\omega_2)\delta(\epsilon-H)+\right. \\ &+ig^R(-\epsilon/\hbar-\omega_1)V(\omega_1)\delta(\epsilon-H)V(\omega_2)ig^a(-\epsilon/\hbar+\omega_2)+ \\ &\left.+\,\delta(\epsilon-H)V(\omega_1)ig^a(-\epsilon/\hbar+\omega_1)V(\omega_2)ig^a(-\epsilon/\hbar+\omega_1+\omega_2)\right\}. \end{aligned} \tag{5.14}$$

This is the expression of Green's function in second order.

5.1.4 Third order

The diagram that represents this order is



which in algebraic terms is

$$iG^C(t,t) = \int_C d\tau_1 \int_C d\tau_2 \int_C d\tau_3 ig^C(t,\tau_1)V(\tau_1)ig^C(\tau_1,\tau_2)V(\tau_2)ig^C(\tau_2,\tau_3)V(\tau_3)ig^C(\tau_3,t). \tag{5.15}$$

After using Langreth's rules, expressing everything in frequency space and eliminating the Dirac deltas, we get

$$\begin{aligned} iG^{<(3)}(\omega) &= \int \frac{d\omega_1}{2\pi}\int \frac{d\omega_2}{2\pi}\int \frac{d\omega_3}{2\pi}(2\pi)\,\delta(\omega_1+\omega_2+\omega_3-\omega)\int \frac{d\omega'}{2\pi} \\ &\times \left\{ ig^R(\omega'-\omega_3-\omega_2-\omega_1)V(\omega_1)ig^R(\omega'-\omega_3-\omega_2)V(\omega_2)ig^R(\omega'-\omega_3)V(\omega_3)ig^<(\omega')+\right. \\ &+ig^R(\omega'-\omega_2-\omega_1)V(\omega_1)ig^R(\omega'-\omega_2)V(\omega_2)ig^<(\omega')V(\omega_3)ig^a(\omega'+\omega_3)+ \\ &+ig^R(\omega'-\omega_1)V(\omega_1)ig^<(\omega')V(\omega_2)ig^a(\omega'+\omega_2)V(\omega_3)ig^a(\omega'+\omega_3+\omega_2)+ \\ &\left.+ig^<(\omega')V(\omega_1)ig^a(\omega'+\omega_1)V(\omega_2)ig^a(\omega'+\omega_1+\omega_2)V(\omega_3)ig^a(\omega'+\omega_1+\omega_2+\omega_3)\right\}. \end{aligned} \tag{5.16}$$

Replacing $ig^<(\omega)$,

$$\begin{aligned} iG^{<(3)}(\omega) &= -\int \frac{d\omega_1}{2\pi}\int \frac{d\omega_2}{2\pi}\int \frac{d\omega_3}{2\pi}(2\pi)\,\delta(\omega_1+\omega_2+\omega_3-\omega)\int_{-\infty}^{\infty} d\epsilon f(\epsilon) \\ &\times \left\{ ig^R(-\epsilon/\hbar-\omega_3-\omega_2-\omega_1)V(\omega_1)ig^R(-\epsilon/\hbar-\omega_3-\omega_2)V(\omega_2)ig^R(-\epsilon/\hbar-\omega_3)V(\omega_3)\delta(\epsilon-H)+\right. \\ &+ig^R(-\epsilon/\hbar-\omega_2-\omega_1)V(\omega_1)ig^R(-\epsilon/\hbar-\omega_2)V(\omega_2)\delta(\epsilon-H)V(\omega_3)ig^a(-\epsilon/\hbar+\omega_3)+ \\ &+ig^R(-\epsilon/\hbar-\omega_1)V(\omega_1)\delta(\epsilon-H)V(\omega_2)ig^a(-\epsilon/\hbar+\omega_2)V(\omega_3)ig^a(-\epsilon/\hbar+\omega_3+\omega_2)+ \\ &\left.+\delta(\epsilon-H)V(\omega_1)ig^a(-\epsilon/\hbar+\omega_1)V(\omega_2)ig^a(-\epsilon/\hbar+\omega_1+\omega_2)V(\omega_3)ig^a(-\epsilon/\hbar+\omega_1+\omega_2+\omega_3)\right\}. \end{aligned} \tag{5.17}$$

This is Green's function in third order.

5.1.5 New notation

By now we see that the expansions are starting to become too unwieldy. At the same time, a certain regularity starts to appear. The interaction terms V always appear sandwiched between two Green's functions, whose type also follows a pattern. There's always one lesser Green's function; to its left there can only be retarded Green's functions and to its right advanced Green's functions. This regularity suggests a new simplifying notation: we need only record the number of retarded Green's functions, since all else is fixed from that. Therefore, define the $W^{x_1 x_2 \cdots x_n}$ function, where the upper indices are to be replaced by R or a to reflect the position of each g^R and g^a, respectively. The $g^<$ is understood to be to the left of all the g^a and to the right of all the g^R. Some examples of this are

$$W^a(\epsilon, \omega_2; \omega_3) = \delta(\epsilon - H) V(\omega_2) i g^a(\omega_3) \tag{5.18}$$

$$W^{RR}(\omega_2, \omega_4, \epsilon; \omega_1, \omega_3) = i g^R(\omega_1) V(\omega_2) i g^R(\omega_3) V(\omega_4) \delta(\epsilon - H) \tag{5.19}$$

$$W^{Raa}(\omega_2, \epsilon, \omega_4, \omega_6; \omega_1, \omega_3, \omega_5) = i g^R(\omega_1) V(\omega_2) \delta(\epsilon - H) V(\omega_4) i g^a(\omega_5) V(\omega_6) i g^a(\omega_7). \tag{5.20}$$

The semicolon separates the arguments that belong to the retarded and advanced Green's functions from the ones that belong to the external interactions and the Dirac delta. The arguments always appear by order. There's still another regularity, this time in the deltas. Looking at the various ω_i as part of a cycle, that is $\omega \to \omega_1 \to \omega_2 \to \cdots \to \omega_{2n+1} \to \omega$, the deltas consist of all the combinations $\delta(\omega_i + \omega_{i+1} - \omega_{i+2})$ of odd i. Let Δ^n be the product of all those combinations multiplied by $(2\pi)^{n+1}$, where n is the order of the perturbation. Some examples:

$$\Delta^1 = (2\pi)^2 \delta(\omega_3 + \omega - \omega_1) \delta(\omega_1 + \omega_2 - \omega_3) \tag{5.21}$$

$$\Delta^2 = (2\pi)^3 \delta(\omega_5 + \omega - \omega_1) \delta(\omega_1 + \omega_2 - \omega_3) \delta(\omega_3 + \omega_4 - \omega_5) \tag{5.22}$$

$$\Delta^3 = (2\pi)^4 \delta(\omega_7 + \omega - \omega_1) \delta(\omega_1 + \omega_2 - \omega_3) \delta(\omega_3 + \omega_4 - \omega_5) \delta(\omega_5 + \omega_6 - \omega_7). \tag{5.23}$$

These considerations allow for a very compact way to write the expansion. Omitting the frequency arguments, the formulas obtained in the previous section are

$$i G^{<(1)}(-\omega) = \int \frac{d\omega_1}{2\pi} \int \frac{d\omega_2}{2\pi} \int \frac{d\omega_3}{2\pi} \left(W^R + W^a \right) \Delta^1 \tag{5.24}$$

$$i G^{<(2)}(-\omega) = \int \frac{d\omega_1}{2\pi} \cdots \frac{d\omega_5}{2\pi} \left(W^{RR} + W^{Ra} + W^{aa} \right) \Delta^2 \tag{5.25}$$

$$i G^{<(3)}(-\omega) = \int \frac{d\omega_1}{2\pi} \cdots \frac{d\omega_7}{2\pi} \left(W^{RRR} + W^{RRa} + W^{Raa} + W^{aaa} \right) \Delta^3. \tag{5.26}$$

We'll be using these expressions later on, so we should make their arguments explicit. Looking at eqs. 5.9, 5.14 and 5.17, we need only match the arguments.

$$iG^{<(1)}(\omega) = -\int_{-\infty}^{\infty} d\epsilon f(\epsilon) \left(W^R(\omega,\epsilon;-\epsilon/\hbar-\omega)+W^a(\epsilon,\omega;-\epsilon/\hbar+\omega)\right) \tag{5.27}$$

$$\begin{aligned} iG^{<(2)}(\omega) = & -\int \frac{d\omega_1}{2\pi}\int \frac{d\omega_2}{2\pi} 2\pi\delta(\omega_1+\omega_2-\omega)\int_{-\infty}^{\infty} d\epsilon f(\epsilon) \\ & \left\{W^{RR}(\omega_1,\omega_2,\epsilon;-\epsilon/\hbar-\omega_1-\omega_2,-\epsilon/\hbar-\omega_2)+\right. \\ & +W^{Ra}(\omega_1,\epsilon,\omega_2;-\epsilon/\hbar-\omega_1,-\epsilon/\hbar+\omega_2)+ \\ & \left.+W^{aa}(\epsilon,\omega_1,\omega_2;-\epsilon/\hbar+\omega_1,-\epsilon/\hbar+\omega_1+\omega_2)\right\} \end{aligned} \tag{5.28}$$

$$\begin{aligned} iG^{<(3)}(\omega) = & -\int \frac{d\omega_1}{2\pi}\int \frac{d\omega_2}{2\pi}\int \frac{d\omega_3}{2\pi}(2\pi)\,\delta(\omega_1+\omega_2+\omega_3-\omega)\int_{-\infty}^{\infty} d\epsilon f(\epsilon) \\ & \times\left\{W^{RRR}(\omega_1,\omega_2,\omega_3,\epsilon;-\epsilon/\hbar-\omega_3-\omega_2-\omega_1,-\epsilon/\hbar-\omega_3-\omega_2,-\epsilon/\hbar-\omega_3)+\right. \\ & +W^{RRa}(\omega_1,\omega_2,\epsilon,\omega_3;-\epsilon/\hbar-\omega_2-\omega_1,-\epsilon/\hbar-\omega_2,-\epsilon/\hbar+\omega_3)+ \\ & +W^{Raa}(\omega_1,\epsilon,\omega_2,\omega_3;-\epsilon/\hbar-\omega_1,-\epsilon/\hbar+\omega_2,-\epsilon/\hbar+\omega_3+\omega_2)+ \\ & \left.+W^{aaa}(\epsilon,\omega_1,\omega_2,\omega_3;-\epsilon/\hbar+\omega_1,-\epsilon/\hbar+\omega_2+\omega_1,-\epsilon/\hbar+\omega_3+\omega_2+\omega_1)\right\}. \end{aligned} \tag{5.29}$$

5.1.6 Even higher orders

Although a rigorous proof is not provided, this notation reveals that the next orders should follow the exact same pattern: the sum of all the W functions integrated over all the frequencies with the appropriate Δ function:

$$iG^{<(n)}(-\omega) = \int \frac{d\omega_1}{2\pi}\cdots\frac{d\omega_{2n+1}}{2\pi}\left(W^{R\cdots R}+\cdots+W^{a\cdots a}\right)\Delta^n. \tag{5.30}$$

Easy to write, the notation hides the true monstrosity that is an n-th order expansion.

5.2 Expansion of the Tight Binding Hamiltonian

So far, this is valid for any time-dependent non-interacting operator $V(t)$. The case we want to study, the tight binding Hamiltonian, is a particular case of this, but one in which the time-dependent interaction is itself a series of the external field A. This makes matters slightly more difficult, because there will be numerous contributions in each order in A from all the terms in the Green's function.

Consider the tight binding Hamiltonian written in the Wannier basis:

$$H = \sum_{\boldsymbol{R}_i,\boldsymbol{R}_j}\sum_{\sigma_1,\sigma_2} t_{\sigma_1\sigma_2}\left(\boldsymbol{R}_i-\boldsymbol{R}_j\right) c^{\dagger}_{\sigma_1}(\boldsymbol{R}_i) c_{\sigma_2}\left(\boldsymbol{R}_j\right). \tag{5.31}$$

The $\boldsymbol{R}_i$ represent the lattice sites and the σ_i the other degrees of freedom unrelated to the translational symmetry, such as the orbitals and spin. This may be expressed in momentum space by defining

$$t_{\sigma_1\sigma_2}\left(\boldsymbol{R}_i-\boldsymbol{R}_j\right)=\frac{1}{V}\sum_{\boldsymbol{k}}\epsilon_{\sigma_1\sigma_2}(\boldsymbol{k})e^{i\boldsymbol{k}\cdot\left(\boldsymbol{R}_i-\boldsymbol{R}_j\right)} \tag{5.32}$$

$$c_\sigma\left(\boldsymbol{R}_i\right)=\frac{1}{V}\sum_{\boldsymbol{k}}c_\sigma\left(\boldsymbol{k}\right)e^{i\boldsymbol{k}\cdot\boldsymbol{R}_i} \tag{5.33}$$

and

$$c_\sigma^\dagger\left(\boldsymbol{R}_i\right)=\frac{1}{V}\sum_{\boldsymbol{k}}c_\sigma^\dagger\left(\boldsymbol{k}\right)e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_i} \tag{5.34}$$

turning the Hamiltonian into

$$H=\frac{1}{V}\sum_{\sigma_1,\sigma_2}\sum_{\boldsymbol{k}}\epsilon_{\sigma_1\sigma_2}(\boldsymbol{k})c_{\sigma_1}^\dagger\left(\boldsymbol{k}\right)c_{\sigma_2}\left(\boldsymbol{k}\right). \tag{5.35}$$

The electromagnetic field is introduced through Peierls' substitution [12], so the Hamiltonian acquires the form

$$H_{\boldsymbol{A}}=\sum_{\boldsymbol{R}_i,\boldsymbol{R}_j}\sum_{\sigma_1,\sigma_2}e^{\frac{-ie}{\hbar}\int_{\boldsymbol{R}_j}^{\boldsymbol{R}_i}\boldsymbol{A}(\boldsymbol{r}',t)\cdot d\boldsymbol{r}'}t_{\sigma_1\sigma_2}\left(\boldsymbol{R}_i-\boldsymbol{R}_j\right)c_{\sigma_1}^\dagger(\boldsymbol{R}_i)c_{\sigma_2}\left(\boldsymbol{R}_j\right). \tag{5.36}$$

If we want to introduce both a magnetic and an electric field, we may use the following vector potential:

$$\boldsymbol{A}(\boldsymbol{r},t)=\boldsymbol{A}_1(\boldsymbol{r})+\boldsymbol{A}_2(t). \tag{5.37}$$

The electric and magnetic fields are obtained from $\boldsymbol{E}(t)=-\frac{\partial\boldsymbol{A}_2(t)}{\partial t}$ and $\boldsymbol{B}(\boldsymbol{r})=\boldsymbol{\nabla}\times\boldsymbol{A}_1(\boldsymbol{r})$. The introduction of the magnetic field only changes the $t_{\sigma\sigma'}$, but the exponent no longer depends on the difference of positions. It is possible to overcome this obstacle by carefully choosing the vector potential, but that would require a whole discussion of its own. For that reason, we'll forget the magnetic field for now and focus on the electric field. The position-dependent part of the vector potential may thus be disregarded:

$$H_{\boldsymbol{A}}=\sum_{\boldsymbol{R}_i,\boldsymbol{R}_j}\sum_{\sigma_1,\sigma_2}e^{\frac{-ie}{\hbar}\boldsymbol{A}(t)\cdot\left(\boldsymbol{R}_i-\boldsymbol{R}_j\right)}t_{\sigma_1\sigma_2}\left(\boldsymbol{R}_i-\boldsymbol{R}_j\right)c_{\sigma_1}^\dagger(\boldsymbol{R}_i)c_{\sigma_2}\left(\boldsymbol{R}_j\right) \tag{5.38}$$

In momentum space this becomes

$$H_{\boldsymbol{A}} = \frac{1}{V}\sum_{\sigma_1,\sigma_2}\sum_{\boldsymbol{k}} \epsilon_{\sigma_1\sigma_2}\left(\boldsymbol{k}+\frac{e}{\hbar}\boldsymbol{A}(t)\right) c^\dagger_{\sigma_1}(\boldsymbol{k})\, c_{\sigma_2}(\boldsymbol{k}) \tag{5.39}$$

which closely resembles the minimal coupling procedure. Expanding the exponential in real space, we get

$$\begin{aligned} H_A \quad (t) = & \sum_{\boldsymbol{R}_i,\boldsymbol{R}_j}\sum_{\sigma_1,\sigma_2}\left(1+\frac{-ie}{\hbar}\boldsymbol{A}(t)\cdot(\boldsymbol{R}_i-\boldsymbol{R}_j)+\left[\frac{-ie}{\hbar}\boldsymbol{A}(t)\cdot(\boldsymbol{R}_i-\boldsymbol{R}_j)\right]^2+\cdots\right) \\ & \times t_{\sigma_1\sigma_2}(\boldsymbol{R}_i-\boldsymbol{R}_j)\, c^\dagger_{\sigma_1}(\boldsymbol{R}_i) c_{\sigma_2}(\boldsymbol{R}_j) \\ = & \sum_{\boldsymbol{R}_i,\boldsymbol{R}_j}\sum_{\sigma_1,\sigma_2} t_{\sigma_1\sigma_2}(\boldsymbol{R}_i-\boldsymbol{R}_j)\, c^\dagger_{\sigma_1}(\boldsymbol{R}_i) c_{\sigma_2}(\boldsymbol{R}_j) + \\ & + \frac{-ie}{\hbar}A^\alpha(t)\sum_{\boldsymbol{R}_i,\boldsymbol{R}_j}\sum_{\sigma_1,\sigma_2}\left(R^\alpha_i-R^\alpha_j\right) t_{\sigma_1\sigma_2}(\boldsymbol{R}_i-\boldsymbol{R}_j)\, c^\dagger_{\sigma_1}(\boldsymbol{R}_i) c_{\sigma_2}(\boldsymbol{R}_j) + \\ & + \frac{1}{2!}\left(\frac{-ie}{\hbar}\right)^2 A^\alpha(t)A^\beta(t)\sum_{\boldsymbol{R}_i,\boldsymbol{R}_j}\sum_{\sigma_1,\sigma_2}\left(R^\alpha_i-R^\alpha_j\right)\left(R^\beta_i-R^\beta_j\right) \\ & \times t_{\sigma_1\sigma_2}(\boldsymbol{R}_i-\boldsymbol{R}_j)\, c^\dagger_{\sigma_1}(\boldsymbol{R}_i) c_{\sigma_2}(\boldsymbol{R}_j)+\cdots \\ = & H_0 + eA^\alpha(t)v^\alpha + \frac{1}{2!}e^2A^\alpha(t)A^\beta(t)v^{\alpha\beta}+\cdots \end{aligned} \tag{5.40}$$

where we have defined

$$\begin{aligned} v^{\alpha_1\cdots\alpha_n} &= \frac{1}{e^n}\frac{\partial}{\partial A^{\alpha_1}}\cdots\frac{\partial}{\partial A^{\alpha_n}} H_A|_{A=0} \\ &= \left(\frac{-i}{\hbar}\right)^n \sum_{\boldsymbol{R}_i,\boldsymbol{R}_j}\sum_{\sigma_1,\sigma_2}(R^{\alpha_1}_i-R^{\alpha_1}_j)\cdots(R^{\alpha_n}_i-R^{\alpha_n}_j) t_{\sigma_1\sigma_2}(\boldsymbol{R}_i-\boldsymbol{R}_j)\, c^\dagger_{\sigma_1}(\boldsymbol{R}_i) c_{\sigma_2}(\boldsymbol{R}_j)\,. \\ &= \left(\frac{-i}{\hbar}\right)^n [R^{\alpha_1},\cdots[R^{\alpha_n},H_{\boldsymbol{A}}]] \end{aligned}$$

In first order, this is just the velocity operator. We can identify the external perturbation from this:

$$H^{\text{ext}}(t) = eA^\alpha(t)v^\alpha + \frac{1}{2!}e^2A^\alpha(t)A^\beta(t)v^{\alpha\beta}+\cdots. \tag{5.41}$$

In a similar fashion, the current $J^\alpha = -\frac{1}{V}\frac{\partial H}{\partial A^\alpha}$ also follows a series expansion:

$$J^\alpha(t) = -\frac{e}{V}\left(v^\alpha + ev^{\alpha\beta}A^\beta_2(t) + \frac{e^2}{2!}v^{\alpha\beta\gamma}A^\beta_2(t)A^\gamma_2(t) + \frac{e^3}{3!}v^{\alpha\beta\gamma\delta}A^\beta_2(t)A^\gamma_2(t)A^\delta_2(t)+\cdots\right). \tag{5.42}$$

If the Hamiltonian is written in momentum space, the $v^{\alpha_1\cdots\alpha_n}$ operators are recognized as the derivatives of $\epsilon_{\sigma_1\sigma_2}(\boldsymbol{k})$.

Their matrix elements are

$$v_{\sigma_1\sigma_2}^{\alpha_1\cdots\alpha_n}(\boldsymbol{k}) = \frac{1}{(-\hbar)^n}\frac{\partial}{\partial k^{\alpha_1}}\cdots\frac{\partial}{\partial k^{\alpha_n}}\epsilon_{\sigma_1\sigma_2}(\boldsymbol{k}). \tag{5.43}$$

This is all the information we need to compute the expected value of J^α. Some care has to be taken, though, as now each term in the perturbative expansion of the previous chapter is itself a whole series. In the next section, we'll take the Green's functions calculated in the previous section and expand the interaction terms in this series.

5.2.1 Green's function series

We're going to take the Green's functions, order by order, and replace each of the V by their series expansion

$$V = \frac{-i}{\hbar}H^{ext} = \frac{-i}{\hbar}\left(ev^\alpha A^\alpha + \frac{e^2}{2!}v^{\alpha\beta}A^\alpha A^\beta + \frac{e^3}{3!}v^{\alpha\beta\gamma}A^\alpha A^\beta A^\gamma + \cdots\right). \tag{5.44}$$

The Green's functions are expressed in frequency space, so we'll need to calculate the Fourier transform of the product of external fields. In second and third orders, these are, respectively

$$\int_{-\infty}^{\infty} dt e^{i\omega t}A^\alpha(t)A^\beta(t) = \int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_2}{2\pi}(2\pi)\,\delta(\omega_1+\omega_2-\omega)A^\alpha(\omega_1)A^\beta(\omega_2) \tag{5.45}$$

and

$$\begin{aligned}&\int_{-\infty}^{\infty} dt e^{i\omega t}A^\alpha(t)A^\beta(t)A^\gamma(t) \\ &\quad= \int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_2}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_3}{2\pi}(2\pi)\,\delta(\omega_1+\omega_2+\omega_3-\omega)A^\alpha(\omega_1)A^\beta(\omega_2)A^\gamma(\omega_3).\end{aligned} \tag{5.46}$$

These will fit nicely with the definition of higher-order conductivities.

5.2.1.1 Green's functions - Zeroth order

In this order, we get exactly the same thing as before because there is no interaction

$$iG^{<(0)}(t,t') = ig^<(t,t'). \tag{5.47}$$

Taking $t' = t$ and moving on to frequency space,

$$iG^{<(0)}(\omega) = -2\pi\int_{-\infty}^{\infty} d\epsilon f(\epsilon)\delta(\epsilon - H)\delta(\omega). \tag{5.48}$$

5.2.1.2 Green's functions - First order in V

Starting from eq. 5.9, we need to replace each $V(t)$ by its series in $A(t)$. To simplify bookkeeping, we shall adopt a notation to distinguish each contribution. Let $iG^{<(V^n,A^m)}$ represent the n-th order expansion in V of the Green's function, which, in its turn has been expanded in m-th order in A. In this notation, we may say, for example, that

$$iG^{<(V^1)} = \sum_{m=0}^{\infty} iG^{<(V,A^m)} \tag{5.49}$$

where $iG^{<(1V)}$ is just eq. 5.9 from before:

$$iG^{<(V^1)}(\omega) = -\int_{-\infty}^{\infty} d\epsilon f(\epsilon) \left(W^R(\omega,\epsilon;-\epsilon/\hbar-\omega) + W^a(\epsilon,\omega;-\epsilon/\hbar+\omega)\right).$$

With this notation in mind, it becomes clear that we need a new notation for the W functions as they now may include different types of $v^{\alpha_1\cdots\alpha_n}$ operators. Each operator will be represented by its indices, using commas to separate the various operators. Their order is preserved. Some examples are

$$\begin{aligned} W_a^{\alpha\beta\gamma}(\epsilon;\omega_3) &= \delta(\epsilon-H)v^{\alpha\beta\gamma}ig^a(\omega_3) \\ W_{RR}^{\alpha,\beta\gamma}(\epsilon;\omega_1,\omega_3) &= ig^R(\omega_1)v^{\alpha}ig^R(\omega_3)v^{\beta\gamma}\delta(\epsilon-H) \\ W_{Raa}^{\alpha,\beta,\gamma}(\epsilon;\omega_1,\omega_3,\omega_5) &= ig^R(\omega_1)v^{\alpha}\delta(\epsilon-H)v^{\beta}ig^a(\omega_5)v^{\gamma}ig^a(\omega_7) \end{aligned}$$

Note that the frequencies belonging to the interactions have been removed because they are now outside the W functions. Up to third order in $\boldsymbol{A}$ we obtain:

$$iG^{<(V^1,A^1)}(\omega) = \frac{ie}{\hbar}\int_{-\infty}^{\infty} d\epsilon f(\epsilon)\left[W_R^{\alpha}(\epsilon;-\epsilon/\hbar-\omega) + W_a^{\alpha}(\epsilon;-\epsilon/\hbar+\omega)\right]A^{\alpha}(\omega)$$

$$\begin{aligned} iG^{<(V^1,A^2)}(\omega) &= \frac{ie^2}{2!\,\hbar}\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_2}{2\pi}(2\pi)\,\delta(\omega_1+\omega_2-\omega)A^{\alpha}(\omega_1)A^{\beta}(\omega_2) \\ &\quad\times\int_{-\infty}^{\infty} d\epsilon f(\epsilon)\left[W_R^{\alpha\beta}(\epsilon;-\epsilon/\hbar-\omega) + W_a^{\alpha\beta}(\epsilon;-\epsilon/\hbar+\omega)\right] \end{aligned}$$

$$\begin{aligned} iG^{<(V^1,A^3)}(\omega) &= \frac{ie^3}{3!\,\hbar}\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_2}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_3}{2\pi}(2\pi)\,\delta(\omega_1+\omega_2+\omega_3-\omega)A^{\alpha}(\omega_1)A^{\beta}(\omega_2)A^{\gamma}(\omega_3) \\ &\quad\times\int_{-\infty}^{\infty} d\epsilon f(\epsilon)\left[W_R^{\alpha\beta\gamma}(\epsilon;-\epsilon/\hbar-\omega) + W_a^{\alpha\beta\gamma}(\epsilon;-\epsilon/\hbar+\omega)\right]. \end{aligned}$$

5.2.1.3 Green's functions - Second order in V

Using eq. 5.12, there are no terms of order lower than second order, since we have two factors of V:

$$\begin{aligned} iG^{<(V^2)}(\omega) &= \int \frac{d\omega_1}{2\pi}\int \frac{d\omega_2}{2\pi} 2\pi\delta(\omega_1+\omega_2-\omega)\int \frac{d\omega'}{2\pi} \\ &\times \left\{ ig^R(\omega'-\omega_1-\omega_2)V(\omega_1)ig^R(\omega'-\omega_2)V(\omega_2)ig^<(\omega')+\right. \\ &+ ig^R(\omega'-\omega_1)V(\omega_1)ig^<(\omega')V(\omega_2)ig^a(\omega'+\omega_2)+ \\ &\left.+\, ig^<(\omega')V(\omega_1)ig^a(\omega'+\omega_1)V(\omega_2)ig^a(\omega'+\omega_1+\omega_2)\right\}. \end{aligned}$$

The term in second-order in A is rather straightforward because there can only be one contribution from each V:

$$\begin{aligned} iG^{<(V^2,A^2)}(\omega) &= -\left(\frac{-ie}{\hbar}\right)^2 \int \frac{d\omega_1}{2\pi}\int \frac{d\omega_2}{2\pi} 2\pi\delta(\omega_1+\omega_2-\omega)A^\alpha(\omega_1)A^\beta(\omega_2)\int_{-\infty}^{\infty} d\epsilon f(\epsilon) \\ &\times \left\{ W_{RR}^{\alpha,\beta}(\epsilon;-\epsilon/\hbar-\omega_1-\omega_2,-\epsilon/\hbar-\omega_2)+\right. \\ &+ W_{Ra}^{\alpha,\beta}(\epsilon;-\epsilon/\hbar-\omega_1,-\epsilon/\hbar+\omega_2)+ \\ &\left.+\, W_{aa}^{\alpha,\beta}(\epsilon;-\epsilon/\hbar+\omega_1,-\epsilon/\hbar+\omega_1+\omega_2)+\right\} \end{aligned}$$

but the third-order term is slightly trickier since we need to replace one of the V by the second-order expression and the other one by the first-order one, and there are two ways of doing that. The result is

$$\begin{aligned} iG^{<(2V,3A)}(\omega) &= \int \frac{d\omega_1}{2\pi}\int \frac{d\omega_2}{2\pi}\int \frac{d\omega_3}{2\pi}\,(2\pi)\,\delta(\omega_1+\omega_2+\omega_3-\omega)A^\alpha(\omega_1)A^\beta(\omega_2)A^\gamma(\omega_3) \\ &\times(-1)\left(\frac{-ie}{\hbar}\right)\left(\frac{-ie^2}{2!\,\hbar}\right)\int_{-\infty}^{\infty} d\epsilon f(\epsilon) \\ &\times \left\{ W_{RR}^{\alpha,\beta\gamma}(\epsilon;-\epsilon/\hbar-\omega_1-\omega_2,-\epsilon/\hbar-\omega_2-\omega_3)+\right. \\ &+ W_{RR}^{\alpha\beta,\gamma}(\epsilon;-\epsilon/\hbar-\omega_1-\omega_2-\omega_3,-\epsilon/\hbar-\omega_3)+ \\ &+ W_{Ra}^{\alpha,\beta\gamma}(,\epsilon;-\epsilon/\hbar-\omega_1,-\epsilon/\hbar+\omega_2+\omega_3)+ \\ &+ W_{Ra}^{\alpha\beta,\gamma}(,\epsilon;-\epsilon/\hbar-\omega_1-\omega_2,-\epsilon/\hbar+\omega_3)+ \\ &+ W_{aa}^{\alpha,\beta\gamma}(\epsilon;-\epsilon/\hbar+\omega_1,-\epsilon/\hbar+\omega_1+\omega_2+\omega_3)+ \\ &\left.+\, W_{aa}^{\alpha\beta,\gamma}(\epsilon;-\epsilon/\hbar+\omega_1+\omega_2,-\epsilon/\hbar+\omega_1+\omega_2+\omega_3)\right\}. \end{aligned}$$

These are all the expansions up to third order in $\boldsymbol{A}$ coming from the second-order Green's functions.

5.2.1.4 Green's functions - Third order in V

This one is the easiest because there is only one term. Using eq. 5.17, all we need to to is replace V by $\frac{-ie}{\hbar}A^\alpha v^\alpha$. The result is

$$\begin{aligned} iG^{<(3V,3A)}(\omega) &= -\left(\frac{-ie}{\hbar}\right)^3 \int \frac{d\omega_1}{2\pi}\int \frac{d\omega_2}{2\pi}\int \frac{d\omega_3}{2\pi}(2\pi)\,\delta(\omega_1+\omega_2+\omega_3-\omega)A^\alpha(\omega_1)A^\beta(\omega_2)A^\gamma(\omega_3) \\ &\times \int_{-\infty}^{\infty} d\epsilon f(\epsilon)\Big\{W^{\alpha\beta\gamma}_{RRR}(\epsilon;-\epsilon/\hbar-\omega_3-\omega_2-\omega_1,-\epsilon/\hbar-\omega_3-\omega_2,-\epsilon/\hbar-\omega_3)+ \\ &\quad +W^{\alpha\beta\gamma}_{RRa}(\epsilon;-\epsilon/\hbar-\omega_2-\omega_1,-\epsilon/\hbar-\omega_2,-\epsilon/\hbar+\omega_3)+ \\ &\quad +W^{\alpha\beta\gamma}_{Raa}(\epsilon;-\epsilon/\hbar-\omega_1,-\epsilon/\hbar+\omega_2,-\epsilon/\hbar+\omega_3+\omega_2)+ \\ &\quad +W^{\alpha\beta\gamma}_{aaa}(\epsilon;-\epsilon/\hbar+\omega_1,-\epsilon/\hbar+\omega_2+\omega_1,-\epsilon/\hbar+\omega_3+\omega_2+\omega_1)\Big\} \end{aligned}$$

Up to third order, we have thus calculated all the terms that will contribute to the current. This will make our next step easier, since we've already isolated all the terms in each order in A. Now we're finally going to use this to calculate the expected value of the current.

5.2.2 Grouping up the terms in A

For referencing purposes, here are all the terms we've calculated so far, grouped by order in A.

5.2.2.1 Green's functions - Zeroth order in A

$$iG^{<(A^0)}(\omega) = -2\pi\int_{-\infty}^{\infty} d\epsilon f(\epsilon)\delta(\epsilon-H)\delta(\omega) \tag{5.50}$$

5.2.2.2 Green's functions - First order in A

$$iG^{<(A^1)}(\omega) = \frac{ie}{\hbar}\int_{-\infty}^{\infty} d\epsilon f(\epsilon)\left[W^\alpha_R(\epsilon;-\epsilon/\hbar-\omega)+W^\alpha_a(\epsilon;-\epsilon/\hbar+\omega)\right]A^\alpha(\omega)$$

5.2.2.3 Green's functions - Second order in A

$$\begin{aligned} iG^{<(A^2)}(\omega) &= \int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_2}{2\pi}(2\pi)\,\delta(\omega_1+\omega_2-\omega)A^\alpha(\omega_1)A^\beta(\omega_2)\int_{-\infty}^{\infty}d\epsilon f(\epsilon) \\ &\quad \times e^2\left\{\frac{i}{2\hbar}\Big[W^{\alpha\beta}_R(\epsilon;-\epsilon/\hbar-\omega)+W^{\alpha\beta}_a(\epsilon;-\epsilon/\hbar+\omega)\Big]+\right. \\ &\quad \frac{1}{\hbar^2}\Big[W^{\alpha,\beta}_{RR}(\epsilon;-\epsilon/\hbar-\omega_1-\omega_2,-\epsilon/\hbar-\omega_2)+ \\ &\quad \left. W^{\alpha,\beta}_{Ra}(\epsilon;-\epsilon/\hbar-\omega_1,-\epsilon/\hbar+\omega_2)+W^{\alpha,\beta}_{aa}(\epsilon;-\epsilon/\hbar+\omega_1,-\epsilon/\hbar+\omega_1+\omega_2)\Big]\right\} \end{aligned}$$

5.2.2.4 Green's functions - Third order in A

$$
\begin{aligned}
iG^{<(A^3)}(\omega) \;=\; & \int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_2}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_3}{2\pi}\,(2\pi)\,\delta(\omega_1+\omega_2+\omega_3-\omega)A^{\alpha}(\omega_1)A^{\beta}(\omega_2)A^{\gamma}(\omega_3)\\
& \times\int_{-\infty}^{\infty}d\epsilon f(\epsilon)\left\{\frac{ie^3}{3!\,\hbar}\left[W_R^{\alpha\beta\gamma}(\epsilon;-\epsilon/\hbar-\omega)+W_a^{\alpha\beta\gamma}(\epsilon;-\epsilon/\hbar+\omega)\right]+\right.\\
& +\frac{e^3}{2!\,\hbar^2}\left[W_{RR}^{\alpha,\beta\gamma}(\epsilon;-\epsilon/\hbar-\omega_1-\omega_2,-\epsilon/\hbar-\omega_2-\omega_3)+\right.\\
& +W_{RR}^{\alpha\beta,\gamma}(\epsilon;-\epsilon/\hbar-\omega_1-\omega_2-\omega_3,-\epsilon/\hbar-\omega_3)+\\
& +W_{Ra}^{\alpha,\beta\gamma}(,\epsilon;-\epsilon/\hbar-\omega_1,-\epsilon/\hbar+\omega_2+\omega_3)+\\
& +W_{Ra}^{\alpha\beta,\gamma}(,\epsilon;-\epsilon/\hbar-\omega_1-\omega_2,-\epsilon/\hbar+\omega_3)+\\
& +W_{aa}^{\alpha,\beta\gamma}(\epsilon;-\epsilon/\hbar+\omega_1,-\epsilon/\hbar+\omega_1+\omega_2+\omega_3)+\\
& \left.+W_{aa}^{\alpha\beta,\gamma}(\epsilon;-\epsilon/\hbar+\omega_1+\omega_2,-\epsilon/\hbar+\omega_1+\omega_2+\omega_3)\right]\\
& \frac{-ie^3}{\hbar^3}\left[W_{RRR}^{\alpha\beta\gamma}(\epsilon;-\epsilon/\hbar-\omega_3-\omega_2-\omega_1,-\epsilon/\hbar-\omega_3-\omega_2,-\epsilon/\hbar-\omega_3)+\right.\\
& +W_{RRa}^{\alpha\beta\gamma}(\epsilon;-\epsilon/\hbar-\omega_2-\omega_1,-\epsilon/\hbar-\omega_2,-\epsilon/\hbar+\omega_3)+\\
& +W_{Raa}^{\alpha\beta\gamma}(\epsilon;-\epsilon/\hbar-\omega_1,-\epsilon/\hbar+\omega_2,-\epsilon/\hbar+\omega_3+\omega_2)+\\
& \left.\left.+W_{aaa}^{\alpha\beta\gamma}(\epsilon;-\epsilon/\hbar+\omega_1,-\epsilon/\hbar+\omega_2+\omega_1,-\epsilon/\hbar+\omega_3+\omega_2+\omega_1)\right]\right\}
\end{aligned}
$$

5.3 Calculation of the current from the Green's functions

First, we need to evaluate the expected value of the $v^{\alpha_1\cdots\alpha_n}$ operators. Expressing them in their second-quantized form, we see that the average falls into the creation and annihilation operators, which yields the lesser Green's function. Written in an arbitrary basis,

$$
\langle v^{\alpha_1\cdots\alpha_n}(t)\rangle=\left\langle\sum_{ij}v_{ij}^{\alpha_1\cdots\alpha_n}c_i^{\dagger}(t)c_j(t)\right\rangle=\sum_{ij}v_{ij}^{\alpha_1\cdots\alpha_n}iG_{ji}^{<}(t,t)=\mathrm{Tr}\left[v^{\alpha_1\cdots\alpha_n}iG^{<}(t,t)\right]. \tag{5.51}
$$

Taking the expected value of the current in eq. 5.42 we get, up to third order

$$
\begin{aligned}
\langle J^{\alpha}(t)\rangle \;=\; & -\frac{e}{V}\langle v^{\alpha}(t)\rangle-\frac{e^2}{V}\left\langle v^{\alpha\beta}(t)\right\rangle A^{\beta}(t)-\frac{1}{2!}\frac{e^3}{V}\left\langle v^{\alpha\beta\gamma}(t)\right\rangle A^{\beta}(t)A^{\gamma}(t)+ \qquad (5.52)\\
& -\frac{1}{3!}\frac{e^4}{V}\left\langle v^{\alpha\beta\gamma\delta}(t)\right\rangle A^{\beta}(t)A^{\gamma}(t)A^{\delta}(t)+\cdots\\
= \; & -\frac{e}{V}\mathrm{Tr}\left[v^{\alpha}iG^{<}(t,t)\right]-\frac{e^2}{V}\mathrm{Tr}\left[v^{\alpha\beta}iG^{<}(t,t)\right]A^{\beta}(t)+\\
& -\frac{1}{2!}\frac{e^3}{V}\mathrm{Tr}\left[v^{\alpha\beta\gamma}iG^{<}(t,t)\right]A^{\beta}(t)A^{\gamma}(t)-\frac{1}{3!}\frac{e^4}{V}\mathrm{Tr}\left[v^{\alpha\beta\gamma\delta}iG^{<}(t,t)\right]A^{\beta}(t)A^{\gamma}(t)A^{\delta}(t)+\cdots
\end{aligned}
$$

or, in frequency space,

$$\begin{aligned}
&\langle J^\alpha(\omega)\rangle \qquad (5.53)\\
&= -\frac{e}{V}\mathrm{Tr}\left[v^\alpha iG^<(\omega)\right] - \frac{e^2}{V}\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\mathrm{Tr}\left[v^{\alpha\beta}iG^<(\omega_1)\right]A^\beta(\omega_2)2\pi\delta(\omega_1+\omega_2-\omega)\\
&-\frac{1}{2!}\frac{e^3}{V}\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\mathrm{Tr}\left[v^{\alpha\beta\gamma}iG^<(\omega_1)\right]A^\beta(\omega_2)A^\gamma(\omega_3)2\pi\delta(\omega_1+\omega_2+\omega_3-\omega)\\
&-\frac{1}{3!}\frac{e^4}{V}\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\frac{d\omega_4}{2\pi}\mathrm{Tr}\left[v^{\alpha\beta\gamma\delta}iG^<(\omega_1)\right]A^\beta(\omega_2)A^\gamma(\omega_3)A^\delta(\omega_4)2\pi\delta(\omega_1+\omega_2+\omega_3+\omega_4-\omega)\\
&+\cdots.
\end{aligned}$$

As if it weren't enough that the Green's function mixes terms from all orders in A, so does the current. What we have to do now is plug in the expansion of the Green's function and collect the terms order by order. But first, let's see how to define the conductivity in higher orders

5.4 Conductivity

The conductivity in momentum space is simply the factor that multiplies the electric field when calculating the expected value of the current. To generalize it, we use the following formula:

$$\begin{aligned}
\langle J^\alpha(\omega)\rangle \;=\; &\sigma^{\alpha\beta}(\omega)E^\beta(\omega) + \int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_2}{2\pi}\sigma^{\alpha\beta\gamma}(\omega_1,\omega_2)E^\beta(\omega_1)E^\gamma(\omega_2)\delta(\omega_1+\omega_2-\omega)\\
&+\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_2}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_3}{2\pi}\sigma^{\alpha\beta\gamma\delta}(\omega_1,\omega_2,\omega_3)\\
&\times E^\beta(\omega_1)E^\gamma(\omega_2)E^\delta(\omega_3)\delta(\omega_1+\omega_2+\omega_3-\omega)+\cdots. \qquad (5.54)
\end{aligned}$$

We are now ready to finally obtain the conductivity.

5.4.1 Zeroth order

As we should expect, there is no zeroth order contribution to the current. There needs to be an applied external field for the current to exist. Using the definition of the velocity operator, the zeroth order current is

$$\langle J^\alpha(t)\rangle = -\frac{e}{V}\mathrm{Tr}\left[v^\alpha\right] = \frac{ie}{V\hbar}\mathrm{Tr}\left[r^\alpha H - Hr^\alpha\right] = 0 \qquad (5.55)$$

where $\boldsymbol{r}$ is the position operator. The cyclic property of the trace guarantees that this term is zero.

5.4.2 First order

Collecting the first order terms in 5.53 we obtain

$$\langle J^\alpha(\omega)\rangle = -\frac{e}{V}\mathrm{Tr}\left[v^\alpha iG^{<(A^1)}(\omega)\right] - \frac{e^2}{V}\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\mathrm{Tr}\left[v^{\alpha\beta}iG^{<(A^0)}(\omega_1)\right]A^\beta(\omega_2)2\pi\delta(\omega_1+\omega_2-\omega). \tag{5.56}$$

Plugging in the required order of the Green's function, we get

$$\begin{aligned}\langle J^\alpha(\omega)\rangle &= -\frac{ie^2}{\hbar V}\int_{-\infty}^{\infty}d\epsilon f(\epsilon)\mathrm{Tr}\left[v^\alpha\left(W_R^\beta(\epsilon;-\epsilon/\hbar-\omega)+W_a^\beta(\epsilon;-\epsilon/\hbar+\omega)\right)\right]\frac{E^\beta(\omega)}{i\omega}\\ &+\frac{e^2}{V}\int_{-\infty}^{\infty}d\epsilon f(\epsilon)\mathrm{Tr}\left[v^{\alpha\beta}\delta(\epsilon-H)\right]\frac{E^\beta(\omega)}{i\omega}.\end{aligned} \tag{5.57}$$

We have already done the replacement $A^\alpha(\omega)=\frac{E^\alpha(\omega)}{i\omega}$ because now we can immediately recognize the factor multiplying $E^\beta(\omega)$ as the conductivity.

$$\begin{aligned}\sigma^{\alpha\beta}(\omega) &= \frac{-4\sigma_0}{V}\int_{-\infty}^{\infty}d\epsilon\frac{f(\epsilon)}{\omega}\mathrm{Tr}\left\{\left[v^\alpha W_R^\beta(\epsilon;-\epsilon/\hbar-\omega)+v^\alpha W_a^\beta(\epsilon;-\epsilon/\hbar+\omega)\right]\right.\\ &\left.+i\hbar\mathrm{Tr}\left[v^{\alpha\beta}\delta(\epsilon-H)\right]\right\}\end{aligned} \tag{5.58}$$

Here we have defined the universal conductivity of graphene $\sigma_0 = e^2/4\hbar$

5.4.3 Second order

Like before, collect the second order contributions

$$\begin{aligned}&\langle J^\alpha(\omega)\rangle = -\frac{e}{V}\mathrm{Tr}\left[v^\alpha iG^{<(A^2)}(\omega)\right] - \frac{e^2}{V}\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\mathrm{Tr}\left[v^{\alpha\beta}iG^{<(A^1)}(\omega_1)\right]A^\beta(\omega_2)2\pi\delta(\omega_1+\omega_2-\omega)\\ &-\frac{1}{2!}\frac{e^3}{V}\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\mathrm{Tr}\left[v^{\alpha\beta\gamma}iG^{<(A^0)}(\omega_1)\right]A^\beta(\omega_2)A^\gamma(\omega_3)2\pi\delta(\omega_1+\omega_2+\omega_3-\omega)\end{aligned} \tag{5.59}$$

The first term is

$$\begin{aligned}-\frac{e}{V}\mathrm{Tr}\left[v^\alpha iG^{<(A^2)}(\omega)\right] &= -\frac{e^3}{V}\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_2}{2\pi}(2\pi)\,\delta(\omega_1+\omega_2-\omega)A^\beta(\omega_1)A^\gamma(\omega_2)\int_{-\infty}^{\infty}d\epsilon f(\epsilon)\\ &\times\left\{\frac{i}{2\hbar}\mathrm{Tr}\left[v^\alpha\left(W_R^{\beta\gamma}(\epsilon;-\epsilon/\hbar-\omega)+W_a^{\beta\gamma}(\epsilon;-\epsilon/\hbar+\omega)\right)\right]+\right.\\ &+\frac{1}{\hbar^2}\mathrm{Tr}\left[v^\alpha\left(W_{RR}^{\beta,\gamma}(\epsilon;-\epsilon/\hbar-\omega_1-\omega_2,-\epsilon/\hbar-\omega_2)+\right.\right.\\ &+W_{Ra}^{\beta,\gamma}(\epsilon;-\epsilon/\hbar-\omega_1,-\epsilon/\hbar+\omega_2)+\\ &\left.\left.\left.+W_{aa}^{\beta,\gamma}(\epsilon;-\epsilon/\hbar+\omega_1,-\epsilon/\hbar+\omega_1+\omega_2)\right)\right]\right\}.\end{aligned} \tag{5.60}$$

The second term:

$$
\begin{aligned}
&-\frac{e^2}{V}\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\mathrm{Tr}\left[v^{\alpha\beta}iG^{<(A^1)}(\omega_1)\right]A^\beta(\omega_2)2\pi\delta(\omega_1+\omega_2-\omega)\\
&=-\frac{ie^3}{V\hbar}\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}2\pi\delta(\omega_1+\omega_2-\omega)A^\beta(\omega_1)A^\gamma(\omega_2)\int_{-\infty}^{\infty}d\epsilon f(\epsilon)\\
&\quad\times\mathrm{Tr}\left[v^{\alpha\beta}\left(W_R^\gamma(\epsilon;-\epsilon/\hbar-\omega_2)+W_a^\gamma(\epsilon;-\epsilon/\hbar+\omega_2)\right)\right]
\end{aligned}
\tag{5.61}
$$

Third term:

$$
\begin{aligned}
&-\frac{1}{2!}\frac{e^3}{V}\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\mathrm{Tr}\left[v^{\alpha\beta\gamma}iG^{<(A^0)}(\omega_1)\right]A^\beta(\omega_2)A^\gamma(\omega_3)2\pi\delta(\omega_1+\omega_2+\omega_3-\omega)\\
&=\frac{1}{2!}\frac{e^3}{V}\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}A^\beta(\omega_1)A^\gamma(\omega_2)2\pi\delta(\omega_1+\omega_2-\omega)\int_{-\infty}^{\infty}d\epsilon f(\epsilon)\mathrm{Tr}\left[v^{\alpha\beta\gamma}\delta(\epsilon-H)\right]
\end{aligned}
\tag{5.62}
$$

Summing it all up, and replacing $A^\alpha(\omega)=\frac{E^\alpha(\omega)}{i\omega}$ we obtain

$$
\begin{aligned}
\langle J^\alpha(\omega)\rangle \;=\; &-\frac{e^3}{V}\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_2}{2\pi}(2\pi)\,\delta(\omega_1+\omega_2-\omega)\frac{E^\beta(\omega_1)}{i\omega_1}\frac{E^\gamma(\omega_2)}{i\omega_2}\int_{-\infty}^{\infty}d\epsilon f(\epsilon)\\
&\times\left\{\frac{i}{2\hbar}\mathrm{Tr}\left[v^\alpha W_R^{\beta\gamma}(\epsilon;-\epsilon/\hbar-\omega)+v^\alpha W_a^{\beta\gamma}(\epsilon;-\epsilon/\hbar+\omega)\right]+\right.\\
&+\frac{1}{\hbar^2}\mathrm{Tr}\left[v^\alpha W_{RR}^{\beta,\gamma}(\epsilon;-\epsilon/\hbar-\omega_1-\omega_2,-\epsilon/\hbar-\omega_2)+\right.\\
&+v^\alpha W_{Ra}^{\beta,\gamma}(\epsilon;-\epsilon/\hbar-\omega_1,-\epsilon/\hbar+\omega_2)+\\
&\left.\left.+v^\alpha W_{Ra}^{\beta,\gamma}(\epsilon;-\epsilon/\hbar-\omega_1,-\epsilon/\hbar+\omega_2)\right)\right]\\
&+\frac{i}{\hbar}\mathrm{Tr}\left[v^{\alpha\beta}W_R^\gamma(\epsilon;-\epsilon/\hbar-\omega_2)+v^{\alpha\beta}W_a^\gamma(\epsilon;-\epsilon/\hbar+\omega_2)\right]\\
&\left.-\frac{1}{2}\mathrm{Tr}\left[v^{\alpha\beta\gamma}\delta(\epsilon-H)\right]\right\}.
\end{aligned}
\tag{5.63}
$$

Comparing with eq. 5.54, we may identify the second order conductivity as

$$
\begin{aligned}
&\sigma^{\alpha\beta\gamma}(\omega_1,\omega_2)\\
&=-\frac{e^3}{Vi\omega_1 i\omega_2}\int_{-\infty}^{\infty}d\epsilon f(\epsilon)\left\{\frac{i}{2\hbar}\mathrm{Tr}\left[v^\alpha\left(W_R^{\beta\gamma}(\epsilon;-\epsilon/\hbar-\omega)+W_a^{\beta\gamma}(\epsilon;-\epsilon/\hbar+\omega)\right)\right]+\right.\\
&+\frac{1}{\hbar^2}\mathrm{Tr}\left[v^\alpha\left(W_{RR}^{\beta,\gamma}(\epsilon;-\epsilon/\hbar-\omega_1-\omega_2,-\epsilon/\hbar-\omega_2)+\right.\right.\\
&\left.\left.+W_{Ra}^{\beta,\gamma}(\epsilon;-\epsilon/\hbar-\omega_1,-\epsilon/\hbar+\omega_2)+W_{aa}^{\beta,\gamma}(\epsilon;-\epsilon/\hbar+\omega_1,-\epsilon/\hbar+\omega_1+\omega_2)\right)\right]\\
&\left.+\frac{i}{\hbar}\mathrm{Tr}\left[v^{\alpha\beta}\left(W_R^\gamma(\epsilon;-\epsilon/\hbar-\omega_2)+W_a^\gamma(\epsilon;-\epsilon/\hbar+\omega_2)\right)\right]-\frac{1}{2}\mathrm{Tr}\left[v^{\alpha\beta\gamma}\delta(\epsilon-H)\right]\right\}.
\end{aligned}
\tag{5.64}
$$

5.4.4 Third order

Collecting the third order contributions, the current is, formally,

$$\begin{aligned}\langle J^\alpha(\omega)\rangle &= -\frac{e}{V}\mathrm{Tr}\left[v^\alpha iG^<(\omega)\right] - \frac{e^2}{V}\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\mathrm{Tr}\left[v^{\alpha\beta}iG^<(\omega_1)\right]A^\beta(\omega_2)2\pi\delta(\omega_1+\omega_2-\omega)\\ &- \frac{1}{2!}\frac{e^3}{V}\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\mathrm{Tr}\left[v^{\alpha\beta\gamma}iG^<(\omega_1)\right]A^\beta(\omega_2)A^\gamma(\omega_3)2\pi\delta(\omega_1+\omega_2+\omega_3-\omega) \qquad (5.65)\\ &- \frac{1}{3!}\frac{e^4}{V}\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\frac{d\omega_4}{2\pi}\mathrm{Tr}\left[v^{\alpha\beta\gamma\delta}iG^<(\omega_1)\right]A^\beta(\omega_2)A^\gamma(\omega_3)A^\delta(\omega_4)2\pi\delta(\omega_1+\omega_2+\omega_3+\omega_4-\omega).\end{aligned}$$

This one is done in exactly the same way as the other ones and is left as an exercise to the reader. This will not be calculated because it is too computationally expensive to use. See Section 6.8 for a more thorough justification.

6 Kernel Polynomial Method - KPM

Up until now, we have obtained expressions for the current using the Keldysh formalism and insisted in expressing them as traces of quantum mechanical operators. This allows us to have a basis-independent description, which is very useful because we can choose the most convenient one when doing the numerical calculations. In this chapter, we'll see how to express these formulas in terms of something we can calculate numerically. To achieve that, we first need to delve into the Kernel Polynomial Method (KPM), which uses Chebyshev polynomials to establish a recursion relation between the numerical objects we need to calculate. This eliminates a whole lot of redundancy and makes KPM an efficient method of calculating traces of operators.

6.1 Chebyshev Polynomials

The point of this section is to introduce the Chebyshev polynomials and to show how a function may be expanded in a series of Chebyshev polynomials. We could have used another set of polynomials, but these satisfy a simple recursion relation and have good convergence properties [4], which make them ideal for numerical calculations.

6.1.1 Definition

The Chebyshev polynomials are defined in the range]-1,1[and the n-th polynomial may be generated using the following definition and the properties of trigonometric functions:

$$T_n(x) = \cos(n \arccos(x)). \tag{6.1}$$

Using this formula, we may find the first few polynomials:

$$\begin{aligned} T_0(x) &= 1 && (6.2)\\ T_1(x) &= x && (6.3)\\ T_2(x) &= 2x^2 - 1 && (6.4)\\ T_3(x) &= 4x^3 - 3x && (6.5) \end{aligned}$$

6.1.2 Recursion relation

The Chebyshev polynomials satisfy the recursion relation

$$T_{m+1}(x) = 2xT_m(x) - T_{m-1}(x) \tag{6.6}$$

which may be proven directly from definition by replacing $x = \cos(\theta)$:

$$\begin{aligned} T_{n+1}(\cos(\theta)) + T_{n-1}(\cos(\theta)) &= \cos((n+1)\theta) + \cos((n-1)\theta) \\ &= \cos(n\theta)\cos(\theta) - \sin(n\theta)\sin(\theta) + \cos(n\theta)\cos(\theta) + \sin(n\theta)\sin(\theta) \\ &= 2\cos(n\theta)\cos(\theta) = 2\cos(\theta)T_n(\cos(\theta)). \end{aligned} \tag{6.7}$$

This means that from just the first two polynomials, all the others may be reconstructed.

6.1.3 Orthogonality

They also satisfy an orthogonality relation,

$$\int_{-1}^{1} \frac{dx}{\pi\sqrt{1-x^2}} T_n(x)T_m(x) = \frac{1+\delta_{n0}}{2}\delta_{nm} \tag{6.8}$$

which is a direct consequence of the orthogonality of Fourier components upon the change of variables $x = \cos(\theta)$:

$$\int_{\pi}^{0} \frac{1}{\pi\sin(\theta)} \cos(n\theta)\cos(m\theta)\left[-\sin(\theta)\right] d\theta = \frac{1}{\pi}\int_{0}^{\pi} \cos(n\theta)\cos(m\theta)d\theta = \frac{1+\delta_{n0}}{2}\delta_{nm} \tag{6.9}$$

It's this close relationship between the Chebyshev and Fourier series that gives them many of their properties. The fact that they're orthogonal to one another means that a function may be easily expanded in terms of Chebyshev polynomials.

6.2 Expansion of functions in terms of Chebyshev polynomials

Any integrable function $f :]-1, 1[\to \mathbb{R}$ may be expressed in terms of a sum of Chebyshev polynomials

$$f(x) = \sum_{n=0}^{\infty} a_n T_n(x). \tag{6.10}$$

These a_n coefficients may be found using the orthogonality relations

$$\int_{-1}^{1} \frac{dx}{\pi\sqrt{1-x^2}} T_m(x)f(x) = \sum_{n=0}^{\infty} a_n \int_{-1}^{1} \frac{dx}{\pi\sqrt{1-x^2}} T_m(x)T_n(x) = \sum_{n=0}^{\infty} a_n \frac{1+\delta_{n0}}{2}\delta_{nm} = a_m\frac{1+\delta_{m0}}{2} \tag{6.11}$$

Therefore the coefficients are

$$a_n = \frac{2}{1+\delta_{n0}} \int_{-1}^{1} \frac{dx}{\pi\sqrt{1-x^2}} T_n(x) f(x). \tag{6.12}$$

In principle, this is enough to obtain the expansion. However, for some practical calculations, it may be easier to use a different set of coefficients:

$$f(x) = \frac{1}{\pi} \frac{1}{\sqrt{1-x^2}} \sum_{n=0}^{\infty} \frac{2b_n}{1+\delta_{n0}} T_n(x). \tag{6.13}$$

That way, we do not have to deal with square roots inside the integral. These new coefficients are

$$b_n = \int_{-1}^{1} dx T_n(x) f(x). \tag{6.14}$$

Let's now apply this to the functions of our interest. Looking at the results obtained in the previous chapter, we see the Dirac deltas and Green's functions are the only objects that depend on the Hamiltonian operator. In general, they cannot be calculated directly, so we'll first expand them in Chebyshev polynomials and then sum the series.

6.2.1 Dirac delta

We're looking to expand $\delta(x-\epsilon)$, which depends on two variables. Later on, one of them will be an operator so let's try and isolate it out by searching for an expansion of the form

$$\delta(x-\epsilon) = \sum_{n=0}^{\infty} \frac{\Delta_n(\epsilon)}{1+\delta_{n0}} T_n(x). \tag{6.15}$$

Assuming both x and ϵ are in the $]-1,1[$ range, the orthogonality relations give us the $\Delta_n(\epsilon)$

$$\int_{-1}^{1} \frac{dx}{\pi\sqrt{1-x^2}} T_m(x)\delta(x-\epsilon) = \sum_{n=0}^{\infty} \int_{-1}^{1} \frac{dx}{\pi\sqrt{1-x^2}} T_m(x)T_n(x) \frac{\Delta_n(\epsilon)}{1+\delta_{n0}} = \frac{\Delta_m(\epsilon)}{2} \tag{6.16}$$

and the left-hand side of the equation may be calculated easily:

$$2\int_{-1}^{1} \frac{dx}{\pi\sqrt{1-x^2}} T_m(x)\delta(x-\epsilon) = \frac{2T_m(\epsilon)}{\pi\sqrt{1-\epsilon^2}} = \Delta_m(\epsilon). \tag{6.17}$$

This means the expansion of the Dirac delta is

$$\delta(x-\epsilon) = \frac{1}{\pi} \frac{1}{\sqrt{1-\epsilon^2}} \left[1 + 2\sum_{n=1}^{\infty} T_n(\epsilon)T_n(x) \right] \tag{6.18}$$

Using the b_n coefficients, we would have obtained

$$\delta(x-\epsilon) = \frac{1}{\pi}\frac{1}{\sqrt{1-x^2}}\left[1 + 2\sum_{n=1}^{\infty} T_n(\epsilon)T_n(x)\right]. \tag{6.19}$$

The only difference is the argument of the square root.

6.2.2 Green's functions

Consider the Green's function with a finite $\lambda > 0$ that accounts for dispersion [13]:

$$g^{\sigma,\lambda}(\epsilon, h) = \frac{-1}{\epsilon - h + i\sigma\lambda} = \sigma i \int_0^{\infty} dt e^{\sigma i(\epsilon+h+i\sigma\lambda)t}. \tag{6.20}$$

This is also a two-variable function in which we want to achieve a separation between ϵ and h in the polynomial expansion, so let us look for an expression of the form

$$g^{\sigma,\lambda}(\epsilon, h) = \sum_{n=0}^{\infty} \frac{g_n^{\sigma,\lambda}(\epsilon)}{1+\delta_{n0}} T_n(h). \tag{6.21}$$

The function $g_n^{\sigma,\lambda}(\epsilon)$ may be calculated applying the orthogonality relations.

$$g_n^{\sigma,\lambda}(\epsilon) = 2\int_{-1}^{1} \frac{dh}{\pi\sqrt{1-h^2}} T_m(h) g^{\sigma,\lambda}(\epsilon, h) \tag{6.22}$$

The calculation will be done using $g^{\sigma,\lambda}$ in its integral form since it's simpler to integrate.

$$g_n^{\sigma,\lambda}(\epsilon) = 2\int_{-1}^{1} \frac{dh}{\pi\sqrt{1-h^2}} T_n(h)\sigma i \int_0^{\infty} dt e^{\sigma i(\epsilon-h+i\sigma\lambda)t} \tag{6.23}$$

Separating the exponential we are able to isolate the term that depends on h and integrate it explicitly.

$$g_n^{\sigma,\lambda}(\epsilon) = 2\sigma i \int_0^{\infty} dt e^{\sigma i(\epsilon+i\sigma\lambda)t} \int_{-1}^{1} \frac{dh}{\pi\sqrt{1-h^2}} T_n(h) e^{-\sigma i h t} \tag{6.24}$$

Now we may identify the second integral as Bessel function.

$$\int_{-1}^{1} \frac{dh}{\pi\sqrt{1-h^2}} T_n(h) e^{-\sigma i h t} = (-\sigma i)^n J_n(t) \tag{6.25}$$

So what remains is just its Laplace transform. To see this, let $z = \lambda - \sigma i\epsilon$:

$$g_n^{\sigma,\lambda}(z) = -2(-\sigma i)^{n+1} \int_0^{\infty} dt e^{-zt} J_n(t). \tag{6.26}$$

This is a tricky calculation which can be checked in the Appendix but the result is

$$g_n^{\sigma,\lambda}(z) = 2\sigma i \frac{e^{-ni \arccos(iz)}}{\sqrt{z^2+1}}. \tag{6.27}$$

This is the result that should be used if we want to include phenomenological scattering. If that's not the case, take the limit $\lambda \to 0^+$, such that $iz = \sigma\epsilon + i0^+$. Because we're using $-1 < \epsilon < 1$, the imaginary factor does nothing in these functions, since we never hit the branch cuts. We may therefore ignore it and consider the functions as if they were functions of real variables. This leaves us with

$$g_n^{\sigma}(\epsilon) = 2\sigma i \frac{e^{-ni\sigma \arccos(\epsilon)}}{\sqrt{1-\epsilon^2}}. \tag{6.28}$$

which means Green's function without scattering in terms of Chebyshev polynomials is

$$g^{\sigma}(\epsilon, h) = \frac{-1}{\epsilon + h + \sigma i 0^+} = \frac{2\sigma i}{\sqrt{1-\epsilon^2}} \sum_{n=0}^{\infty} \frac{e^{-ni\sigma \arccos(\epsilon)}}{1+\delta_{n0}} T_n(h). \tag{6.29}$$

6.3 Truncated series and the use of kernels

Naturally, we cannot expect to be able to sum the whole series, so we have to truncate it at some order N. Near points where the derivative of the function isn't continuous, this gives rise to an undesired oscillatory behavior known as Gibbs oscillations[1]. A simple fix to this is to modify the coefficients of the expansion $b_n \to w_n b_n$, choosing the w_n to take into account the finite order of the series. That is an additional approximation to the function we're calculating, but just like the one we're doing by truncating the series, its difference to the exact result should approach zero in the limit $N \to \infty$. To see where these coefficients come from and how they're chosen, we'll have to introduce the concept of an integral kernel and see how the truncated series expansion may be obtained from the original function by convolving it with the kernel.

Let $f_{KPM}(x)$ denote this truncated series with the modified coefficients.

$$f_{KPM}(x) = \frac{1}{\pi} \frac{1}{\sqrt{1-x^2}} \sum_{n=0}^{N-1} \frac{2}{1+\delta_{n0}} w_n b_n T_n(x) \tag{6.30}$$

If we define the kernel $K_N(x,y)$ as

$$K_N(x,y) = \sum_{n=0}^{N-1} \frac{2}{1+\delta_{n0}} w_n \frac{T_n(x)}{\pi\sqrt{1-x^2}} \frac{T_n(y)}{\pi\sqrt{1-y^2}} \tag{6.31}$$

[1] This is the same phenomenon that happens in Fourier expansions, which isn't surprising given the close relationship between the Chebyshev and Fourier expansions.

it may be checked directly that

$$f_{KPM}(x) = \int_{-1}^{1} \pi\sqrt{1-y^2} K_N(x,y) f(y) dy. \tag{6.32}$$

This kernel gives us a mapping between the function we're seeking to approximate, $f(x)$, and its approximation with the modified coefficients, $f_{KPM}(x)$. It can also be used to obtain the m-th order term of the Chebyshev series if we use the weight $w_n = \delta_{nm}$:

$$f_n(x) = \frac{1}{\pi\sqrt{1-x^2}} \frac{2}{1+\delta_{n0}} T_n(x) \int_{-1}^{1} T_n(y) f(y) dy. \tag{6.33}$$

With this in mind, we show here some common ways to choose these coefficients. Their derivation may be seen in [4].

6.3.1 Dirichlet kernel

The Dirichlet kernel K_N^D is simply 6.31 with 1the coefficients

$$w_n^D = 1 \tag{6.34}$$

and is equivalent to the bare truncation of the series. If the function does not contain discontinuities, this one should be enough to obtain a good result. But how can we evaluate the convergence of $f_{KPM}(x)$? We can use the notion of an integral scalar product

$$\langle f \,|\, g \rangle = \int_{-1}^{1} \pi\sqrt{1-x^2} f(x) g(x) dx \tag{6.35}$$

to define the norm $\|f\| = \sqrt{\langle f \,|\, f \rangle}$. With this norm, we may say that

$$\|f - f_{KPM}\|^2 = \int_{-1}^{1} \pi\sqrt{1-x^2} \left[f(x) - f_{KPM}(x)\right]^2 dx \xrightarrow{N\to\infty} 0 \tag{6.36}$$

since we know that f_{KPM} approaches f. Using the fact that power series converge absolutely[2] inside their radius of convergence, we can learn that for **any** given point x,

$$\frac{1}{\pi\sqrt{1-x^2}} \sum_{n=0}^{N} \frac{2a_n}{1+\delta_{n0}} T_n(x) \xrightarrow{N\to\infty} f(x) \tag{6.37}$$

As this is a point-wise condition, for different values of x, the series may converge at different rates. If we want to avoid oscillations, we need to impose a global condition. Fig. 6.3 shows how the truncated approximation by Chebyshev polynomials using the Dirichlet kernel to two different functions affects the convergence. Just as advertised, near the discontinuity there appears strong oscillations even at high orders.

[2] Absolute convergence is a stronger condition of convergence and it simply means that $\sum_{n=0}^{\infty} |a_n x^n|$ also converges.

6.3.2 Fejér kernel

It was shown by Fejér [14] that using the kernel

$$K_N^F(x,y) = \frac{1}{N}\sum_{\nu=0}^{N} K_\nu^D(x,y) \tag{6.38}$$

on continuous functions guarantees uniform convergence[3] of f_{KPM} in any interval $[-1+\epsilon, 1-\epsilon]$ (for any $\epsilon > 0$ in which this makes sense). In other words, this condition means that the whole function converges to f at uniform speed. In terms of the weight functions, this translates to

$$w_n^F = 1 - n/N. \tag{6.39}$$

The higher order terms, which would give rise to the oscillations, have a smaller weight in f_{KPM}, which is an important factor in removing the oscillations. Comparing in Fig. 6.3 we can immediately see that the oscillations are gone but the convergence is slower for the continuous function.

6.3.3 Jackson kernel

Building on the previous kernel, these coefficients are further adjusted to minimize the spreading of sharp features of the function.

$$w_n^J = \frac{(N-n+1)\cos\frac{\pi n}{N+1} + \sin\frac{\pi n}{N+1}\cot\frac{\pi}{N+1}}{N+1} \tag{6.40}$$

In our case, we'll be expanding Dirac deltas, so it seems relevant to see just how the features of this kernel affect its convergence [13]. Using the Jackson kernel, the Dirac delta has the following expression:

$$\delta_{KPM}(x-\epsilon) = \frac{1}{\pi\sqrt{1-x^2}}\sum_{n=0}^{M-1}\frac{2w_n^J}{1+\delta_{n0}}T_n(x)T_n(\epsilon) \tag{6.41}$$

Not much can be inferred from just looking at this, so let's examine its average and variance. Hopefully this will give us some information about δ_{KPM} as a distribution. Choosing $\epsilon = 0$, all the odd moments vanish due to the parity of the function.

[3] This is an even stronger condition for convergence. Let $\{F_n\}$ be a sequence of functions. The sequence is said to converge uniformly to F within a set S of values of x if for all $\epsilon > 0$, we can find an integer N such that $|F_n(x) - F(x)| < \epsilon$ for all $n \geq N$ and all $x \in S$. A series converges uniformly if the sequence of partial sums $\sum_{k=0}^{n} f_k = F_n$ converges uniformly.

To evaluate these averages, it is useful to express x^2 in terms of Chebyshev polynomials, for then we may use the orthogonality relations to our advantage.

$$x^2 = \frac{T_2(x) + 1}{2} \tag{6.42}$$

With this, the calculations result in

$$\langle x^2 \rangle = \int_{-1}^{1} dx \delta_{KPM}(x) x^2 = \frac{N \sin^2(\frac{\pi}{N+1})}{N+1}. \tag{6.43}$$

Since $\langle x \rangle = 0$, we may immediately say that its standard deviation is $\sigma = \sqrt{\langle x^2 \rangle}$. For large N, we may just as well use

$$\sigma\left(\delta_{KPM}\right) \approx \left|\sin\left(\frac{\pi}{N}\right)\right| \approx \frac{\pi}{N}. \tag{6.44}$$

A finite-order expansion necessarily exhibits a broadening of the Dirac delta, which gets sharper with higher N. Fig 6.1 shows that near the peak, δ_{KPM} is very well approximated by a Gaussian curve with standard deviation σ.

$$\delta_{KPM} \approx \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{x^2}{2\sigma^2}\right) \tag{6.45}$$

The differences start to show near the tails, but is that difference relevant?

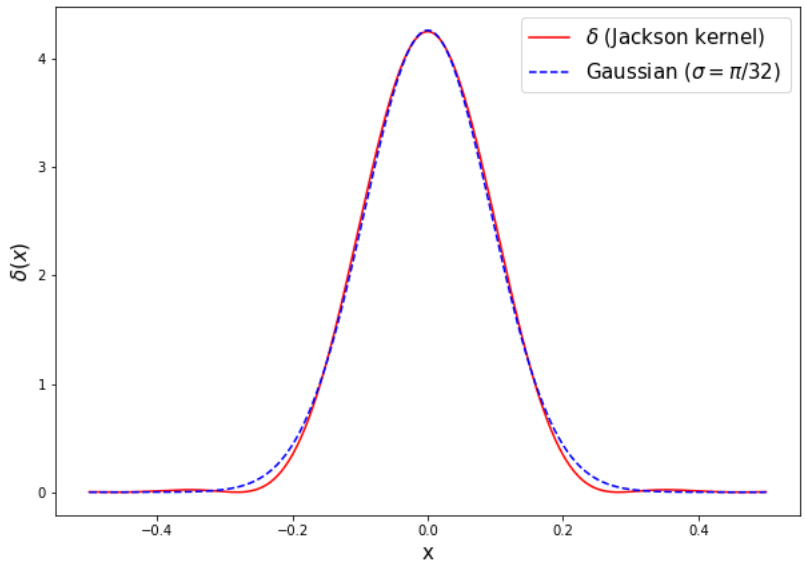


Figure 6.1: δ_{KPM} with the Jackson kernel and respective Gaussian approximation for $N = 32$.

To answer that question, we should check what happens with the fourth moment of δ_{KPM}. Using

$$x^4 = \frac{T_4(x) + 4T_2(x) + 3T_0(x)}{8} \tag{6.46}$$

we can find $\langle x^4 \rangle$:

$$\langle x^4 \rangle = \int_{-1}^{1} dx \delta_{KPM}(x) x^4 = \frac{8 + 3N + (2 + 4N)\cos(2\Delta) + (N-2)\cos(4\Delta)}{8(N+1)}. \tag{6.47}$$

In the limit of large N, this simplifies to

$$\langle x^4 \rangle \approx \cos^4\left(\frac{\pi}{N}\right) \approx 1 - 2\left(\frac{\pi}{N}\right)^2. \tag{6.48}$$

Right here we can see that the similarities between the Gaussian and δ_{KPM} start to break down. In this case, we approach a constant, while the Gaussian's fourth moment should go to zero when $N \to \infty$:

$$\langle x^4 \rangle_{\text{Gauss}} = 3\sigma^4 \approx 3\left(\frac{\pi}{N}\right)^4 \to 0. \tag{6.49}$$

The repercussions of this become noticeable when we try to evaluate something such as $x^4\delta(x)$, which is the integrand of the $\langle x^4 \rangle$. It could originate from something we'd want to calculate, such as the fourth moment of the distribution of energies. Fig. 6.2 shows that $x^2\delta(x)$ has some oscillations but still converges, while the oscillations for $x^4\delta(x)$ completely destroy the shape of the function. Maybe we need more polynomials to ensure it converges? The right side of Fig. 6.2 clearly says no. Increasing the number of polynomials only makes matters worse as the oscillations take over the graph.

If $\delta_{KPM}(x)$ actually converged to a Gaussian, we'd have no issues with oscillations at any $\langle x^n \rangle$ because it'd decay very quickly. Near the peak, the resemblance is uncanny, but caution should be taken before using this as a Gaussian. If we had used $x = 0$ and studied δ_{KPM} as a function of ϵ, we would have obtained a similar result.

6.3.4 Lorentz kernel

Sometimes, the functions we're expanding have some important features that must be present in the expansion. In the previous case, we said that using the Jackson kernel produces Gaussian peaks in sharp features. While useful for Dirac deltas, when dealing with Green's functions this is undesirable because its imaginary part should approach a Lorentzian curve, not a Gaussian. This is the main reason that leads to the definition of the Lorentz kernel coefficients.

$$w_n^L = \frac{\sinh\left[\lambda(1 - n/N)\right]}{\sinh(\lambda)} \tag{6.50}$$

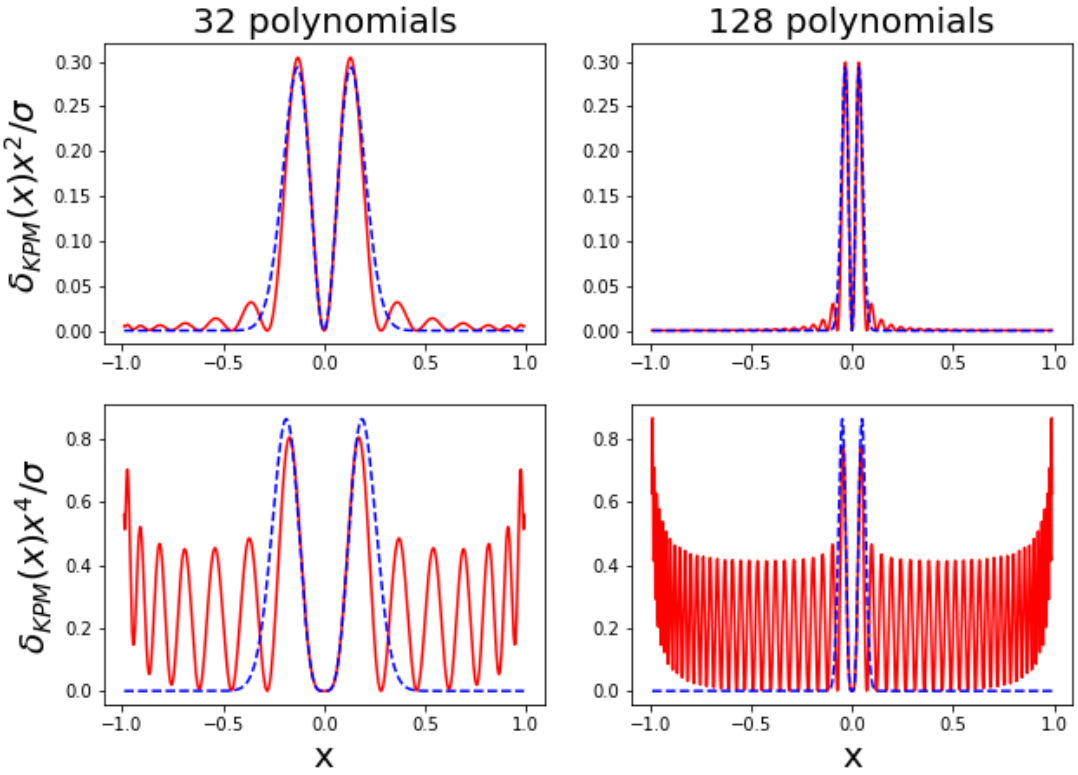


Figure 6.2: Representation of the integrands in the second and fourth moments of $\delta_{KPM}(x)$. $\delta_{KPM}(x)x^2$ (top) and $\delta_{KPM}(x)x^4$ (bottom); 32 Chebyshev polynomials (left), 128 Chebyshev polynomials (right)

We end up with a free parameter that is a compromise between good resolution and damping of oscillations. Fig. 6.3 shows the Lorentz kernel for $\lambda = 3$. A higher λ results in more weight to the lower terms and a slower convergence, while the limit $\lambda \to 0$ recovers the Fejér kernel. Usually we're going to be trying to approximate the imaginary part of the Green's function, which is a Lorentzian:

$$\Im g^a(x) = \Im \frac{-1}{\epsilon + i\sigma} = \frac{\sigma}{x^2 + \sigma^2} = L_\sigma(x) \tag{6.51}$$

In our expressions, we always use $\sigma \to 0$. In this limit, the function becomes singular, so KPM will never converge. A higher number of polynomials will indeed return a better approximation with sharper peaks, but it can never converge to a real singularity. One way to overcome this is to use a finite σ. Now the function is no longer singular and KPM will converge, so a higher number of polynomials will not sharpen the peaks. In that case, we may even forget about the usage of kernels if we have enough polynomials. However, if we insist on using the limit $\sigma \to 0$

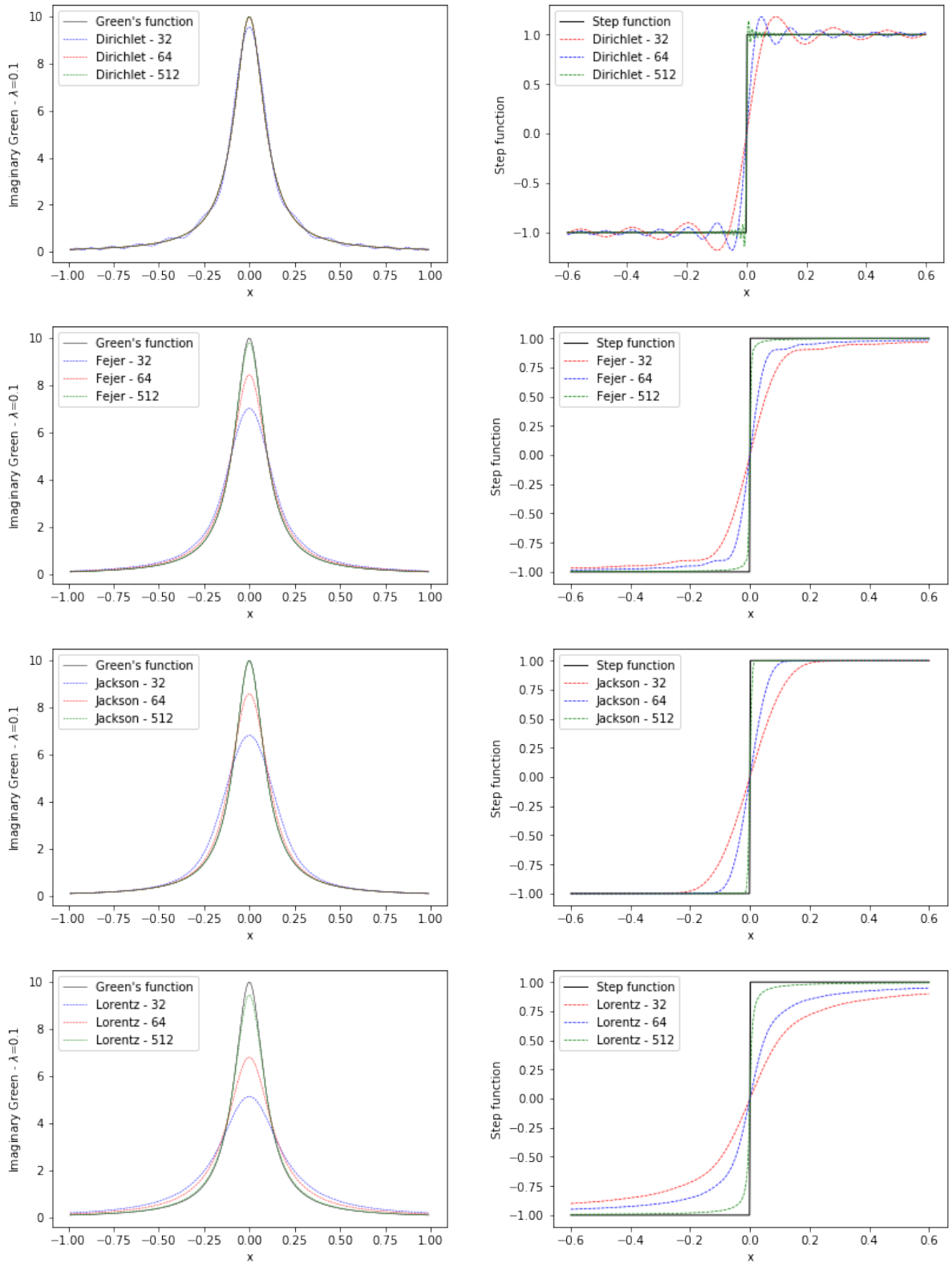


Figure 6.3: Comparison of the truncated series of the imaginary part of Green's function (left) and the step function (right) for varying numbers of polynomials and various kernels. The parameter used for the Lorentz kernel is $\lambda = 4$.

but still want some broadening[4], we may use the Lorentz kernel to our advantage. A suitable choice of λ can emulate a finite σ. Unlike the previous discussion about the Jackson kernel, we cannot evaluate the moments of a Lorentzian, so instead we'll compare the two curves by their width. A natural choice is the width at half maximum, which is 2σ. This parameter may be found by evaluating the Chebyshev expansion of the Green's function at zero since that's where we expect its maximum to lie. Then, we have to match the maximum values, which also fixes the width. Start with the expansion of the (advanced) Green's function with real arguments coupled to the Lorentz kernel:

$$g_M^L(\epsilon, h) = \sum_{n=0}^{M-1} w_n^L g_n^a(\epsilon) \frac{T_n(h)}{1+\delta_{n0}} = \sum_{n=0}^{M-1} \frac{\sinh[\lambda(1-n/M)]}{\sinh(\lambda)} \frac{2i}{\sqrt{1-\epsilon^2}} \frac{(-1)^n e^{-ni\sigma \arccos(\epsilon)}}{1+\delta_{n0}} T_n(h) \tag{6.52}$$

Setting $h = 0$ produces a function of ϵ centered at zero. To find its maximum, evaluate $g_M^L(0,0)$. The height of the Lorentzian is the imaginary part of $g_M^L(0,0)$.

$$\Im\left[g_M^L(0,0)\right] = \Im\left[\sum_{n=0}^{M-1} w_n^L g_n^a(0) \frac{T_n(0)}{1+\delta_{n0}}\right] \tag{6.53}$$

It's a simple matter of using the definitions and some identities on hyperbolic functions to obtain

$$\Im\left[g_M^L(0,0)\right] = \begin{cases} \frac{\tanh\left(\frac{\lambda}{2}\right)}{\tanh\left(\frac{\lambda}{M}\right)} & M \text{ even} \\ \frac{\cosh(\lambda)\cosh\left(\frac{\lambda}{M}\right)-1}{\sinh\left(\frac{\lambda}{M}\right)\sinh(\lambda)} & M \text{ odd} \end{cases}. \tag{6.54}$$

In either case, for large M and small λ, we obtain

$$\Im\left[\delta_M^L(0,0)\right] = \frac{M}{\lambda}\tanh\left(\frac{\lambda}{2}\right). \tag{6.55}$$

Equating eq. 6.54 to the height of the Lorentzian for even M, we get the desired relation between λ and σ:

$$\sigma = \frac{\tanh\left(\frac{\lambda}{M}\right)}{\tanh\left(\frac{\lambda}{2}\right)}. \tag{6.56}$$

This is an important result because it tells us that if we want to keep the same finite resolution while increasing the number of polynomials, we have to change λ. For small λ this function

[4] It's actually useful to have some breadth in the singularities. For a sufficiently high number of polynomials, we are able to use KPM to distinguish between individual energy levels, which take the form of Dirac deltas. From a theoretical stand, we use infinite systems, which results in a continuum of states, so we never see individual peaks. Even experimentally, we cannot distinguish between individual peaks because of the resolution. It makes sense to want a similar thing with KPM, and that may be done by broadening the peaks.

approaches $2/M$ and for large λ it approaches λ/M. If instead we keep λ fixed, σ becomes smaller and smaller as M increases, indicating a sharpening of the peaks. In Fig. 6.4 we may see just how the Lorentz kernel coupled to the real-energy Green's function approaches a Lorentzian curve. For small λ, g^L does converge, but not to a Lorentzian. The percent error is very large even for a high number of polynomials. An increase in λ is compatible with a better approximation for higher-order expansions.

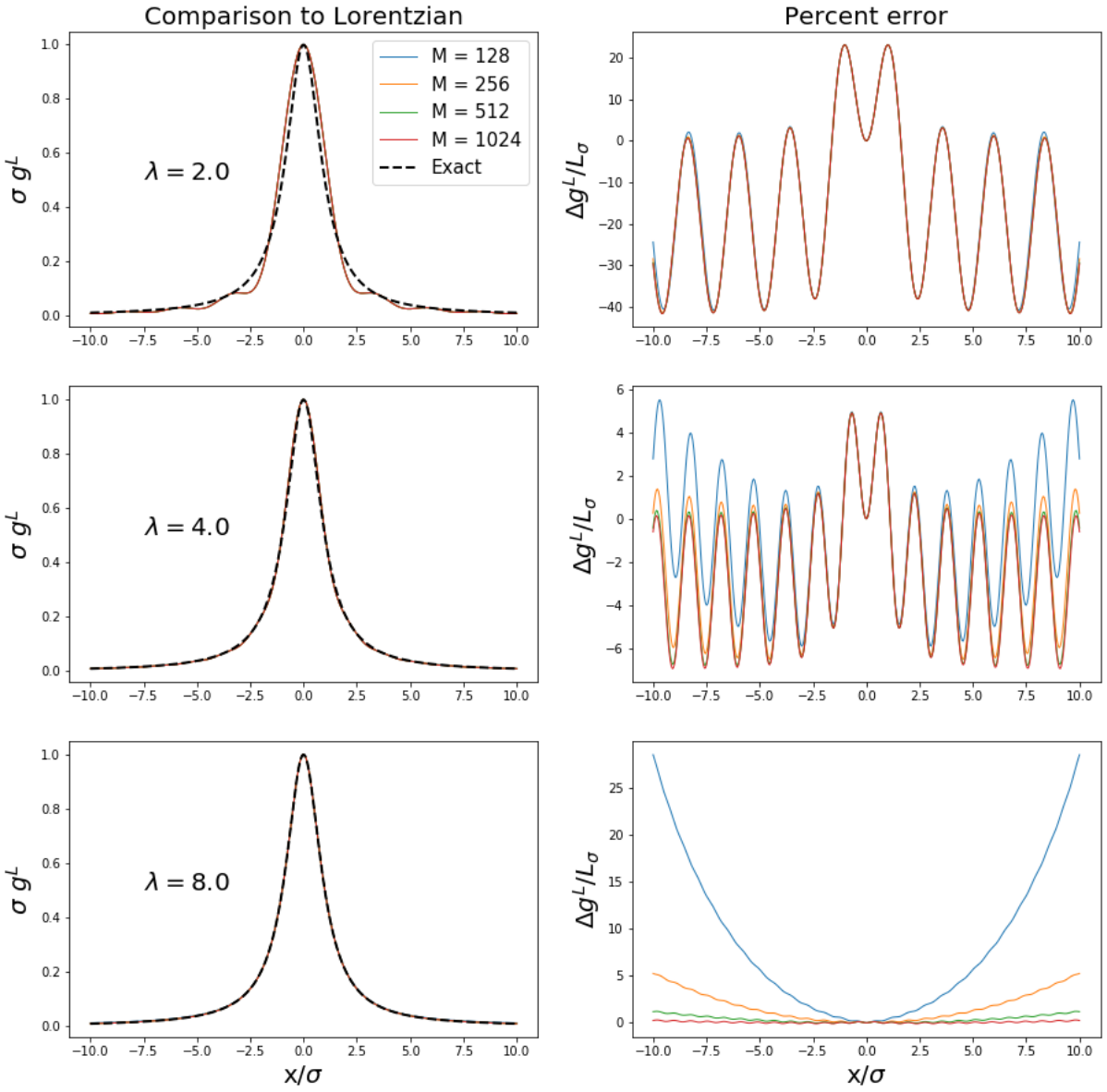


Figure 6.4: Approximation of a Lorentzian curve using the KPM expansion of the imaginary part of Green's function. The graphs are scaled by σ, so all the Lorentzian curves are $1/(1+x^2)$ in this scale. On the left, the curves are superimposed, while on the left we see the percent error.

6.4 From functions to operators

What we've done in these previous sections is targeted towards functions in the $]-1,1[$ range, but this is not quite what we want. We're working with functions of operators, not functions of complex variables. The Green's functions obtained from the Keldysh formalism are actually functions of the Hamiltonian, and as such, are operators themselves. We should take a short moment to remember how these are defined. Functions of operators are defined in terms of their Taylor series, which is assumed to converge to the function inside a certain radius. This is why we may say that if $|n\rangle$ is an eigenvector of H with eigenvalue ϵ_n, then for any function f:

$$f(H)\,|n\rangle = f(\epsilon_n)\,|n\rangle \tag{6.57}$$

is well-defined. Summing the series of operators first and then acting with $|n\rangle$ or acting with $|n\rangle$ through the whole series produces the same result. Since inside that radius the series converges absolutely, we may simply reorder the terms into Chebyshev polynomials.

What about the fact that Chebyshev polynomials are only defined in the range $]-1,1[$? Since the functions used are only defined in that range, that means that the eigenvalues of the Hamiltonian must also lie between that same range[5]. This can be imposed by a suitable rescaling of the Hamiltonian and all the energy scales [4].

$$\tilde{H} = (H-b)/\lambda \tag{6.58}$$

$$\tilde{E} = (E-b)/\lambda \tag{6.59}$$

With these formulas, we may use the extremal eigenvalues E_{min} and E_{max} to define the scales. Using

$$\begin{aligned} \lambda &= (E_{max}-E_{min})/(2-\epsilon) \\ b &= (E_{max}+E_{min})/2 \end{aligned}$$

we can be sure that the new eigenvalues will all lie in the desired $]-1,1[$ range. The $\epsilon > 0$ factor is important to guarantee that the new eigenvalues do not include the boundaries of the $]-1,1[$ interval, which could cause numerical problems. If the eigenvalues of the original Hamiltonian already fit in that interval, this rescaling may still be performed to improve energy resolution, although it is not necessary.

[5] These eigenvalues are necessarily bounded because we're dealing with finite matrices when doing the numerical calculations.

To see this in action consider a typical term of the expansion, such as

$$\frac{-e^2}{\hbar V\omega}\int_{-\infty}^{\infty} d\epsilon f(\epsilon)\mathrm{Tr}\left[v^\alpha i g^R\left(-\frac{\epsilon}{\hbar}-\omega\right)v^\beta\delta(\epsilon-H)\right]$$
$$=\frac{-e^2}{\hbar V\omega}\int_{E_{min}}^{E_{max}} d\epsilon\frac{1}{1+e^{\beta(\epsilon-\mu)}}\mathrm{Tr}\left[v^\alpha\frac{-i}{-\frac{\epsilon}{\hbar}-\omega+\frac{H}{\hbar}-i0^+}v^\beta\delta(\epsilon-H)\right] \quad .$$

The limits of integration may be taken to be E_{min} and E_{max} because outside that range, the Dirac delta will always yield zero. Using the transformations 6.58 and 6.59, the above formula becomes

$$\frac{-e^2}{\hbar V\omega}\int_{-1}^{1}\lambda d\tilde{E}\frac{1}{1+e^{\beta(\lambda\tilde{E}+b-\mu)}}\mathrm{Tr}\left[v^\alpha\frac{-i}{-\lambda\frac{\tilde{E}}{\hbar}-\omega+\lambda\frac{\tilde{H}}{\hbar}-i0^+}v^\beta\delta(\lambda\tilde{E}-\lambda\tilde{H})\right]. \tag{6.60}$$

Now remember that all the quantities that depend on the energy scales must be rescaled. That includes the velocity operator, temperature, chemical potential and external frequencies. The rescaled quantities are $v^\alpha=\lambda\tilde{v}^\alpha$, $\beta=\tilde{\beta}/\lambda$, $\mu=\lambda\tilde{\mu}+b$ and $\omega=\lambda\tilde{\omega}$. With these new quantities, we get the desired result

$$\frac{-e^2}{\hbar V\tilde{\omega}}\int_{-1}^{1} d\tilde{E}\frac{1}{1+e^{\tilde{\beta}(\tilde{E}-\tilde{\mu})}}\mathrm{Tr}\left[\tilde{v}^\alpha\frac{-i}{-\frac{\tilde{E}}{\hbar}-\tilde{\omega}+\frac{\tilde{H}}{\hbar}-i0^+}\tilde{v}^\beta\delta(\tilde{E}-\tilde{H})\right]. \tag{6.61}$$

The expression is formally identical to the original one except for the limits of integration. This pattern will repeat itself at higher orders. For every v operator, there's also a Green's function or a Dirac delta that accompanies it, which cancels the energy scales. The scale coming from the integral was canceled in this case due to the presence of a frequency in the denominator. According to the definition of higher-order conductivities, there will be more frequencies in the denominator, which cannot cancel anything, so there will be surplus scale factors. In second order, for example, this means (dropping the tildes)

$$\begin{aligned}
&\sigma^{\alpha\beta\gamma}(\omega_1,\omega_2)\\
&=-\frac{e^3}{\lambda V i\omega_1 i\omega_2}\int_{-\infty}^{\infty} d\epsilon f(\epsilon)\left\{\frac{i}{2\hbar}\mathrm{Tr}\left[v^\alpha\left(W_R^{\beta\gamma}(\epsilon;-\epsilon/\hbar-\omega)+W_a^{\beta\gamma}(\epsilon;-\epsilon/\hbar+\omega)\right)\right]+\right.\\
&+\frac{1}{\hbar^2}\mathrm{Tr}\left[v^\alpha\left(W_{RR}^{\beta,\gamma}(\epsilon;-\epsilon/\hbar-\omega_1-\omega_2,-\epsilon/\hbar-\omega_2)+\right.\right.\\
&\left.\left.+W_{Ra}^{\beta,\gamma}(\epsilon;-\epsilon/\hbar-\omega_1,-\epsilon/\hbar+\omega_2)+W_{aa}^{\beta,\gamma}(\epsilon;-\epsilon/\hbar+\omega_1,-\epsilon/\hbar+\omega_1+\omega_2)\right)\right]\\
&\left.+\frac{i}{\hbar}\mathrm{Tr}\left[v^{\alpha\beta}\left(W_R^{\gamma}(\epsilon;-\epsilon/\hbar-\omega_2)+W_a^{\gamma}(\epsilon;-\epsilon/\hbar+\omega_2)\right)\right]-\frac{1}{2}\mathrm{Tr}\left[v^{\alpha\beta\gamma}\delta(\epsilon-H)\right]\right\}
\end{aligned} \tag{6.62}$$

after rescaling. Note the extra λ factor. For a concrete example, consider a tight-binding Hamiltonian with hopping $\gamma_0=2.33eV$. The Hamiltonian will depend on this factor, which is bigger than one, so we cannot expect the eigenvalues to lie in the range $]-1,1[$. Let's work with a new

hopping $\tilde{\gamma}_0 = 0.1$. This means that the scale factor is $\lambda = 23.3$ eV.

6.5 Evaluation of traces

The previous sections have showed that the objects we need to calculate are traces of products of operators such as

$$\mathrm{Tr}\left[v^\alpha i g^R\left(-\frac{\epsilon}{\hbar}-\omega\right)v^\beta \delta(\epsilon - H)\right]. \tag{6.63}$$

At first glance, it may seem that we need to calculate this trace of operators for all different values of energies and frequencies. This is not the case, thanks to the expansion of those functions in terms of Chebyshev polynomials.

6.5.1 Isolation of the operators

In fact, plugging in the expansions for the Green's function (6.21) and the Dirac delta (6.15) we obtain

$$\sum_{n,m=0}^{\infty} \Delta_n(\epsilon) g_m^R(-\frac{\epsilon}{\hbar}-\omega)\mathrm{Tr}\left[v^\alpha \frac{T_m(h)}{1+\delta_{m0}} v^\beta \frac{T_n(h)}{1+\delta_{n0}}\right]. \tag{6.64}$$

Here we see the usefulness of separating the variables used in the expansions of the Dirac delta and the Green's function, as we only need to calculate the trace once. It is assumed that these factors Δ_n and g_m have already been multiplied by the w coefficients coming from the choice of kernel.

6.5.2 Use of the recursion relations

Now it is obvious that the fundamental objects we need to calculate are traces of Chebyshev polynomials with some other operator A, $\mathrm{Tr}\left[T_n(H)A\right]$. For now, let's consider traces with only one Chebyshev polynomial. It will be easy to generalize to a higher number of polynomials. Let's see how these special polynomials can help us calculate this trace. For arbitrary states $|\psi\rangle$ and $|\phi\rangle$, define

$$\mu_n^{\psi\phi} = \langle\psi| AT_n(H) |\phi\rangle. \tag{6.65}$$

Letting $\langle\psi_A| = \langle\psi| A$ and $|\phi_n\rangle = T_n(H)|\phi\rangle$, this coefficient is simply $\mu_n = \langle\psi_A|\phi_n\rangle$. This is useful because, by definition, these $|\phi_n\rangle$ satisfy the same recurrence relation as the Chebyshev polynomials themselves. We may therefore use $|\phi_{n+1}\rangle = 2H|\phi_n\rangle - |\phi_{n-1}\rangle$ to iteratively obtain all the $|\phi_n\rangle$. Then, all we need to do is take the dot product with $\langle\psi_A|$ to find $\mu_n^{\psi\phi}$. The great advantage here is that all we need to do to obtain the next μ_n is a simple matrix product. If these

polynomials didn't satisfy a recurrence relation, we'd have to calculate the whole polynomial to evaluate each μ_n, which would be hopelessly time-consuming. If we have two polynomials, such as in 6.64, we'll have to calculate

$$\mu_{nm}^{\psi\phi} = \langle\psi| AT_n(H)BT_m(H) |\phi\rangle . \tag{6.66}$$

In this case start by fixing a value of m, store $|\phi_m\rangle = T_m(H)|\phi\rangle$ and then multiply it by B, defining $\left|\phi_m^B\right\rangle$. We are left with

$$\mu_{nm}^{\psi\phi} = \langle\psi| AT_n(H) \left|\phi_m^B\right\rangle . \tag{6.67}$$

This is precisely the previous case with just one Chebyshev polynomial, and may be treated in precisely the same way. Then the process is repeated for $m+1$, where the stored vectors $|\phi_m\rangle$ and $|\phi_{m-1}\rangle$ may be used to obtain $|\phi_{m+1}\rangle$. If we have more than two polynomials, the procedure is entirely analogous.

6.5.3 Stochastic evaluation of traces

Now suppose that the vectors used are actually random vectors. Given a basis $\{|\phi_i\rangle\}$, let $|r\rangle = \sum_{i=0}^{D-1} \xi_{ri} |\phi_i\rangle$ be a random vector, where the ξ_{ri} are complex random variables assumed to be independent and identically distributed. D is the number of states. Furthermore, we'll require that

$$\begin{aligned} \langle \xi_{ir} \rangle &= 0 \\ \left\langle \xi_{ir} \xi_{jr'} \right\rangle &= 0 \\ \left\langle \xi_{ir}^* \xi_{jr'} \right\rangle &= \delta_{ij}\delta_{rr'}. \end{aligned}$$

Applying this to an arbitrary matrix B gives

$$\langle r| B |r\rangle = \sum_{ij} \xi_{ri}^* \xi_{rj} B_{ij}. \tag{6.68}$$

Thanks to the conditions imposed to the random variables, taking the average of this yields precisely the trace of B!

$$\langle \langle r| B |r\rangle \rangle = \sum_{ij} \langle \xi_{ri}^* \xi_{rj} \rangle B_{ij} = \sum_i B_{ii} \tag{6.69}$$

6.5.3.1 Variance

So far, all we know is that by doing this, we'll get the correct value on average, but how good of an estimate is it? Let's see what happens when we average over multiple realizations of the random

vector $|r\rangle$. Let $\Theta = \frac{1}{R}\sum_{r=0}^{R-1}\langle r|\,B\,|r\rangle$ be the estimate with R vectors. What is the variation around the average value? Evaluating $(\delta\Theta)^2 = \langle\Theta^2\rangle - \langle\Theta\rangle^2$ we get[4]

$$(\delta\Theta)^2 = \frac{1}{R}\left[\mathrm{Tr}\left(B^2\right) + \left(\left\langle|\xi_{ri}|^4\right\rangle - 2\right)\sum_{j=0}^{D-1} B_{jj}^2\right]. \tag{6.70}$$

This formula depends explicitly on $\left\langle|\xi_{ri}|^4\right\rangle$, which means that the choice of distribution for the ξ_{ri} will in general influence the fluctuations around the average. An interesting choice of distribution is one in which $\left\langle|\xi_{ri}|^4\right\rangle = 2$, which would cancel the second term and make the result completely basis-independent. But naturally, we'd want the smallest possible fluctuations, so it seems logical to choose a distribution that minimizes $\left\langle|\xi_{ri}|^4\right\rangle$. Due to the constraints imposed on the ξ_{ri}, its minimum possible value[6] is 1, so the smallest possible variance is

$$(\delta\Theta)^2_{\min} = \frac{1}{R}\left[\mathrm{Tr}\left(B^2\right) - \sum_{j=0}^{D-1} B_{jj}^2\right]. \tag{6.71}$$

If we perform the calculations in the eigen basis of B, the variance would be zero! But if we knew the eigen basis of B, we wouldn't need perturbation theory in the first place. In order to fulfill all the constraints imposed on the distribution, we choose the ξ_{ri} to lie in the unit complex circle, with the angle uniformly distributed. This has the additional advantage to guarantee $\left\langle|\xi_{ri}|^4\right\rangle = 1$, yielding the smallest possible variance[7].

6.5.3.2 Relative error

The next step is to see how the relative error changes with the size of the Hamiltonian matrix and the number of random vectors. Because the systems we're studying have translational symmetry, the trace of the matrices will be of order N, where N is the number of states. Therefore, the relative error is of order

$$\frac{\delta\Theta}{\Theta} = \frac{\sqrt{\frac{1}{R}\left[\mathrm{Tr}\left(B^2\right) - \sum_{j=0}^{D-1} B_{jj}^2\right]}}{\mathrm{Tr}\left(B\right)} \sim \frac{1}{\sqrt{RN}}. \tag{6.72}$$

For a two-dimensional system where $N \sim L^2$ the relative error decreases as $1/L$. This comes to show that for very large systems, we may use a small R and the method will still converge.

[6] To see why, let $x = |\xi_{ri}|$ and consider the variance of x^2, $\sigma^2(x^2) = \left\langle\left(x^2 - \langle x^2\rangle\right)^2\right\rangle = \langle x^4\rangle - \langle x^2\rangle^2$. The requirement $\langle x^2\rangle = 1$ coupled with the fact that the variance is necessarily positive means that $\langle x^4\rangle - 1 > 0$.

[7] The conditions are indeed satisfied. In fact, for all integer n, $\langle\xi_{ri}^n\rangle = \frac{1}{2\pi}\int_0^{2\pi} e^{in\theta}d\theta = 0$ and $\langle|\xi_{ri}|^n\rangle = \frac{1}{2\pi}\int_0^{2\pi}\left|e^{i\theta}\right|^n d\theta = 1$. The remaining conditions are satisfied because the ξ_{ri} are independent and identically distributed.

6.6 Calculation of the conductivity

This section has a simple goal: starting from the expressions for the conductivity obtained in the previous chapter, we'll rewrite them in terms of the new language developed in this chapter. There's just one last small ingredient missing: the $v^{\alpha_1 \cdots \alpha_n}$ defined in the previous chapter are slightly different from the ones we use in KPM. Some of the Hamiltonians used make no mention to imaginary numbers (for example, when there's no magnetic field) so it makes sense to use only real numbers to cut on unnecessary computational time that would be spent calculating complex functions instead of real ones. That's the reason that leads to the definition of $v_{KPM}^{\alpha_1 \cdots \alpha_n} = \hbar^{-n} [r^{\alpha_1}, \cdots [r^{\alpha_n}, H]]$. Comparing to the v operators, we find $v_{KPM}^{\alpha_1 \cdots \alpha_n} = i^n v^{\alpha_1 \cdots \alpha_n}$. It's very important to note that, unlike $v^{\alpha_1 \cdots \alpha_n}$, $v_{KPM}^{\alpha_1 \cdots \alpha_n}$ is not hermitian. That becomes relevant when we want to evaluate something such as $\langle \psi | v_{KPM}$. Lastly, many authors express the lengths in units of the distance between unit cells, instead of the distance between neighbouring atoms. To facilitate conversions between the two cases, we express everything in terms of the distance between atoms, introducing a scale factor η in every quantity that depends on the scale. We'll get one for each index in the v operators as this is the number of r operators inside the nested commutators. The other contribution to this factor comes from the volume V in the denominator, which for our case of two-dimensional systems is actually an area and contributes with η^2. We'll end up with conductivities expressed solely in terms of dimensionless quantities and scales.

6.6.1 First order

Let $V = V_c N$, where V_c is the volume of a unit cell and N is the number of unit cells. Using eq. 5.58

$$\sigma^{\alpha\beta}(\omega) = \frac{-4\sigma_0}{V_c} \int_{-1}^{1} d\epsilon \frac{f(\epsilon)}{\omega} \frac{\mathrm{Tr}}{N} \left[v^{\alpha} \left(W_R^{\beta}(\epsilon; -\epsilon/\hbar - \omega) + W_a^{\beta}(\epsilon; -\epsilon/\hbar + \omega) \right) + i\hbar \frac{\mathrm{Tr}}{N} \left[v^{\alpha\beta} \delta(\epsilon - H) \right] \right] \tag{6.73}$$

start by unwinding the definition of the W functions

$$\begin{aligned} \sigma^{\alpha\beta}(\omega) \quad = \quad & \frac{-4\sigma_0}{V_c} \int_{-1}^{1} d\epsilon \frac{f(\epsilon)}{\omega} \frac{\mathrm{Tr}}{N} \Big[v^{\alpha} i g^R(-\epsilon/\hbar - \omega) v^{\beta} \delta(\epsilon - H) + \\ & + v^{\alpha} \delta(\epsilon - H) v^{\beta} i g^a(-\epsilon/\hbar + \omega) + i\hbar v^{\alpha\beta} \delta(\epsilon - H) \Big] . \end{aligned} \tag{6.74}$$

Then, replacing v by v_{KPM}, extracting the length scale and plugging in the expansion of the Dirac deltas and the Green's functions, we get

$$\begin{aligned}\sigma^{\alpha\beta}(\omega) &= \frac{4\sigma_0 i}{V_c}\int_{-1}^{1} d\epsilon \frac{f(\epsilon)}{\omega}\left\{\sum_{mn} g_n^R(-\epsilon/\hbar-\omega)\Delta_m(\epsilon)\frac{\mathrm{Tr}}{N}\left[v^\alpha_{KPM}\frac{T_n(H)}{1+\delta_{n0}}v^\beta_{KPM}\frac{T_m(H)}{1+\delta_{m0}}\right]\right. \\ &+\sum_{mn} g_m^a(-\epsilon/\hbar+\omega)\Delta_n(\epsilon)\frac{\mathrm{Tr}}{N}\left[v^\alpha_{KPM}\frac{T_n(H)}{1+\delta_{n0}}v^\beta_{KPM}\frac{T_m(H)}{1+\delta_{m0}}\right]+ \\ &\left.+\sum_n \Delta_n(\epsilon)\hbar\frac{\mathrm{Tr}}{N}\left[v^{\alpha\beta}_{KPM}\frac{T_n(H)}{1+\delta_{n0}}\right]\right\}. \end{aligned} \tag{6.75}$$

Although the scales are not present, all these quantities are now completely dimensionless except for the physical constants. These traces suggest a new notation. Define the Gamma matrices in a similar fashion to the W operators, with commas separating the various indices:

$$\Gamma^{\alpha_1^1\cdots\alpha_{n_1}^1,\cdots,\alpha_1^m\cdots\alpha_{n_m}^m}_{n_1\cdots n_m} = \frac{\mathrm{Tr}}{N}\left[v^{\alpha_1^1\cdots\alpha_{n_1}^1}_{KPM}\frac{T_{n_1}(H)}{1+\delta_{n_1 0}}\cdots v^{\alpha_1^m\cdots\alpha_{n_m}^m}_{KPM}\frac{T_{n_m}(H)}{1+\delta_{n_m 0}}\right]. \tag{6.76}$$

Omitting the sum, this yields the final result for the conductivity in first order

$$\boxed{\sigma^{\alpha\beta}(\omega) = \frac{4\sigma_0 i}{V_c\omega}\int_{-1}^{1} d\epsilon f(\epsilon)\Delta_n(\epsilon)\left\{g_m^R(-\epsilon/\hbar-\omega)\Gamma^{\alpha\beta}_{mn} + g_m^a(-\epsilon/\hbar+\omega)\Gamma^{\alpha\beta}_{nm} + \hbar\Gamma^{\alpha\beta}_n\right\}.} \tag{6.77}$$

Interestingly, this conductivity is independent of the scales chosen. This is because it is expressed in terms of σ_0, which already has units of conductivity.

6.6.2 Second order

Starting from eq. 5.64 still with length dimensions,

$$\begin{aligned}\sigma^{\alpha\beta\gamma}(\omega_1,\omega_2) &= -\frac{e^3}{\lambda V_c i\omega_1 i\omega_2}\int_{-1}^{1} d\epsilon f(\epsilon)\left\{\frac{i}{2\hbar}\frac{\mathrm{Tr}}{N}\left[v^\alpha\left(W_R^{\beta\gamma}(\epsilon;-\epsilon/\hbar-\omega)+W_a^{\beta\gamma}(\epsilon;-\epsilon/\hbar+\omega)\right)\right]+\right. \\ &+\frac{1}{\hbar^2}\frac{\mathrm{Tr}}{N}\left[v^\alpha\left(W_{RR}^{\beta,\gamma}(\epsilon;-\epsilon/\hbar-\omega_1-\omega_2,-\epsilon/\hbar-\omega_2)+\right.\right. \\ &\left.\left.+W_{Ra}^{\beta,\gamma}(\epsilon;-\epsilon/\hbar-\omega_1,-\epsilon/\hbar+\omega_2)+W_{aa}^{\beta,\gamma}(\epsilon;-\epsilon/\hbar+\omega_1,-\epsilon/\hbar+\omega_1+\omega_2)\right)\right] \\ &\left.+\frac{i}{\hbar}\frac{\mathrm{Tr}}{N}\left[v^{\alpha\beta}\left(W_R^\gamma(\epsilon;-\epsilon/\hbar-\omega_2)+W_a^\gamma(\epsilon;-\epsilon/\hbar+\omega_2)\right)\right]-\frac{1}{2}\frac{\mathrm{Tr}}{N}\left[v^{\alpha\beta\gamma}\delta(\epsilon-H)\right]\right\}\end{aligned} \tag{6.78}$$

the process is entirely analogous, and the result is

$$\begin{aligned}\sigma^{\alpha\beta\gamma}(\omega_1,\omega_2) &= \frac{-ie^3\eta}{\lambda V_c\omega_1\omega_2}\int_{-1}^{1} d\epsilon f(\epsilon)\Delta_n(\epsilon)\left\{\frac{1}{\hbar}g_m^R(-\epsilon/\hbar-\omega_2)\,\Gamma_{mn}^{\alpha\beta,\gamma}\right.\\ &+\frac{1}{\hbar}g_m^a(-\epsilon/\hbar+\omega_2)\,\Gamma_{nm}^{\alpha\beta,\gamma}+\frac{1}{2}\Gamma_n^{\alpha\beta\gamma}\\ &+\frac{1}{2\hbar}g_m^R(-\epsilon/\hbar-\omega_1-\omega_2)\,\Gamma_{mn}^{\alpha,\beta\gamma}\\ &+\frac{1}{2\hbar}g_m^a(-\epsilon/\hbar+\omega_1+\omega_2)\,\Gamma_{nm}^{\alpha,\beta\gamma}\\ &+\frac{1}{\hbar^2}g_m^R(-\epsilon/\hbar-\omega_1-\omega_2)\,g_p^R(-\epsilon/\hbar-\omega_2)\,\Gamma_{mpn}^{\alpha,\beta,\gamma}+\\ &+\frac{1}{\hbar^2}g_m^R(-\epsilon/\hbar-\omega_1)\,g_p^a(-\epsilon/\hbar+\omega_2)\,\Gamma_{mnp}^{\alpha,\beta,\gamma}+\\ &\left.+\frac{1}{\hbar^2}g_m^a(-\epsilon/\hbar+\omega_1+\omega_2)\,g_p^a(-\epsilon/\hbar+\omega_1)\,\Gamma_{npm}^{\alpha,\beta,\gamma}\right\}. \end{aligned} \tag{6.79}$$

Unlike the first-order conductivity, the second-order one depends on both the energy and the length scales. To overcome this, we may define something similar to the universal conductivity of graphene, $\sigma_2 = e^3a/4\hbar t$. Extracting the scales from a and t inside σ_2, the previous equation becomes

$$\begin{aligned}\frac{\sigma^{\alpha\beta\gamma}(\omega_1,\omega_2)}{\sigma_2} &= \frac{-4it}{V_c\omega_1\omega_2\hbar a}\int_{-1}^{1} d\epsilon f(\epsilon)\Delta_n(\epsilon)\left\{\frac{1}{2}\Gamma_n^{\alpha\beta\gamma}+\right.\\ &+g_m^a(-\epsilon/\hbar+\omega_2)\,\Gamma_{nm}^{\alpha\beta,\gamma}+g_m^R(-\epsilon/\hbar-\omega_2)\,\Gamma_{mn}^{\alpha\beta,\gamma}+\\ &+\frac{1}{2}g_m^a(-\epsilon/\hbar+\omega_1+\omega_2)\,\Gamma_{nm}^{\alpha,\beta\gamma}+\frac{1}{2}g_m^R(-\epsilon/\hbar-\omega_1-\omega_2)\,\Gamma_{mn}^{\alpha,\beta\gamma}+\\ &+\frac{1}{\hbar}g_m^R(-\epsilon/\hbar-\omega_1-\omega_2)\,g_p^R(-\epsilon/\hbar-\omega_2)\,\Gamma_{mpn}^{\alpha,\beta,\gamma}+\\ &+\frac{1}{\hbar}g_m^R(-\epsilon/\hbar-\omega_1)\,g_p^a(-\epsilon/\hbar+\omega_2)\,\Gamma_{mnp}^{\alpha,\beta,\gamma}+\\ &\left.+\frac{1}{\hbar}g_m^a(-\epsilon/\hbar+\omega_1+\omega_2)\,g_p^a(-\epsilon/\hbar+\omega_1)\,\Gamma_{npm}^{\alpha,\beta,\gamma}\right\}. \end{aligned}$$

Now it is duly dimensionless.

6.6.3 Third order

This one is done in the same fashion as the other two, and it is left as an exercise for the (really) interested reader.

6.7 Density of states

Although we're using it to calculate conductivities, KPM is also very useful in calculating the density of states (DOS). Indeed, the density of states does not need to be expanded in series.

$$\rho(\epsilon) = \frac{1}{\lambda\eta^2 V}\sum_n \delta(\epsilon - \epsilon_n) = \frac{1}{\lambda\eta^2 V}\mathrm{Tr}\left[\delta(\epsilon - H)\right] = \frac{1}{\lambda\eta^2 V_c}\sum_n \Delta_n(\epsilon)\frac{\mathrm{Tr}}{N}\left[\frac{T_n(H)}{1+\delta_{n0}}\right] \tag{6.80}$$

Remember that the density of states also depends on both the energy and the length scales, due to its normalization.

6.8 Remark

The Γ matrices introduced in the previous section require a lot of storage space. Assuming that we're using double-precision numbers, each one of them will take up 8 bytes. But we need complex numbers, so that's 16 bytes per number. If we want a decent resolution, we'll using something like 1024 Chebyshev polynomials. Therefore, for a single n-th order Γ matrix with 1024 polynomials, the required storage is $1024^n \times 16$. Plugging in $n = 1$ for the density of states, that's 16 KB, so calculating it is very easy. $n = 2$ for Γ_{nm} is 16 MB, so calculating the first order current is still easy. Plugging in $n = 3$ for a matrix such as Γ_{nmp} already requires 16 GB, so the second-order conductivity is starting to show some large numbers. If we want to obtain a third-order response, we're out of luck, because we'll need 16 TB of storage for one single matrix, not to mention the time that it'll take. This is why we stick to obtaining the first and second-order conductivities. The third-order one isn't feasible.

7 Applications

The conductivities obtained so far apply to a very general array of systems. They are valid both with and without periodic boundary conditions because those may be introduced through the Hamiltonian. As a matter of fact, we make no mention of translation invariance anywhere because we're using the full Hamiltonian in our formulas, so it is also valid for systems where we may introduce disorder by changing some of the Hamiltonian's matrix elements. Through Peierls' substitution, we may also introduce magnetic field by changing the hoppings. The only thing we're assuming is that the electrons do not interact with one another. If we were to consider that case, we'd have to take into account the S^V in the Keldysh formalism, which would introduce more Feynman diagrams through an additional perturbation expansion on the coupling between the interaction and the solvable Hamiltonian. With this being said, the time has come to apply this to concrete systems: Graphene and Hexagonal Boron-Nitride (h-BN).

7.1 Graphene

Graphene is a two-dimensional crystal composed solely of carbon, with the atoms arranged in a honeycomb lattice [15] (see Fig. 7.1). It may be seen as the superposition of two sub-lattices A and B. The unit cell is composed of two neighbouring atoms, one from each sub-lattice.

Let a be the distance between consecutive atoms. Then, the primitive vectors between unit cells are

$$\begin{aligned} \boldsymbol{a}_1 &= a\left(0, \sqrt{3}\right) \\ \boldsymbol{a}_2 &= \frac{a}{2}\left(3, \sqrt{3}\right) \end{aligned}$$

and the distance vectors between neighbours are

$$\begin{aligned} \boldsymbol{\delta}_1 &= \frac{a}{2}\left(-1, \sqrt{3}\right) \\ \boldsymbol{\delta}_2 &= \frac{a}{2}\left(-1, -\sqrt{3}\right) \\ \boldsymbol{\delta}_3 &= a\left(1, 0\right). \end{aligned} \tag{7.1}$$

We need to calculate the area A_c occupied by a single unit cell to plug into the conductivity. Since we know the primitive vectors, the area of the unit cell is simply the area of the parallelogram formed by the vectors, that is: $A_c = |\boldsymbol{a}_1 \times \boldsymbol{a}_2| = \frac{3\sqrt{3}}{2}a^2$.

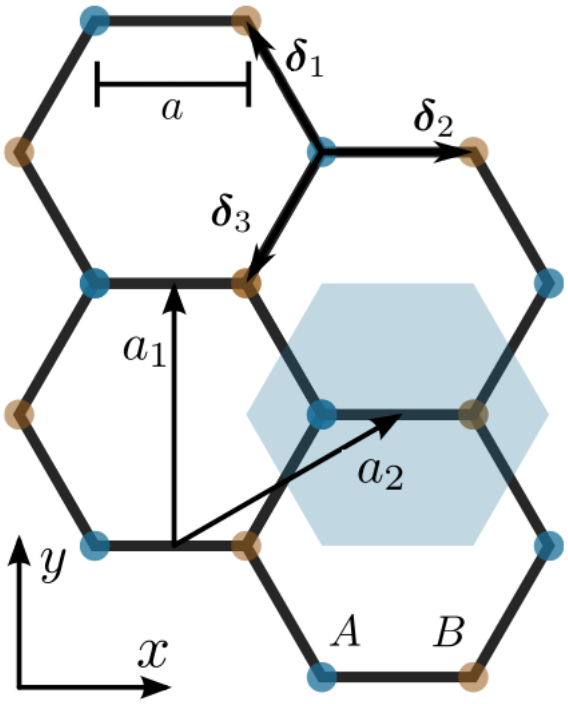


Figure 7.1: Graphene honeycomb lattice. The carbon atoms are labeled by the sub-lattice to which they belong. $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ represent the primitive vectors of the crystal and the deltas represent the distance vectors between nearest neighbours.

7.1.1 Graphene Hamiltonian

Consider a general tight-binding Hamiltonian in a system with translation invariance. The hopping parameter only depends on the difference of positions and on the orbitals μ and ν.

$$H = \sum_{\boldsymbol{R}_n, \boldsymbol{R}_m} \sum_{\mu\nu} t_{\mu\nu} \left(\boldsymbol{R}_m - \boldsymbol{R}_n \right) c_\mu^\dagger \left(\boldsymbol{R}_m \right) c_\nu \left(\boldsymbol{R}_n \right) \tag{7.2}$$

The simplest description of graphene consists of two orbitals[1] and a nearest-neighbour hopping. Looking at Fig. 7.1, that means that an electron that's in atom A (B) may only hop to any of the neighbouring B (A) atoms. Furthermore, we assume that all the (non-zero) hoppings are the same and are real. Therefore, the inter-orbital hoppings are

$$t_{AB} \left(\boldsymbol{\delta}_1 \right) = t_{AB} \left(\boldsymbol{\delta}_2 \right) = t_{AB} \left(\boldsymbol{\delta}_3 \right) = -t. \tag{7.3}$$

The remaining hoppings are found by using the fact that H is hermitian: $t_{AB} = t_{BA}$. The

[1] Usually, when we speak of orbitals, we're thinking of the various atomic orbitals that may be occupied by an electron. Take an electron in the Hydrogen atom, for example. It may be in any of the $1s$, $2s$, $2p_x$, etc. orbitals. It may hop between orbitals or to other orbitals in a different atom. In this description of graphene, each carbon atom has only one orbital. But since there are two carbon atoms per unit cell, we might as well consider them as two orbitals of one single atom.

on-site energies $t_{AA}(\mathbf{0})$ and $t_{BB}(\mathbf{0})$ are taken to be the same but we might as well say they're zero because they only introduce a shift in the eigen energies.

We have not said anything about the electron's spin, but it's still there nevertheless. Since we're tracing over all the states in the system and half of them are the same because of spin degeneracy, we have to add a factor of 2 to the conductivity. Thus, the formula for the first-order conductivity (eq. 6.77) in graphene becomes[2]:

$$\sigma^{\alpha\beta}(\omega) = \frac{16\sigma_0 i}{3\sqrt{3}\omega}\int_{-1}^{1} d\epsilon f(\epsilon)\Delta_n(\epsilon)\left\{g_m^R(-\epsilon/\hbar-\omega)\Gamma_{mn}^{\alpha\beta} + g_m^a(-\epsilon/\hbar+\omega)\Gamma_{nm}^{\alpha\beta} + \hbar\Gamma_n^{\alpha\beta}\right\}. \tag{7.4}$$

And the density of states is

$$\rho(\epsilon) = \frac{4}{3\sqrt{3}\lambda\eta^2}\int_{-1}^{1} d\epsilon\Delta_n(\epsilon)\frac{\mathrm{Tr}}{N}\left[\frac{T_n(H)}{1+\delta_{n0}}\right] \tag{7.5}$$

These are the precise expressions used in our program.

7.1.2 Dispersion relation

From the information in the previous section, we may calculate the dispersion relation of graphene. Start by writing the Hamiltonian's matrix elements in the momentum basis (eq. 5.35).

$$H = \frac{1}{V}\sum_{\sigma_1,\sigma_2}\sum_{\boldsymbol{k}}\epsilon_{\sigma_1\sigma_2}(\boldsymbol{k})c_{\sigma_1}^{\dagger}(\boldsymbol{k})\,c_{\sigma_2}(\boldsymbol{k}) \tag{7.6}$$

The ϵ matrix may be calculated from its definition:

$$\epsilon_{\sigma_1\sigma_2}(\boldsymbol{k}) = \sum_{\boldsymbol{R}} t_{\sigma_1\sigma_2}(\boldsymbol{R})\,e^{i\boldsymbol{k}\cdot\boldsymbol{R}}. \tag{7.7}$$

These position vectors refer to the distance between interacting atoms, so they correspond to the distance vectors (eq. 7.1)

$$\epsilon_{AB}(\boldsymbol{k}) = \sum_{\boldsymbol{R}} t_{\sigma_1\sigma_2}(\boldsymbol{R})\,e^{i\boldsymbol{k}\cdot\boldsymbol{R}} = -t\left(e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_1} + e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_2} + e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_3}\right) \tag{7.8}$$

Note that $\epsilon_{AB}(-\boldsymbol{k}) = \epsilon_{AB}^*(\boldsymbol{k})$. The Hamiltonian in $\boldsymbol{k}$ space therefore is

$$H(\boldsymbol{k}) = \begin{bmatrix} 0 & \epsilon_{AB}(\boldsymbol{k}) \\ \epsilon_{AB}^*(\boldsymbol{k}) & 0 \end{bmatrix}. \tag{7.9}$$

[2] Although this is dependent on the numerical implementation and not on the formula itself, it is very important to make sure we know what is the N used in the denominator of the Γ matrices. Care should be taken because we defined it as the number of unit cells, but sometimes it is used as the number of states. As there are two orbitals per unit cell, this distinction introduces a factor of 2 in the case of graphene.

Diagonalizing in this subspace we arrive at graphene's dispersion relation

$$\epsilon_{\pm}(\boldsymbol{k}) = \pm|\epsilon_{AB}(\boldsymbol{k})| = \pm t\sqrt{3 + 2\cos\left(k_y a\sqrt{3}\right) + 4\cos\left(\frac{k_x 3a}{2}\right)\cos\left(\frac{k_y\sqrt{3}a}{2}\right)}. \tag{7.10}$$

This consists of two bands, one at negative energies and one at positive energies, but the crucial piece of information here is that this function has zeroes (for example at $\boldsymbol{k} = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}\right)$), so these two bands meet and there is no gap.

7.1.3 Density of states and first-order conductivity

Using the Hamiltonian 7.2, we are able to compute the density of states $\rho(\epsilon)$ (Fig. 7.1.3) and the first-order longitudinal conductivity σ^{xx} (Fig. 7.1.3) of graphene.

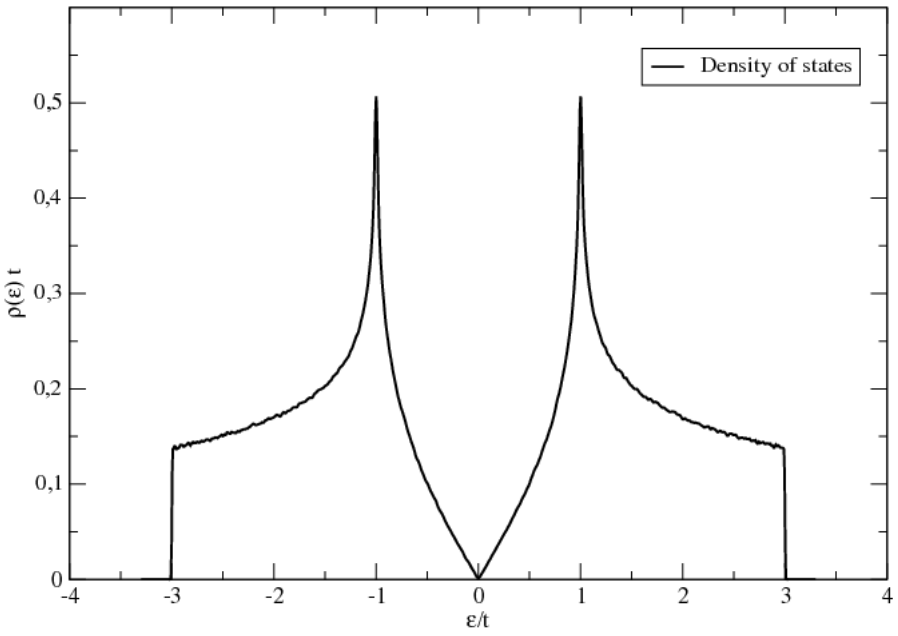


Figure 7.2: KPM simulation of the density of states $\rho(\epsilon)$ of graphene for a hopping parameter $t = 2.33$ eV. The axes are in units of t. System size: 2048×2048 unit cells, number of Chebyshev polynomials used: 1024. We used the Jackson kernel for the Dirac deltas.

7.1.4 Second-order conductivity

There's nothing to see here, as the second-order conductivity in graphene is zero. To see why, we'll have to analyze the Γ matrices that give rise to the second-order conductivity. Consider for

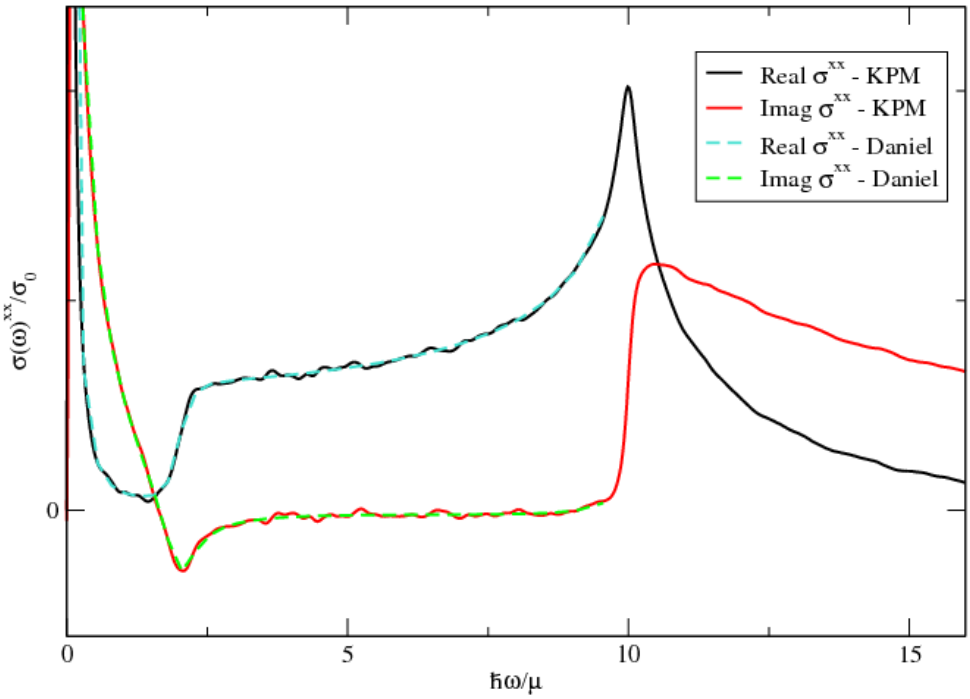


Figure 7.3: KPM simulation of the first-order conductivity in graphene. The curves are plotted against a reference (dashed lines). The graph is in units of the graphene universal conductivity σ_0 and the chemical potential. System size: 2048×2048 unit cells, number of Chebyshev polynomials used: 1024, chemical potential $\mu = 0.466$ eV, $t = 2.33$ eV, temperature $T = 200$K, infinitesimal scattering parameter Γ: 0.0388 eV. We use the Jackson kernel for the Dirac deltas but no kernel for the Green's functions. Instead, we introduce a broadening by replacing $\omega \to \omega + i\Gamma$.

example $\Gamma^{\alpha,\beta,\gamma}_{nmp}$:

$$\Gamma^{\alpha,\beta,\gamma}_{nmp} = \frac{\mathrm{Tr}}{N}\left[v^{\alpha}\frac{T_n(H)}{1+\delta_{n0}}v^{\beta}\frac{T_m(H)}{1+\delta_{m0}}v^{\gamma}\frac{T_p(H)}{1+\delta_{p0}}\right] \tag{7.11}$$

This matrix is composed of sums of matrices of the form

$$X^{\alpha,\beta,\gamma}_{nmp} = \mathrm{Tr}\left[v^{\alpha}H^{n}v^{\beta}H^{m}v^{\gamma}H^{p}\right] \tag{7.12}$$

In momentum space, this trace may be evaluated

$$X_{nmp}^{\alpha,\beta,\gamma} = \sum_{\boldsymbol{k}} \tilde{\mathrm{Tr}} \left[v^{\alpha}(\boldsymbol{k}) H^{n}(\boldsymbol{k}) v^{\beta}(\boldsymbol{k}) H^{m}(\boldsymbol{k}) v^{\gamma}(\boldsymbol{k}) H^{p}(\boldsymbol{k}) \right] \tag{7.13}$$

where we denoted the trace over the remaining degrees of freedom in the $\boldsymbol{k}$ subspace by a tilde. It is important to know what is the explicit form of these matrices. Noting[3] that $H^2(\boldsymbol{k}) = |\varepsilon(\boldsymbol{k})|^2$, the n-th power of the Hamiltonian may be written as

$$H^{n}(\boldsymbol{k}) = \begin{cases} |\epsilon_{AB}(\boldsymbol{k})|^{n} & n \text{ even} \\ |\epsilon_{AB}(\boldsymbol{k})|^{n-1} H(\boldsymbol{k}) & n \text{ odd} \end{cases} \tag{7.14}$$

And the product $v^{\alpha_1 \cdots \alpha_k}(\boldsymbol{k}) H^{n}(\boldsymbol{k})$ becomes

$$\begin{aligned} & v^{\alpha_1 \cdots \alpha_a}(\boldsymbol{k}) H^{n}(\boldsymbol{k}) \\ &= \begin{cases} \left(-\frac{1}{\hbar}\right)^{a} |\epsilon_{AB}(\boldsymbol{k})|^{n} \begin{bmatrix} 0 & \boldsymbol{\nabla}_{\boldsymbol{k}}^{\alpha_1 \cdots \alpha_a} \epsilon_{AB}(\boldsymbol{k}) \\ \boldsymbol{\nabla}_{\boldsymbol{k}}^{\alpha_1 \cdots \alpha_a} \epsilon_{AB}^{*}(\boldsymbol{k}) & 0 \end{bmatrix} = E_{a}^{n}(\boldsymbol{k}) & \text{n even} \\ \left(-\frac{1}{\hbar}\right)^{a} |\epsilon_{AB}(\boldsymbol{k})|^{n-1} \begin{bmatrix} \epsilon_{AB}^{*}(\boldsymbol{k}) \boldsymbol{\nabla}_{\boldsymbol{k}}^{\alpha_1 \cdots \alpha_a} \epsilon_{AB}(\boldsymbol{k}) & 0 \\ 0 & \epsilon_{AB}(\boldsymbol{k}) \boldsymbol{\nabla}_{\boldsymbol{k}}^{\alpha_1 \cdots \alpha_a} \epsilon_{AB}^{*}(\boldsymbol{k}) \end{bmatrix} = O_{a}^{n}(\boldsymbol{k}) & \text{n odd} \end{cases} \end{aligned}$$

In the new E and O matrices, the specific indices of the $v^{\alpha_1 \cdots \alpha_a}(\boldsymbol{k})$ matrices have been omitted because they are not relevant for this discussion. These are the building blocks of the Γ matrices, so now we may see what happens when we trace over products of these objects. Each time we multiply two of these objects together, we'll get matrix entries with a number of derivatives equal to the sum of the number of derivatives of the matrices that gave origin to it.

Odd number of E

Any product with an odd number of E produces a traceless matrix, independently of $\boldsymbol{k}$. This shows that for any X matrix, if the sum of the degrees of the polynomials is odd, that entry will be zero.

Even number of E

Any product which has an even number of E matrices becomes diagonal. It is easy to see that the diagonals are complex conjugates of each other[4] so the trace will be real and the transformation

[3] For simplicity of notation, this is to be understood as multiplied by the identity matrix $\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$.

[4] Any product of matrices of the type $A = \begin{bmatrix} 0 & a \\ a^{*} & 0 \end{bmatrix}$ or $B = \begin{bmatrix} b & 0 \\ 0 & b^{*} \end{bmatrix}$ results in one or the other. The product of any two matrices of the same type produces a matrix of type B, while the product of any two matrices of

$\boldsymbol{k} \to -\boldsymbol{k}$ will simply introduce a minus sign for every derivative. The number of derivatives is equal to the degree of the Γ matrix. Therefore, for Γ matrices of odd degree, there will be an odd number of derivatives, which means the whole trace is anti-symmetrical in the exchange $\boldsymbol{k} \to -\boldsymbol{k}$. When summed over all the $\boldsymbol{k}$, this yields zero.

This exhausts all the possibilities and proves that any Γ of odd degree is zero in the tight-binding graphene. This was only possible because the Hamiltonian had a very simple form and we were able to easily find its n-th power. For more complicated Hamiltonians, this analysis is in general not possible.

7.2 Hexagonal Boron Nitride (h-BN)

Just like graphene, h-BN consists of an hexagonal array of atoms, but this time there are Boron atoms in sublattice A and Nitrogen atoms in sublattice B. The hoppings between nearest neighbours are identical, but each site now has a different self-energy. Everything else is identical to graphene. Same lattice vectors, same distance vectors and same unit cell area. Therefore, the conductivity and density of states will have the exact same expressions, keeping in mind that the Hamiltonian is different.

$$\sigma^{\alpha\beta}_{h-BN}(\omega) = \frac{16\sigma_0 i}{3\sqrt{3}\omega}\int_{-1}^{1} d\epsilon f(\epsilon)\Delta_n(\epsilon)\left\{g^R_m(-\epsilon/\hbar-\omega)\Gamma^{\alpha\beta}_{mn} + g^a_m(-\epsilon/\hbar+\omega)\Gamma^{\alpha\beta}_{nm} + \hbar\Gamma^{\alpha\beta}_{n}\right\} \tag{7.15}$$

$$\rho_{h-BN}(\epsilon) = \frac{4}{3\sqrt{3}\lambda}\int_{-1}^{1} d\epsilon \Delta_n(\epsilon)\frac{\mathrm{Tr}}{N}\left[\frac{T_n\left(H_{h-BN}\right)}{1+\delta_{n0}}\right] \tag{7.16}$$

The on-site energies $t_{AA}(\mathbf{0})$ and $t_{BB}(\mathbf{0})$ are no longer zero. For this model, we'll use $t_{AA}(\mathbf{0}) = \Delta/2$ and $t_{BB}(\mathbf{0}) = -\Delta/2$. Due to the new terms in the Hamiltonian, we have no reason to expect that the second-order conductivity remain zero. Replacing the area and taking into account the spin degeneracy, eq. 6.79 becomes

$$\begin{aligned}
\frac{\sigma^{\alpha\beta\gamma}_{h-BN}(\omega_1,\omega_2)}{\sigma_2} = \frac{-16it}{3\sqrt{3}\omega_1\omega_2 a}\int_{-1}^{1} d\epsilon f(\epsilon)\Delta_n(\epsilon)\Bigg\{&\frac{\hbar}{2}\Gamma^{\alpha\beta\gamma}_n + \\
&+ g^a_m(-\epsilon/\hbar+\omega_2)\Gamma^{\alpha\beta,\gamma}_{nm} + g^R_m(-\epsilon/\hbar-\omega_2)\Gamma^{\alpha\beta,\gamma}_{mn} + \\
&+ \frac{1}{2}g^R_m(-\epsilon/\hbar-\omega_1-\omega_2)\Gamma^{\alpha,\beta\gamma}_{mn} + \frac{1}{2}g^a_m(-\epsilon/\hbar+\omega_1+\omega_2)\Gamma^{\alpha,\beta\gamma}_{nm} + \\
&+ \frac{1}{\hbar}g^R_m(-\epsilon/\hbar-\omega_1-\omega_2)g^R_p(-\epsilon/\hbar-\omega_2)\Gamma^{\alpha,\beta,\gamma}_{mpn} + \\
&+ \frac{1}{\hbar}g^R_m(-\epsilon/\hbar-\omega_1)g^a_p(-\epsilon/\hbar+\omega_2)\Gamma^{\alpha,\beta,\gamma}_{mnp} + \\
&+ \frac{1}{\hbar}g^a_m(-\epsilon/\hbar+\omega_1+\omega_2)g^a_p(-\epsilon/\hbar+\omega_1)\Gamma^{\alpha,\beta,\gamma}_{npm}\Bigg\}
\end{aligned} \tag{7.17}$$

different types produces a matrix of type A.

Symmetry considerations [16] demand that there be only two independent components of $\sigma^{\alpha\beta\gamma}$ and that one of them be zero, so we only need to care about σ^{xxx}. As we'll see, this will simplify eq. 7.17 considerably.

7.2.1 Dispersion relation and evaluation of traces

The Hamiltonian in $\boldsymbol{k}$ space may be described by

$$H(\boldsymbol{k}) = \begin{bmatrix} \Delta/2 & \epsilon_{AB}(\boldsymbol{k}) \\ \epsilon^*_{AB}(\boldsymbol{k}) & -\Delta/2 \end{bmatrix} \tag{7.18}$$

Diagonalizing, we get the dispersion relation

$$\epsilon_{\pm}(\boldsymbol{k}) = \pm\sqrt{|\epsilon_{AB}(\boldsymbol{k})|^2 + \frac{\Delta^2}{4}} \tag{7.19}$$

Note how the bands no longer meet, so there is a gap of size Δ. Now we'll do an analysis of the Γ matrices similar to the one we used in graphene to see why the matrices with an odd number of indices were zero. This time, we do not expect the second-order conductivity to be zero, but there will be some simplifications to be had. Although this Hamiltonian is more complicated, it too becomes diagonal after multiplying by itself. As for the case of graphene, we may use this to find the explicit form for the n-th power of the Hamiltonian

$$H^n(\boldsymbol{k}) = \begin{cases} \epsilon^n(\boldsymbol{k}) & n \text{ even} \\ \epsilon^{n-1}(\boldsymbol{k}) H(\boldsymbol{k}) & n \text{ odd} \end{cases} \tag{7.20}$$

This simple formula allows us to calculate the product of $v^{\alpha_1\cdots\alpha_a}\ H^n$, the building blocks of the Γ matrices

$$\begin{aligned} & v^{\alpha_1\cdots\alpha_a}(\boldsymbol{k})\, H^n(\boldsymbol{k}) \\ &= \begin{cases} |\epsilon_{AB}(\boldsymbol{k})|^n \begin{bmatrix} 0 & v^{\alpha_1\cdots\alpha_a}_{AB}(\boldsymbol{k}) \\ v^{\alpha_1\cdots\alpha_a *}_{AB}(\boldsymbol{k}) & 0 \end{bmatrix} = E^n_a(\boldsymbol{k}) & \text{n even} \\ |\epsilon_{AB}(\boldsymbol{k})|^{n-1} \begin{bmatrix} v^{\alpha_1\cdots\alpha_a}_{AB}(\boldsymbol{k})\epsilon^*_{AB}(\boldsymbol{k}) & -v^{\alpha_1\cdots\alpha_a}_{AB}(\boldsymbol{k})\Delta/2 \\ v^{\alpha_1\cdots\alpha_a *}_{AB}(\boldsymbol{k})\Delta/2 & v^{\alpha_1\cdots\alpha_a *}_{AB}(\boldsymbol{k})\epsilon_{AB}(\boldsymbol{k}) \end{bmatrix} = O^n_a(\boldsymbol{k}) & \text{n odd} \end{cases} \end{aligned}$$

In order to analyze these expressions, we shall adopt a simpler notation

$$v^{\alpha_1\cdots\alpha_a}(\boldsymbol{k})\,H^n(\boldsymbol{k}) = \begin{cases} \begin{bmatrix} 0 & A_a^n(\boldsymbol{k}) \\ A_a^{n*}(\boldsymbol{k}) & 0 \end{bmatrix} = E_a^n(\boldsymbol{k}) & \text{n even} \\ \begin{bmatrix} B_a^n(\boldsymbol{k}) & -C_a^{n*}(\boldsymbol{k}) \\ C_a^n(\boldsymbol{k}) & B_a^{n*}(\boldsymbol{k}) \end{bmatrix} = O_a^n(\boldsymbol{k}) & \text{n odd} \end{cases} \tag{7.21}$$

where we defined

$$A_a^n(\boldsymbol{k}) = |\epsilon_{AB}(\boldsymbol{k})|^n\, v_{AB}^{\alpha_1\cdots\alpha_a}(\boldsymbol{k}) \tag{7.22}$$
$$B_a^n(\boldsymbol{k}) = |\epsilon_{AB}(\boldsymbol{k})|^{n-1}\, v_{AB}^{\alpha_1\cdots\alpha_a}(\boldsymbol{k})\epsilon_{AB}^*(\boldsymbol{k}) \tag{7.23}$$
$$C_a^n(\boldsymbol{k}) = |\epsilon_{AB}(\boldsymbol{k})|^{n-1}\, v_{AB}^{\alpha_1\cdots\alpha_a *}(\boldsymbol{k})\Delta/2 \tag{7.24}$$

The upper indices of the $v^{\alpha_1\cdots\alpha_a}$ operators have been neglected because they are not relevant for now. The only thing needed is the number of indices, which is equal to the number of derivatives. When swapping $\boldsymbol{k}\to-\boldsymbol{k}$, these transform as

$$A_a^n(-\boldsymbol{k}) = (-1)^a\, A_a^{n*}(\boldsymbol{k}) \tag{7.25}$$
$$B_a^n(-\boldsymbol{k}) = (-1)^a\, B_a^{n*}(\boldsymbol{k}) \tag{7.26}$$
$$C_a^n(-\boldsymbol{k}) = (-1)^a\, C_a^{n*}(\boldsymbol{k}) \tag{7.27}$$

Now let's evaluate the traces of products of E and O matrices. Omitting their arguments and the indices pertaining to H^n, the traces up to three indices are

$$\mathrm{Tr}\,[E_a^n] = 0 \tag{7.28}$$
$$\mathrm{Tr}\,[O_a^n] = 2\Re(B_a) \tag{7.29}$$
$$\mathrm{Tr}\,[E_a^n O_b^m] = 2\Im(A_a C_b) \tag{7.30}$$
$$\mathrm{Tr}\,[O_a^n O_b^m] = 2\Re(B_a B_b - C_a^* C_b) \tag{7.31}$$
$$\mathrm{Tr}\,[E_a^n E_b^m] = 2\Re(A_a A_b^*) \tag{7.32}$$
$$\mathrm{Tr}\,[E_a^n E_b^m E_c^p] = 0 \tag{7.33}$$
$$\mathrm{Tr}\,[E_a^n E_b^m O_c^p] = 2\Re(A_a A_b^* B_c) \tag{7.34}$$
$$\mathrm{Tr}\,[O_a^n O_b^m E_c^p] = 2\Im(C_a B_b A_c + C_b B_a^* A_c) \tag{7.35}$$
$$\mathrm{Tr}\,[O_a^n O_b^m O_c^p] = 2\Re(B_a B_b B_c - B_a C_b^* C_c - C_a^* B_b^* C_c - C_b^* C_a B_c^*) \tag{7.36}$$

If we swap $\boldsymbol{k} \to -\boldsymbol{k}$ we get the following behaviours

$$\begin{aligned}
\mathrm{Tr}\left[E_a^n\left(-\boldsymbol{k}\right)\right] &= 0 && (7.37)\\
\mathrm{Tr}\left[O_a^n\left(-\boldsymbol{k}\right)\right] &= (-1)^a\,\mathrm{Tr}\left[O_a^n\left(\boldsymbol{k}\right)\right] && (7.38)\\
\mathrm{Tr}\left[E_a^n\left(-\boldsymbol{k}\right)E_b^m\left(-\boldsymbol{k}\right)\right] &= (-1)^{a+b}\,\mathrm{Tr}\left[E_a^n\left(\boldsymbol{k}\right)E_b^m\left(\boldsymbol{k}\right)\right] && (7.39)\\
\mathrm{Tr}\left[E_a^n\left(-\boldsymbol{k}\right)O_b^m\left(-\boldsymbol{k}\right)\right] &= (-1)^{a+b+1}\,\mathrm{Tr}\left[E_a^n\left(\boldsymbol{k}\right)O_b^m\left(\boldsymbol{k}\right)\right] && (7.40)\\
\mathrm{Tr}\left[O_a^n\left(-\boldsymbol{k}\right)O_b^m\left(-\boldsymbol{k}\right)\right] &= (-1)^{a+b}\,\mathrm{Tr}\left[O_a^n\left(\boldsymbol{k}\right)O_b^m\left(\boldsymbol{k}\right)\right] && (7.41)\\
\mathrm{Tr}\left[E_a^n\left(-\boldsymbol{k}\right)E_b^m\left(-\boldsymbol{k}\right)E_c^p\left(-\boldsymbol{k}\right)\right] &= 0 && (7.42)\\
\mathrm{Tr}\left[E_a^n\left(-\boldsymbol{k}\right)E_b^m\left(-\boldsymbol{k}\right)O_c^p\left(-\boldsymbol{k}\right)\right] &= (-1)^{a+b+c}\,\mathrm{Tr}\left[E_a^n\left(\boldsymbol{k}\right)E_b^m\left(\boldsymbol{k}\right)O_c^p\left(\boldsymbol{k}\right)\right] && (7.43)\\
\mathrm{Tr}\left[O_a^n\left(-\boldsymbol{k}\right)O_b^m\left(-\boldsymbol{k}\right)E_c^p\left(-\boldsymbol{k}\right)\right] &= (-1)^{a+b+c+1}\,\mathrm{Tr}\left[E_a^n\left(\boldsymbol{k}\right)E_b^m\left(\boldsymbol{k}\right)O_c^p\left(\boldsymbol{k}\right)\right] && (7.44)\\
\mathrm{Tr}\left[O_a^n\left(-\boldsymbol{k}\right)O_b^m\left(-\boldsymbol{k}\right)O_c^p\left(-\boldsymbol{k}\right)\right] &= (-1)^{a+b+c}\,\mathrm{Tr}\left[O_a^n\left(\boldsymbol{k}\right)O_b^m\left(\boldsymbol{k}\right)O_c^p\left(\boldsymbol{k}\right)\right] && (7.45)
\end{aligned}$$

Remember that we want to examine the second-order conductivity, which has three indices, so $a+b+c=3$. When there is only one v operator, there is no b or c, so $a=3$. For two, there is no c so $a+b=3$. We can either have $a=1$ and $b=2$ or the other way around. For three operators, we get $a+b+c=3$. After summing over all $\boldsymbol{k}$, only terms unchanged by $\boldsymbol{k} \to -\boldsymbol{k}$ remain, so that leaves only two:

$$\begin{aligned}
\mathrm{Tr}\left[E_a^n O_b^m\right] &= 2\Im\left(A_a C_b\right) && (7.46)\\
\mathrm{Tr}\left[O_a^n O_b^m E_c^p\right] &= 2\Im\left(C_a B_b A_c + C_b B_a^* A_c\right) && (7.47)
\end{aligned}$$

Replace these objects by their definitions

$$\begin{aligned}
\mathrm{Tr}\left[E_a^n O_b^m\right] &= \left|\epsilon_{AB}\right|^{n+m-1}\Delta\Im\left(v_{AB}^{\alpha_1\cdots\alpha_a}v_{AB}^{\alpha_1\cdots\alpha_b *}\right) && (7.48)\\
\mathrm{Tr}\left[O_a^n O_b^m E_c^p\right] &= \left|\epsilon_{AB}\right|^{m+n+p-2}\Delta 2\Re\left(v_{AB}^{\alpha_1\cdots\alpha_b}\epsilon_{AB}^*\right)\Im\left[v_{AB}^{\alpha_1\cdots\alpha_c}v_{AB}^{\alpha_1\cdots\alpha_a *}\right] && (7.49)
\end{aligned}$$

To simplify these, let's particularize to the case we're studying, σ^{xxx}. The second trace is now zero because we're computing the imaginary part of $v_{AB}^x v_{AB}^{x*}$, which is real. The only survivor is the first trace, which may have two forms:

$$\left|\epsilon_{AB}\right|^{n+m-1}\Delta\Im\left(v_{AB}^x v_{AB}^{xx*}\right) \tag{7.50}$$

and

$$\left|\epsilon_{AB}\right|^{n+m-1}\Delta\Im\left(v_{AB}^{xx} v_{AB}^{x*}\right) \tag{7.51}$$

The same argument does not apply here, so we have no reason to believe this is zero. After all of this, we conclude that all the Γ matrices of one and three indices vanish. The second-order conductivity $\sigma^{xxx}(\omega_1, \omega_2)$ therefore simplifies tremendously for the case of h-BN.

$$\sigma^{xxx}_{h-BN}(\omega_1,\omega_2) = \frac{-16i\sigma_2}{3\sqrt{3}\lambda\omega_1\omega_2}\int_{-1}^{1} d\epsilon f(\epsilon)\Delta_n(\epsilon)\left\{g^a_m(-\epsilon/\hbar+\omega_2)\,\Gamma^{xx,x}_{nm}\right. \tag{7.52}$$
$$\left. +g^R_m(-\epsilon/\hbar-\omega_2)\,\Gamma^{xx,x}_{mn} + \frac{1}{2}g^R_m(-\epsilon/\hbar-\omega_1-\omega_2)\,\Gamma^{x,xx}_{mn} + \frac{1}{2}g^a_m(-\epsilon/\hbar+\omega_1+\omega_2)\,\Gamma^{x,xx}_{nm}\right\}$$

The computations thus become much simpler because the hardest objects to calculate are gone.

7.2.2 Density of states

The dispersion relation of h-BN has a gap, which is evident in the density of states of Fig. 7.2.2.

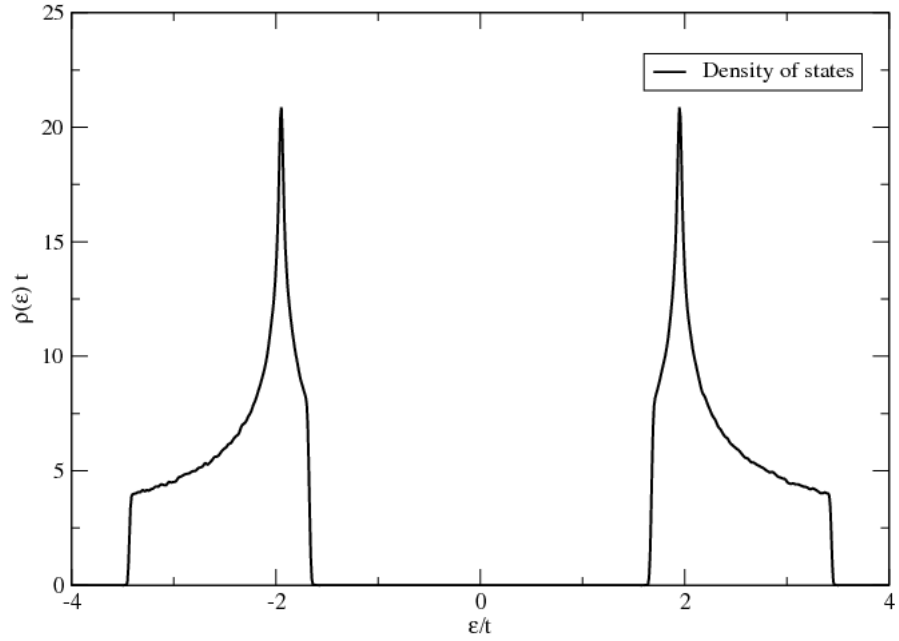


Figure 7.4: KPM simulation of the density of states $\rho(\epsilon)$ of h-BN for a hopping parameter $t = 2.33$ eV. The axes are in units of t. System size: 1024×1024 unit cells, number of Chebyshev polynomials used: 1024. We use the Jackson kernel for the Dirac delta.

7.2.3 First-order conductivity

If we choose the chemical potential to lie inside the gap, we expect no divergence at $\omega = 0$, which is exactly what we see in Fig. 7.5. To remove the peaks at low frequencies, we'd need bigger

systems with more Chebyshev polynomials.

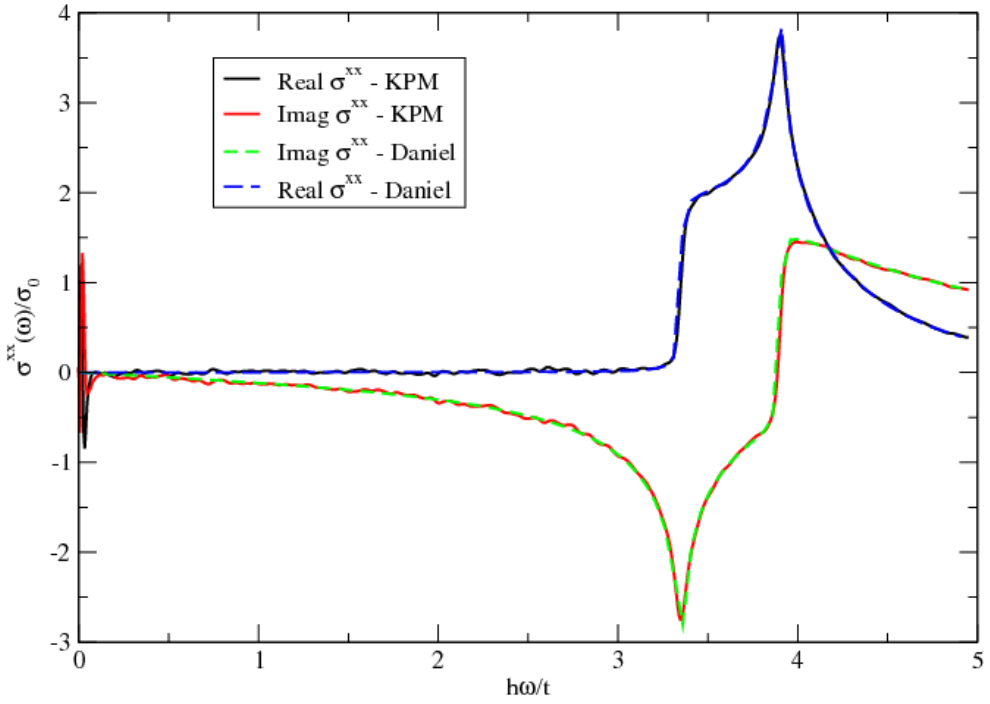


Figure 7.5: KPM simulation of the first-order conductivity in h-BN. The curves are plotted against a reference (dashed lines). The graph is in units of the graphene universal conductivity σ_0 and the hopping t. System size: 2048×2048 unit cells, number of Chebyshev polynomials used: 1024, chemical potential $\mu = 0$, gap $\Delta = 7.8$ eV, hopping $t = 2.33$ eV, infinitesimal $\Gamma = 0.03$ eV, temperature $T = 300K$. The kernels used here are the same as the ones for the conductivity in graphene.

7.2.4 Second-order conductivity

There are two frequency arguments in the second-order conductivity. In order to represent it in a simple graph, we're going to analyze the DC component of the second-order conductivity σ^{xxx}. To see where this comes from, consider a simple sinusoidal electric field $E(t) = E_0 \cos(\omega_0 t)$ along the x direction. In frequency space, $E(\omega) = \pi E_0 (\delta(\omega - \omega_0) + \delta(\omega + \omega_0))$. Replacing in the expression for the second-order current,

$$\begin{aligned}\langle J^{\alpha}(\omega)\rangle &= \frac{E_0^2}{4}\left[\sigma^{\alpha xx}(\omega_0,\omega_0)\delta(2\omega_0-\omega) + \left[\sigma^{\alpha xx}(-\omega_0,\omega_0)+\sigma^{\alpha xx}(\omega_0,-\omega_0)\right]\delta(\omega) + \right. \\ &\left. +\sigma^{\alpha xx}(-\omega_0,-\omega_0)\delta(2\omega_0+\omega)\right].\end{aligned}$$

There are three distinct contributions to the current, but here we'll focus on the longitudinal DC case, where $\omega = 0$ and the current has the same direction as the field: $\sigma^{xxx}(-\omega_0, \omega_0)$. The other two cases would correspond to the second harmonic generation (SHG). Calculation of the DC component turns eq. 7.52 into:

$$\frac{\sigma^{xxx}_{h-BN}}{\sigma_2}(-\omega,\omega) = \frac{16it}{3\sqrt{3}\omega_1^2 a}\int_{-1}^{1} d\epsilon f(\epsilon)\Delta_n(\epsilon)\{g_m^a(-\epsilon/\hbar+\omega)\Gamma^{xx,x}_{nm} \tag{7.53}$$
$$+g_m^R(-\epsilon/\hbar-\omega)\Gamma^{xx,x}_{mn} + \frac{1}{2}g_m^R(-\epsilon/\hbar)\Gamma^{x,xx}_{mn} + \frac{1}{2}g_m^a(-\epsilon/\hbar)\Gamma^{x,xx}_{nm}\Big\}.$$

This is the formula used to obtain Fig. 7.2.4. This result is compared with the conductivity obtained by Daniel. The two curves have the same profile, although the frequency scale seems a bit off. We weren't able to find a satisfactory explanation for this difference, but the issue is still being investigated.

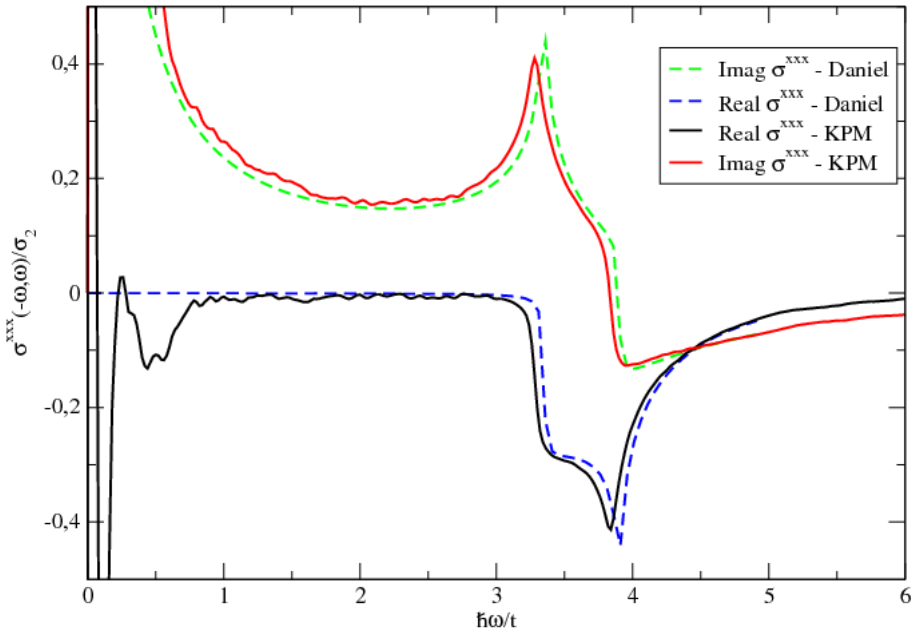


Figure 7.6: KPM simulation of the second-order DC conductivity in h-BN. The curves are plotted against a reference (dashed lines). System size: 4096×4096 unit cells, number of Chebyshev polynomials used: 1024, chemical potential $\mu = 0$, gap $\Delta = 7.8$ eV, hopping $t = 2.33$ eV, infinitesimal $\Gamma = 0.03$ eV, temperature $T = 300K$. The kernels used here are the same as the ones for the conductivity in graphene.

7.3 Conclusion

Along this work, we have developed the tools necessary to deal with the Keldysh formalism. Along the way, we used Kubo's formula to study the first-order response, using it to compare our expressions with various others across the literature. Through the Keldysh formalism, we were able to find a general expression for the n-th order Green's function. Expanding the current in the various orders in the external field, we expressed these quantities in terms of said Green's functions. This is useful because the Kernel Polynomial Method (KPM) precisely allows us to calculate the Green's function numerically. With these tools, we obtained the density of states and first-order conductivity for graphene and hexagonal Boron Nitride (h-BN). The second-order conductivity was obtained for h-BN. The agreement was good but not perfect, so it requires further investigation, but serves as a proof-of-concept for the method developed in this work. Even higher-order conductivites, although possible to calculate, prove to be a formidable computational task, so we had to limit ourselves to the second order.

8 Appendix

8.1 Conventions

To make sure we're all on the same page, this section deals with some conventions.

8.1.1 Continuous Fourier Transform

Define the forward and inverse Fourier transforms as follows:

$$\begin{aligned} f(t) &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} f(\omega) \\ f(\omega) &= \int_{-\infty}^{\infty} dt e^{i\omega t} f(t) \end{aligned}$$

These definitions are used to give meaning to the Fourier transform of the complex exponential

$$\int_{-\infty}^{\infty} dt e^{i\omega t} = 2\pi\delta(\omega) \tag{8.1}$$

8.1.2 Discrete Fourier Transform

A similar convention is followed when dealing with the discrete analogue

$$f(\boldsymbol{R}) = \frac{1}{N} \sum_{\boldsymbol{k}} f(\boldsymbol{k}) e^{i\boldsymbol{k}\cdot\boldsymbol{R}} \tag{8.2}$$

$$f(\boldsymbol{k}) = \sum_{\boldsymbol{R}} f(\boldsymbol{R}) e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \tag{8.3}$$

Where N is the number of $\boldsymbol{k}$ (or $\boldsymbol{R}$) states and may be thought as the volume. These are consistent with the sum rules for real and reciprocal spaces:

$$\sum_{\boldsymbol{R}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}} = N\delta_{\boldsymbol{k},\boldsymbol{0}} \tag{8.4}$$

$$\sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}} = N\delta_{\boldsymbol{R},\boldsymbol{0}} \tag{8.5}$$

8.2 Fourier transform of two complex exponentials

The integral we want to evaluate is

$$\int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt' e^{i(\omega+\omega_{pss'})t} e^{-i(\omega'+\omega_{pss'})t'} \tag{8.6}$$

At first glance, we see that this does not converge. This can be overcome by introducing a convergence factor each time we integrate a variable. For example, if we want to integrate t', we introduce $e^{-\epsilon|t'|}$ and take the limit $\epsilon \to 0^+$ in the end:

$$\lim_{\epsilon\to 0^+} \int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt' e^{i(\omega+\omega_{pss'})t} e^{-i(\omega'+\omega_{pss'})t'-\epsilon|t'|} \tag{8.7}$$

Although doable, this is a very cumbersome approach. It may be avoided if we are able to complete the integral in t' so it spans across the whole real line. This way, we may interpret the integral as a simple Fourier transform of the identity. Introducing the integral representation of the Heaviside function $\Theta(t) = \int_{-\infty}^{\infty} \frac{d\omega''}{2\pi i} \frac{e^{i\omega'' t}}{\omega''-i\epsilon}$ allows us to do exactly that.

$$\int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt' e^{i(\omega+\omega_{pss'})t} e^{-i(\omega'+\omega_{pss'})t'} = \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} \frac{d\omega''}{2\pi i} \frac{e^{i\omega'(t-t')}}{\omega''-i\epsilon} e^{i(\omega+\omega_{pss'})t} e^{-i(\omega'+\omega_{pss'})t'} \tag{8.8}$$

The time integrations are now trivial and yield Dirac deltas.

$$\begin{aligned}
&\int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} \frac{d\omega''}{2\pi i} \frac{e^{i\omega'(t-t')}}{\omega''-i\epsilon} e^{i(\omega+\omega_{pss'})t} e^{-i(\omega'+\omega_{pss'})t'} \\
&= \int_{-\infty}^{\infty} \frac{d\omega''}{2\pi i} \frac{1}{\omega''-i\epsilon} 2\pi\delta(\omega+\omega''+\omega_{pss'}) 2\pi\delta(\omega'+\omega''+\omega_{pss'})
\end{aligned}$$

Finally, performing the integration in ω'' returns

$$\int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt' e^{i(\omega+\omega_{pss'})t} e^{-i(\omega'+\omega_{pss'})t'} = \frac{2\pi i\delta(\omega-\omega')}{\omega+\omega_{pss'}+i\epsilon} \tag{8.9}$$

8.3 Calculation of the commutator $\left\langle \left[c_a^\dagger(t)c_b(t), c_c^\dagger(t')c_d(t')\right]\right\rangle_0$

As the title suggests, the objective here is to calculate the commutator $\left\langle \left[c_a^\dagger(t)c_b(t), c_c^\dagger(t')c_d(t')\right]\right\rangle_0$. The time labels are removed for ease of notation, since they can be inferred from the operators' labels. The first step is to write out the commutator explicitly

$$\left\langle \left[c_a^\dagger c_b, c_c^\dagger c_d\right]\right\rangle_0 = \left\langle c_a^\dagger c_b c_c^\dagger c_d - c_c^\dagger c_d c_a^\dagger c_b\right\rangle_0 \tag{8.10}$$

Now we're going to take each of the terms and anti-commute the inner-most two operators of each

$$\left\langle \left[c_a^\dagger c_b, c_c^\dagger c_d\right]\right\rangle_0 = \left\langle c_a^\dagger \left(\left\{c_b, c_c^\dagger\right\} - c_c^\dagger c_b\right) c_d - c_c^\dagger \left(\left\{c_d, c_a^\dagger\right\} - c_a^\dagger c_d\right) c_b\right\rangle_0 \tag{8.11}$$

Doing this has the advantage of removing all terms with four operators, since those cancel. Simplifying and collecting terms, we arrive at

$$\left\langle \left[c_a^\dagger c_b, c_c^\dagger c_d\right]\right\rangle_0 = \left\{c_b, c_c^\dagger\right\}\left\langle c_a^\dagger c_d\right\rangle_0 - \left\{c_d, c_a^\dagger\right\}\left\langle c_c^\dagger c_b\right\rangle_0 \tag{8.12}$$

The explicit time-dependence may now be reestablished:

$$\left\langle \left[c_a^\dagger(t)c_b(t), c_c^\dagger(t')c_d(t')\right]\right\rangle_0 = \left\{c_b(t), c_c^\dagger(t')\right\}\left\langle c_a^\dagger(t)c_d(t')\right\rangle_0 - \left\{c_d(t'), c_a^\dagger(t)\right\}\left\langle c_c^\dagger(t')c_b(t)\right\rangle_0 \tag{8.13}$$

8.4 Calculation of the Green's functions from the Keldysh formalism

These functions will be used copiously throughout the text so it is useful to determine their full expression in both real and frequency spaces, as well as written in terms of quantum mechanical operators.

8.4.1 Expressions in real and frequency spaces

They are the lesser, greater, retarded and advanced Green's functions and they originate from averaging the product of a creation and a destruction operators over a non-interacting time-independent Hamiltonian. This means that their evolution in the eigen basis of the Hamiltonian is trivial.

$$c_n(t_1) = c_n e^{-i\epsilon_n t_1/\hbar} \tag{8.14}$$
$$c_m^\dagger(t_2) = c_m^\dagger e^{i\epsilon_m t_2/\hbar} \tag{8.15}$$

Using this fact, the time dependency of the average becomes easy to calculate.

$$\left\langle c_m^\dagger(t_2)c_n(t_1)\right\rangle_0 = \left\langle c_m^\dagger c_n\right\rangle_0 e^{-i\epsilon_n t_1/\hbar}e^{i\epsilon_m t_2/\hbar} \tag{8.16}$$
$$\left\langle c_n(t_1)c_m^\dagger(t_2)\right\rangle_0 = \left\langle c_n c_m^\dagger\right\rangle_0 e^{-i\epsilon_n t_1/\hbar}e^{i\epsilon_m t_2/\hbar} \tag{8.17}$$

Next, Wick's theorem for finite temperatures (2.142 and 2.143) tells us how to calculate these averages

$$\left\langle c_m^\dagger c_n\right\rangle_0 = -\delta_{nm} f(\epsilon_n) \tag{8.18}$$
$$\left\langle c_n c_m^\dagger\right\rangle_0 = \delta_{nm}\left[1 - f(\epsilon_n)\right] \tag{8.19}$$

Putting all this together, we are able to find the expressions for the lesser and greater Green's functions in the energy basis, whose definition is given in eq. 4.21:

$$ig_{nm}^<(t_1,t_2) = -\left\langle c_m^\dagger(t_2)c_n(t_1)\right\rangle_0 = -\delta_{nm} f(\epsilon_n)e^{i\epsilon_m(t_2-t_1)/\hbar} \tag{8.20}$$

$$ig_{nm}^>(t_1,t_2) = \left\langle c_n(t_1)c_m^\dagger(t_2)\right\rangle_0 = \delta_{nm}\left[1 - f(\epsilon_n)\right]e^{i\epsilon_m(t_2-t_1)/\hbar} \tag{8.21}$$

The retarded and advanced Green's functions are calculated based on these two, using definitions 4.23 and 4.24:

$$ig^R_{nm}(t_1,t_2) = i\Theta(t_1-t_2)\left[g^>_{nm}(t_1,t_2)-g^<_{nm}(t_1,t_2)\right] = \Theta(t_1-t_2)\delta_{nm}e^{i\epsilon_m(t_2-t_1)/\hbar} \quad (8.22)$$

$$ig^a_{nm}(t_1,t_2) = -i\Theta(t_2-t_1)\left[g^>_{nm}(t_1,t_2)-g^<_{nm}(t_1,t_2)\right] = -\Theta(t_2-t_1)\delta_{nm}e^{i\epsilon_m(t_2-t_1)/\hbar} \quad (8.23)$$

The most important feature about this is that all these functions are diagonal in the energy basis. Therefore, they actually depend only on the difference of times.

$$ig^<_{nm}(t_1,t_2) = ig^<_{nm}(t_1-t_2) \quad (8.24)$$
$$ig^>_{nm}(t_1,t_2) = ig^>_{nm}(t_1-t_2) \quad (8.25)$$
$$ig^R_{nm}(t_1,t_2) = ig^R_{nm}(t_1-t_2) \quad (8.26)$$
$$ig^a_{nm}(t_1,t_2) = ig^a_{nm}(t_1-t_2) \quad (8.27)$$

We can exploit that fact to obtain their Fourier transform. The lesser and greater Green's functions are essentially Dirac deltas

$$ig^<_{nm}(\omega) = \int_{-\infty}^{\infty} dt ig^<_{nm}(t)e^{i\omega t} = -\delta_{nm}f(\epsilon_n)\,(2\pi)\,\delta(\omega-\epsilon_n/\hbar) \quad (8.28)$$

$$ig^>_{nm}(\omega) = \int_{-\infty}^{\infty} dt ig^>_{nm}(t)e^{i\omega t} = \delta_{nm}\left[1-f(\epsilon_n)\right](2\pi)\,\delta(\omega-\epsilon_n/\hbar) \quad (8.29)$$

whilst the retarded and advanced Green's functions can be evaluated if we use the integral representation of the Heaviside function

$$\begin{aligned} ig^R_{nm}(\omega) &= \int_{-\infty}^{\infty} dt ig^R_{nm}(t)e^{i\omega t} = \delta_{nm}\int_{-\infty}^{\infty} dt e^{i\omega t}\Theta(t)e^{-i\epsilon_m t/\hbar} \\ &= \delta_{nm}\int_{-\infty}^{\infty} dt e^{i\omega t}\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi i}\frac{e^{-i\omega' t}}{\omega'+i0^+}e^{-i\epsilon_m t/\hbar} = \frac{-i\delta_{nm}}{\omega-\epsilon_m/\hbar+i0^+} \end{aligned} \quad (8.30)$$

The derivation for the advanced Green's function is almost identical and yields

$$ig^a_{nm}(\omega) = \int_{-\infty}^{\infty} dt ig^a_{nm}(t)e^{i\omega t} = \frac{-i\delta_{nm}}{\omega-\epsilon_m/\hbar-i0^+} \quad (8.31)$$

In summary, these functions have the following form when expressed in terms of time:

$$
\begin{aligned}
ig^{<}_{nm}(t_1,t_2) &= -\delta_{nm} f(\epsilon_n) e^{i\epsilon_m(t_2-t_1)/\hbar} && (8.32)\\
ig^{>}_{nm}(t_1,t_2) &= \delta_{nm}\left[1-f(\epsilon_n)\right] e^{i\epsilon_m(t_2-t_1)/\hbar} && (8.33)\\
ig^{R}_{nm}(t_1,t_2) &= \Theta(t_1-t_2)\delta_{nm} e^{i\epsilon_m(t_2-t_1)/\hbar} && (8.34)\\
ig^{a}_{nm}(t_1,t_2) &= -\Theta(t_2-t_1)\delta_{nm} e^{i\epsilon_m(t_2-t_1)/\hbar} && (8.35)
\end{aligned}
$$

And in frequency space:

$$
\begin{aligned}
ig^{<}_{nm}(\omega) &= -\delta_{nm} f(\epsilon_n)\,(2\pi)\,\delta(\omega-\epsilon_m/\hbar) && (8.36)\\
ig^{>}_{nm}(\omega) &= \delta_{nm}\left[1-f(\epsilon_n)\right](2\pi)\,\delta(\omega-\epsilon_m/\hbar) && (8.37)\\
ig^{R}_{nm}(\omega) &= \frac{-i\delta_{nm}}{\omega-\epsilon_m/\hbar+i0^+} && (8.38)\\
ig^{a}_{nm}(\omega) &= \frac{-i\delta_{nm}}{\omega-\epsilon_m/\hbar-i0^+} && (8.39)
\end{aligned}
$$

8.4.2 Expressing in terms of operators

All these expressions have been obtained by working in the energy basis. Now it's relatively easy to express them in terms of operators, namely the Hamiltonian. All we need to to is replace every instance of an energy eigenvalue by the matrix element of the Hamiltonian. Starting with the retarded Green's function, define $g^R(\omega)=\frac{-1}{\omega-H+i0^+}$. It is easy to check that its matrix elements give precisely our definition of g^R_{nm}

$$
ig^{R}_{nm}(\omega)=\frac{-i\delta_{nm}}{\omega-\epsilon_m+i0^+}=\langle n|\,\frac{-i}{\omega-H+i0^+}\,|m\rangle=\langle n|\,ig^R(\omega)\,|m\rangle \tag{8.40}
$$

Likewise, defining $g^a(\omega)=\frac{-1}{\omega-H-i0^+}$, the advanced Green's function becomes

$$
ig^{a}_{nm}(\omega)=\langle n|\,ig^a(\omega)\,|m\rangle \tag{8.41}
$$

To do the same with the lesser Green's function, note that $f(\epsilon_n)=\int_{-\infty}^{\infty}d\epsilon f(\epsilon)\delta(\epsilon-\epsilon_n)$, which places all the dependency in ϵ_n inside one single Dirac delta. This delta is then promoted to a matrix element of $\delta(\epsilon-H)$

$$
\begin{aligned}
ig^{<}_{nm}(\omega) &= -\delta_{nm} f(\epsilon_n)\,(2\pi)\,\delta(\omega-\epsilon_n/\hbar) = -2\pi\delta_{nm}\int_{-\infty}^{\infty}d\epsilon f(\epsilon)\delta(\omega-\epsilon/\hbar)\delta(\epsilon-\epsilon_n)\\
&= -2\pi\int_{-\infty}^{\infty}d\epsilon f(\epsilon)\delta(\omega-\epsilon/\hbar)\,\langle n|\,\delta(\epsilon-H)\,|m\rangle
\end{aligned}
$$

The greater Green's function is done in precisely the same way and gives

$$ig^{>}_{nm}(\omega) = 2\pi \int_{-\infty}^{\infty} d\epsilon \left[1 - f(\epsilon)\right] \delta(\omega - \epsilon/\hbar) \left\langle n\right| \delta(\epsilon - H) \left|m\right\rangle . \tag{8.42}$$

In summary:

$$\begin{aligned} ig^{<}_{nm}(\omega) &= -2\pi \int_{-\infty}^{\infty} d\epsilon f(\epsilon) \delta(\omega - \epsilon/\hbar) \left\langle n\right| \delta(\epsilon - H) \left|m\right\rangle \\ ig^{>}_{nm}(\omega) &= 2\pi \int_{-\infty}^{\infty} d\epsilon \left[1 - f(\epsilon)\right] \delta(\omega - \epsilon/\hbar) \left\langle n\right| \delta(\epsilon - H) \left|m\right\rangle \\ ig^{R}_{nm}(\omega) &= \left\langle n\right| ig^{R}(\omega) \left|m\right\rangle \\ ig^{a}_{nm}(\omega) &= \left\langle n\right| ig^{a}(\omega) \left|m\right\rangle \end{aligned} \tag{8.43}$$

8.5 Expansion of Green's functions in terms of Chebychev polynomials

Consider the Green's function with a finite $\lambda > 0$ that accounts for dispersion. $\sigma = -1$ gives the advanced and $\sigma = 1$ the retarded Green's function.

$$g^{\sigma,\lambda}(\epsilon, h) = \frac{-1}{\epsilon - h + i\sigma\lambda} = \sigma i \int_0^\infty dt e^{\sigma i(\epsilon - h + i\sigma\lambda)t} \tag{8.44}$$

This is a two-variable function and we want to achieve a separation between ϵ and h in the polynomial expansion, so let us look for an expression of the form

$$g^{\sigma,\lambda}(\epsilon, h) = \sum_{n=0}^{\infty} g_n^{\sigma,\lambda}(\epsilon) \frac{T_n(h)}{1 + \delta_{n0}} \tag{8.45}$$

The function $g_n^{\sigma,\lambda}(\epsilon)$ may be found by applying the orthogonality relations

$$2\int_{-1}^{1} \frac{dh}{\pi\sqrt{1-h^2}} T_m(h) g^{\sigma,\lambda}(\epsilon, h) = \sum_{n=0}^{\infty} \frac{2g_n^{\sigma,\lambda}(\epsilon)}{1 + \delta_{n0}} \int_{-1}^{1} \frac{dh}{\pi\sqrt{1-h^2}} T_m(h) T_n(h) = g_n^{\sigma,\lambda}(\epsilon) \tag{8.46}$$

Now we express the Green's function in its integral form, which enables us to calculate $g_n^{\sigma,\lambda}(\epsilon)$ explicitly

$$\begin{aligned} g_n^{\sigma,\lambda}(\epsilon) &= 2\int_{-1}^{1} \frac{dh}{\pi\sqrt{1-h^2}} T_n(h) \sigma i \int_0^\infty dt e^{\sigma i(\epsilon - h + i\sigma\lambda)t} \\ &= 2\sigma i \int_0^\infty dt e^{\sigma i(\epsilon + i\sigma\lambda)t} \int_{-1}^{1} \frac{dh}{\pi\sqrt{1-h^2}} T_n(h) e^{-\sigma i h t} \end{aligned}$$

The first step is thus to calculate the second integral, which resembles the application of the orthogonality relations to the imaginary exponential.

8.5.1 Second integral

$$\int_{-1}^{1} \frac{dh}{\pi\sqrt{1-h^2}} T_n(h) e^{-\sigma i h t} \tag{8.47}$$

A change of variables $h = \cos(\theta)$ helps shed some light into what this integral really is

$$\int_{-1}^{1} \frac{dh}{\pi\sqrt{1-h^2}} T_n(h) e^{-\sigma i h t} = \int_0^\pi \frac{d\theta}{\pi} \cos(n\theta) e^{-\sigma i \cos(\theta) t} \tag{8.48}$$

Using the fact that

$$\int_{-\pi}^{\pi} d\theta \cos(n\theta) e^{-\sigma i \cos(\theta) t} = \int_{-\pi}^{\pi} d\theta e^{i(n\theta - \sigma t \cos(\theta))} \tag{8.49}$$

the previous integral may be identified as

$$\int_{-1}^{1} \frac{dh}{\pi\sqrt{1-h^2}} T_n(h) e^{-\sigma i h t} = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta e^{i(n\theta - \sigma t \cos(\theta))} \tag{8.50}$$

This is starting to look like the definition of a Bessel function, but it's still not quite there. A series of changes of variables should make it clearer. Using the change $\phi = \pi/2 - \theta$ we arrive at an integral with some odd limits

$$\int_{-\pi}^{\pi} d\theta e^{i(n\theta - \sigma t \cos(\theta))} = \int_{-\pi}^{\pi} d\theta e^{i\left(n\theta - \sigma t \sin(\frac{\pi}{2} - \theta)\right)} = \int_{-\pi/2}^{3\pi/2} d\phi e^{i\left(n(\frac{\pi}{2} - \phi) - \sigma t \sin(\phi)\right)} \tag{8.51}$$

Note that since n is an integer, the integrand has period 2π and is being integrated over a whole period. This means we can shift the integration limits as long as they span a period. With that in mind, the previous integral becomes

$$\int_{-\pi}^{\pi} d\theta e^{i(n\theta - \sigma t \cos(\theta))} = \int_{-\pi}^{\pi} d\phi e^{i\left(n(\frac{\pi}{2} - \phi) - \sigma t \sin(\phi)\right)} \tag{8.52}$$

For integer n, the factor that does not depend on ϕ may be brought outside the exponential to yield i^n

$$\int_{-\pi}^{\pi} d\theta e^{i(n\theta - \sigma t \cos(\theta))} = \int_{-\pi}^{\pi} d\phi e^{i(n\phi + \sigma t \sin(\phi))} i^n. \tag{8.53}$$

Finally, doing the change of variables $\theta = \sigma\phi$ we can identify this as the integral definition of a Bessel function

$$\int_{-\pi}^{\pi} d\phi e^{i(n\phi + \sigma t \sin(\phi))} = \int_{-\pi}^{\pi} d\theta e^{i(-n\sigma\theta - t \sin(\theta))} = 2\pi J_{-n\sigma}(t) = 2\pi \left(-\sigma\right)^n J_n(t) \tag{8.54}$$

Tracing back our steps, we find that

$$\boxed{\int_{-1}^{1} \frac{dh}{\pi\sqrt{1-h^2}} T_n(h) e^{-\sigma i h t} = (-\sigma i)^n J_n(t)} \tag{8.55}$$

All that remains is

$$g_n^{\sigma,\lambda}(\epsilon) \quad = \quad -2(-\sigma i)^{n+1} \int_0^{\infty} dt e^{\sigma i(\epsilon + i\sigma\lambda)t} J_n(t) \tag{8.56}$$

This is basically the Laplace transform of the Bessel function. Let $z = -\sigma i(\epsilon + i\sigma\lambda) = \lambda - \sigma i\epsilon$. Therefore what we must calculate now is

$$\int_0^{\infty} dt e^{-zt} J_n(t) \tag{8.57}$$

8.5.2 Laplace transform of the Bessel function

This is a tricky calculation, but it can be done using integration in the complex plane. First, express the Bessel function in its integral form. Then, the integral in t may be easily performed, leaving an integration in the angle θ

$$\int_0^\infty dt e^{-zt} J_n(t) = \int_{-\pi}^{\pi} \frac{d\theta}{2\pi} e^{in\theta} \int_0^\infty dt e^{-(i\sin(\theta)+z)t} = \int_{-\pi}^{\pi} \frac{d\theta}{2\pi} e^{in\theta} \frac{1}{i\sin(\theta)+z} \tag{8.58}$$

This is valid assuming that $\Re(z) > 0$, which is always true because $\lambda > 0$. Now we resort to the Residue Theorem to compute this integral. Performing the change of variables $\omega = e^{i\theta}$, the integral runs along the unit circle in the complex plane.

$$\int_0^\infty dt e^{-zt} J_n(t) = \frac{1}{2\pi} \oint \frac{d\omega}{i\omega} \omega^n \frac{1}{i\frac{\omega - \frac{1}{\omega}}{2i} + z} = \frac{1}{\pi i} \oint d\omega \frac{\omega^n}{\omega^2 + 2z\omega - 1} \tag{8.59}$$

This integrand has poles at $\omega^\pm = -z \pm \sqrt{z^2+1}$. $\Re(z) > 0$ also guarantees[1] that the only the root that lies inside the unit circle is $\omega^+ = -z + \sqrt{z^2+1}$. If we use the principal branch of the square root, we need not worry about the branch cut, since z is assumed to have a positive real part. Applying the Residue Theorem, we arrive at

$$\begin{aligned} \frac{1}{\pi i} \oint d\omega \frac{\omega^n}{\omega^2 + 2z\omega - 1} &= \frac{2\pi i}{\pi i} \mathrm{Res}\left(\frac{\omega^n}{\omega^2 + 2z\omega - 1}, \omega = -z + \sqrt{z^2+1} \right) \\ &= 2 \lim_{\omega \to \omega^+} \frac{(\omega - \omega^+)\,\omega^n}{(\omega - \omega^-)\,(\omega - \omega^+)} = 2\frac{\omega^{+n}}{\omega^+ - \omega^-} \end{aligned}$$

Using $\omega^+ - \omega^- = 2\sqrt{z^2+1}$ and $e^{i \arcsin(iz)} = \sqrt{1+z^2} - z$, we are able to finish the evaluation of the integral

$$\boxed{\int_0^\infty dt e^{-zt} J_n(t) = \frac{e^{ni \arcsin(iz)}}{\sqrt{z^2+1}}} \tag{8.60}$$

This expression is valid in the right half of the Argand plane, excluding the imaginary axis.

[1] First of all, note that $\omega^+\omega^- = -1$. Therefore, $|\omega^+|$ and $|\omega^-|$ are inverses of one another. That is, if one is inside the complex unit circle, the other is necessarily outside. We only need to guarantee that if one of those roots is inside the unit circle, as we change z, it stays inside. This may be proved by finding all the solutions that lie precisely in the unit circle and guaranteeing that these are never reached. For that purpose, let's find all $\omega = e^{i\theta}$ with θ real such that $\omega^2 + 2z\omega - 1 = 0$. The solution to that is $z = -i\sin(\theta)$. This tells us that if the roots lie in the unit circle, then z must lie in the interval $[-1, 1]$ in the imaginary axis. Furthermore, we know that the roots (ω^-, ω^+) of a complex polynomial are continuous functions of its coefficients[17]. So, by continuity, if a root crosses the unit circle that's because z must have crossed the imaginary $[-1, 1]$ interval. But since $\Re(z) > 0$, this will never happen. Finally, checking that, for example for $z = 1/2$, $\omega^+ = \left(\sqrt{3} - 1\right)/2 < 1$ is enough to say that this root will always stay inside the unit circle and ω^- will never be inside.

8.5.3 Green's function

Going back to eq. 8.56, we finally have all the ingredients to say

$$g_n^{\sigma,\lambda}(\epsilon) = -2(-\sigma i)^{n+1} \frac{e^{ni \arcsin(\sigma\epsilon + i\lambda)}}{\sqrt{1 - (\sigma\epsilon + i\lambda)^2}} \tag{8.61}$$

In some practical calculations, we are not interested in this result for a general λ. Instead, we use the limit $\lambda \to 0^+$. Since we'll be assuming $-1 < \epsilon < 1$, the imaginary factor does nothing in these functions, since we never hit the branch cuts. We may therefore ignore it and consider the functions as if they were real functions of real variables. This simplifies the previous expression to

$$g_n^{\sigma}(\epsilon) = -2(-\sigma i)^{n+1} \frac{e^{ni \arcsin(\sigma\epsilon)}}{\sqrt{1 - \epsilon^2}} \tag{8.62}$$

Using the identity $\frac{\pi}{2} - \arccos(z) = \arcsin(z)$, we are able to get rid of some of the $(\sigma i)^{n+1}$ lurking outside the exponential.

$$g_n^{\sigma}(\epsilon) = 2\sigma i \frac{e^{-ni\sigma \arccos(\epsilon)}}{\sqrt{1 - \epsilon^2}} \tag{8.63}$$

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