Nonlinear Optics

Optical Properties in the Semiclassical Approximation

Bachelor's Thesis

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Abstract

In this thesis I will make use of the Boltzmann equation describing electron movements in materials to find a general formula for the current density. I will then move on to determining the current density for a free electron model, followed by another model type of model, the tight binding model. Since the tight bind model depends on how the crystalline structure of the material is, I will work with just two different types of crystal structures. I will start with the simple cubic structure, and then move on to the more commonly observed face centered cubic structure. I will conclude with considering how this work in the future can be used to find the current densities for other materials, as well as how it is possible to incorporate anomalous behaviors such as the ones from Weyl semi metals.

Contents

1 Introduction

In this thesis I will be analysing how materials respond to electric fields by making use of the Boltzmann equation in the low temperature limit of the semi classical approach. This allows me to find conductivities of different types of materials, using both the free electron model, as well as the tight binding model. These conductivities are important in different areas of physics, such as optical physics and solid state physics. This work was motivated by wanting to properly understand this type of base model, such that it can expanded upon later to include anomalous effects, such as the effects for the exotic material called "Weyl semi-metals". These effects can be somewhat easily included into the formulas by changing the semi classical formula for the electron velocities to include an extra anomalous velocity. This is an interesting area because Weyl semi-metals have been observed to be great materials to use for photo-electrical effects like the ones in solar panels, and light sensors.

2 The Boltzmann equation

All throughout this thesis I will make use of the Boltzmann equation to describe how electrons in materials respond to an external stimuli in the form of electric fields, which can be provided by light. The equation is as follows

$$\frac{\partial f}{\partial t} + \frac{\partial f}{\partial \boldsymbol{r}} \cdot \frac{d\boldsymbol{r}}{dt} + \frac{\partial f}{\partial \boldsymbol{k}} \cdot \frac{d\boldsymbol{k}}{dt} = \left(\frac{df}{dt}\right)_{coll}. \tag{1}$$

Here f is the distribution function, $\boldsymbol{r}$ is the normal position vector of space, $\boldsymbol{k}$ is the wave vector, describing the momentum, and $\left(\frac{df}{dt}\right)_{coll}$ is the collision integral, which I will not go into detail with in this thesis. However we can describe it by introducing a relaxation time for collisions such that the collision integral is

$$\left(\frac{df}{dt}\right)_{coll} = -\frac{f - f_{FD}}{\tau}, \tag{2}$$

with f_{FD} being the Fermi-Dirac distribution.
To further describe electrons I will throughout the thesis make use of the semi-classical formulae

$$\dot{\boldsymbol{r}} = \boldsymbol{v} = \frac{1}{\hbar}\frac{\partial \epsilon}{\partial \boldsymbol{k}} \tag{3}$$

$$\dot{\boldsymbol{k}} = \frac{-e}{\hbar}(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}), \tag{4}$$

which when combined with the Boltzmann equation allows us to write

$$-\frac{f - f_{FD}}{\tau} = \frac{\partial f}{\partial t} - \frac{e}{\hbar}\boldsymbol{E} \cdot \boldsymbol{\nabla}_k f. \tag{5}$$

To get this I have also assumed that f is spatially uniform ($\frac{\partial f}{\partial \boldsymbol{r}} = \mathbf{0}$), and that there is no magnetic field ($\boldsymbol{B} = \mathbf{0}$), which is reasonable as long as the electric field from the light is not too large.

3 Finding a solution to the Boltzmann equation

To work with the Boltzmann equation, I will first assume that we can describe the applied electric field as

$$\boldsymbol{E}(t) = \boldsymbol{E}_0 e^{-i\omega t}. \tag{6}$$

I will also use the method of Parker et al. [1], and assume that the distribution function can be written as a infinite sum of exponentials

$$f(t) = \sum_{n=-\infty}^{\infty} f_n e^{-in\omega t}. \tag{7}$$

By doing so I can insert this in the Boltzmann equation (5) to get a recursive formula

$$\frac{-\sum_{n=-\infty}^{\infty} f_n e^{-in\omega t} + f_0}{\tau} = \sum_{n=-\infty}^{\infty} (-in\omega) f_n e^{-in\omega t} - \frac{e}{\hbar} \sum_{n=-\infty}^{\infty} e^{-i(n+1)\omega t} \boldsymbol{E}_0 \cdot \boldsymbol{\nabla}_{\boldsymbol{k}} f_n \tag{8}$$

$$\Rightarrow \frac{-\sum_{n=-\infty}^{\infty} f_n e^{-in\omega t} + f_0}{\tau} = \sum_{n=-\infty}^{\infty} (-in\omega) f_n e^{-in\omega t} - \frac{e}{\hbar} \sum_{n=-\infty}^{\infty} e^{-in\omega t} \boldsymbol{E}_0 \cdot \boldsymbol{\nabla}_{\boldsymbol{k}} f_{n-1} \tag{9}$$

To find a solution from this I will simply compare terms proportional to $e^{-in\omega t}$, such that for n = 0, we see that if we choose $f_0 = f_{FD}$

$$0 = -\frac{e}{\hbar} \boldsymbol{E}_0 \cdot \boldsymbol{\nabla}_{\boldsymbol{k}} f_{-1}. \tag{10}$$

From this we see that there is a solution of the form $f_{-1} = 0$.
And if we then move on to the other terms ($n \neq 0$), we see that the recursive formula tells us that

$$-\frac{f_n}{\tau} = -in\omega f_n - \frac{e}{\hbar} \boldsymbol{E}_0 \cdot \boldsymbol{\nabla}_{\boldsymbol{k}} f_{n-1} \tag{11}$$

$$\Rightarrow f_n = \frac{e}{\hbar} \frac{\boldsymbol{E}_0 \cdot \boldsymbol{\nabla}_{\boldsymbol{k}} f_{n-1}}{1/\tau - in\omega} \tag{12}$$

By then looking at the term for n = -1, we see that

$$f_{-1} = 0 = \frac{e}{\hbar} \frac{\boldsymbol{E}_0 \cdot \boldsymbol{\nabla}_{\boldsymbol{k}} f_{-2}}{1/\tau - in\omega}. \tag{13}$$

Which again allows us to find a solution of the form $f_{-2} = 0$. This can of course be continued such that for all negative numbers we see that we can find solutions of the form

$$f_{-n'} = 0 \quad for \quad n' \in \mathbb{N} \tag{14}$$

Which means we only need to consider the positive terms for our distribution function

$$f(t) = \sum_{n=0}^{\infty} f_n e^{-in\omega t} = f_0 + \sum_{n=1}^{\infty} \frac{e}{\hbar} \frac{\boldsymbol{E}_0 \cdot \boldsymbol{\nabla}_k f_{n-1}}{1/\tau - in\omega} e^{-in\omega t} \tag{15}$$

4 Electric transport

To describe electric transport in materials it is usually best describe it with the use of the current. Therefore I will here use that we can write the current density as [3]

$$\boldsymbol{j} = -e \int [d\boldsymbol{k}] \boldsymbol{v} (f - f_0). \tag{16}$$

I will throughout make use of $[d\boldsymbol{k}]$ as the integral over k-space, times 2 from the fact that electrons are spin $1/2$ particles, and divided by the appropriate factors of 2π, such that if we have a d-dimensional k-space then $[d\boldsymbol{k}] = d^d\boldsymbol{k}\, \frac{2}{(2\pi)^d}$.

If we define the current density in the α direction (with $\alpha \in \{x, y, z\}$) as j^α then we can write the current density as

$$j^\alpha = \sum_{n=1}^{\infty} \left\{ -e \int [d\boldsymbol{k}] v^\alpha f_n e^{-in\omega t} \right\} \tag{17}$$

$$\equiv \sum_{n=1}^{\infty} j^\alpha_{(n)} \tag{18}$$

We see that the integral involves factors of the distribution function, so I will start by finding a solution for f_n.

Starting from n = 1, we see

$$f_1 = \frac{e}{\hbar} \frac{(E_0)_\alpha}{1/\tau - i\omega} \frac{\partial f_0}{\partial k_\alpha} \tag{19}$$

$$= \frac{e}{\hbar} \frac{(E_0)_\alpha \frac{\partial \epsilon}{\partial k_\alpha}}{1/\tau - i\omega} \frac{\partial f_0}{\partial \epsilon}. \tag{20}$$

Quickly moving on to the second term of the distribution function (n=2) we we see that we can write this as

$$f_2 = \frac{e}{\hbar} \frac{(E_0)_\alpha}{1/\tau - 2i\omega} \frac{\partial}{\partial k_\alpha} \left(\frac{e}{\hbar} \frac{(E_0)_\beta}{1/\tau - i\omega} \frac{\partial f_0}{\partial k_\beta} \right) \tag{21}$$

$$= \frac{e^2}{\hbar^2} \frac{(E_0)_\alpha (E_0)_\beta}{(1/\tau - 2i\omega)(1/\tau - i\omega)} \frac{\partial^2 f_0}{\partial k_\alpha \partial k_\beta}. \tag{22}$$

And from this we see that a pattern emerges, that allows us to write any term with n>0 in the distribution on the form

$$f_n = \frac{e^n}{\hbar^n} \frac{\partial^n f_0}{\partial k_{\alpha_1} \dots \partial k_{\alpha_n}} \prod_{m=1}^{n} \frac{(E_0)_{\alpha_m}}{(1/\tau - mi\omega)}, \tag{23}$$

where α_i is any given direction, and note that I am using the Einstein summation convention, such that all α_i's are summed over. Using this in equation (17), we get that the current density is

$$j^\alpha = \sum_{n=1}^{\infty} -e \int [d\boldsymbol{k}] v^\alpha \frac{e^n}{\hbar^n} \frac{\partial^n f_0}{\partial k_{\alpha_1} \dots \partial k_{\alpha_n}} \prod_{m=1}^{n} \frac{(E_0)_{\alpha_m}}{(1/\tau - mi\omega)} e^{-in\omega t} \tag{24}$$

$$= \sum_{n=1}^{\infty} \frac{-e^{n+1}}{\hbar^n} \prod_{m=1}^{n} \left(\frac{E_{\alpha_m}}{(1/\tau - mi\omega)} \right) \int [d\boldsymbol{k}] v^\alpha \frac{\partial^n f_0}{\partial k_{\alpha_1} \dots \partial k_{\alpha_n}}. \tag{25}$$

Which means that, by the way I have defined the n'th term of the current density, we can write these terms as

$$j^\alpha_{(n)} = \frac{-e^{n+1}}{\hbar^n} \prod_{m=1}^{n} \left(\frac{E_{\alpha_m}}{(1/\tau - mi\omega)} \right) \int [d\boldsymbol{k}] v^\alpha \frac{\partial^n f_0}{\partial k_{\alpha_1} \dots \partial k_{\alpha_n}}. \tag{26}$$

We notice that the terms involves derivatives of the Fermi Dirac distribution. But since the derivatives of the distribution function are difficult quantities to work with, I will use the fact that we can use integration by parts to move the derivatives of the distribution function to the velocity instead. I will tacitly assume that all boundary terms in in the integration by parts play no role for the current. By doing so we see that we can write the current density as

$$j^\alpha_{(n)} = \frac{-e^{n+1}}{\hbar^n} \prod_{m=1}^{n} \left(\frac{E_{\alpha_m}}{(1/\tau - mi\omega)} \right) (-1)^n \int [d\boldsymbol{k}] f_0 \frac{\partial^n v^\alpha}{\partial k_{\alpha_1} \dots \partial k_{\alpha_n}}. \tag{27}$$

We notice that since partial derivatives commute, if we define the n'th order conductivity such that $j^\alpha_{(n)} = \sigma^{\alpha\alpha_1 \dots \alpha_n} E_{\alpha_1} \dots E_{\alpha_n}$. Then the conductivity has to be symmetric in the upper indices, which I will make use of later on.
It is however most often more useful to find the current density using integration by parts only n-1 times, such that the current density terms are

$$j^\alpha_{(n)} = \frac{(-1)^{n-1} e^{n+1}}{\hbar^{n+1}} \prod_{m=1}^{n} \left(\frac{E_{\alpha_m}}{(1/\tau - mi\omega)} \right) \int [d\boldsymbol{k}] \left(-\frac{\partial f_0}{\partial \epsilon} \right) \frac{\partial \epsilon}{\partial k_{\alpha_1}} \frac{\partial^n \epsilon}{\partial k_\alpha \partial k_{\alpha_2} \dots \partial k_{\alpha_n}}. \tag{28}$$

The reason that this is more useful, is that if we assume that we are in the low temperature limit ($k_B T << \epsilon$), then we can rewrite the derivative of the Fermi-Dirac distribution as a delta function instead, such that the current density is

$$j^\alpha_{(n)} \approx \frac{(-1)^{n-1} e^{n+1}}{\hbar^{n+1}} \prod_{m=1}^{n} \left(\frac{E_{\alpha_m}}{(1/\tau - mi\omega)} \right) \int [d\boldsymbol{k}] \delta(\epsilon(\boldsymbol{k}) - \epsilon_F) \frac{\partial \epsilon}{\partial k_{\alpha_1}} \frac{\partial^n \epsilon}{\partial k_\alpha \partial k_{\alpha_2} \dots \partial k_{\alpha_n}}. \tag{29}$$

To make this easier to work with, I will use that we can change the variable of the delta function.

$$\delta(\epsilon(\boldsymbol{k}) - \epsilon_F) = \frac{\delta(\boldsymbol{k} - \boldsymbol{k}(\epsilon_F))}{\left| \frac{\partial \epsilon(\boldsymbol{k})}{\partial \boldsymbol{k}} \Big|_{\boldsymbol{k}=\boldsymbol{k}(\epsilon_F))} \right|} = \frac{\delta(\boldsymbol{k} - \boldsymbol{k}_F)}{\hbar v(\boldsymbol{k}_F)} = \frac{\delta(\boldsymbol{k} - \boldsymbol{k}_F)}{\sqrt{\sum_{\alpha'} \left(\frac{\partial \epsilon}{\partial k_{\alpha'}} \right)^2}} \tag{30}$$

Inserting this change of variable we see that the current density terms instead becomes

$$j^{\alpha}_{(n)} \approx \frac{(-1)^{n-1}e^{n+1}}{\hbar^{n+1}} \frac{2}{(2\pi)^d} \prod_{m=1}^{n} \left(\frac{E_{\alpha_m}}{(1/\tau - mi\omega)} \right) \oint_{C_F} d^{d-1}\boldsymbol{k} \frac{1}{\sqrt{\sum_{\alpha'} \left(\frac{\partial \epsilon}{\partial k_{\alpha'}} \right)^2}} \frac{\partial \epsilon}{\partial k_{\alpha_1}} \frac{\partial^n \epsilon}{\partial k_{\alpha} \partial k_{\alpha_2} \ldots \partial k_{\alpha_n}}. \tag{31}$$

Here C_F is the contour of the Fermi surface, which in a 2D k-space is a line, and in 3D k-space a surface.

5 Recovering the Drude conductivity

Now that we have a general formula for the current density terms, let us instead take a step back from all the different orders for the current, and only consider the first order. This in turn should let us recover the well known Drude conductivity.

I will start with finding the static conductivity, i.e $\omega = 0$. I will do this by starting with equation (27) for the current density.

$$j^{\alpha}_{(1)}(\omega = 0) = \frac{e^2}{\hbar} \tau E_{\beta} \int [d\boldsymbol{k}] f_0 \frac{\partial v^{\alpha}}{\partial k_{\beta}} \tag{32}$$

Here I will start off by using that we can define an effective mass such that $\frac{1}{m_*} = \frac{1}{\hbar^2} \frac{\partial^2 \epsilon}{\partial k^2}$. By then assuming that the mass is not a function of the wave vector k, we can move it outside of the integral.

$$j^{\alpha}_{(1)}(\omega = 0) = e^2 (m_*^{-1})^{\alpha\beta} \tau E_{\beta} \int [d\boldsymbol{k}] f_0 \tag{33}$$

Then we can use that the integral over just the distribution function, is simply the same as the electron density n, so we see that

$$j^{\alpha}_{(1)}(\omega = 0) = ne^2 \tau (m_*^{-1})^{\alpha\beta} E_{\beta}. \tag{34}$$

This formula of course lets us define that the conductivity is of the form

$$\sigma_0^{\alpha\beta} \equiv ne^2 \tau (m_*^{-1})^{\alpha\beta} \tag{35}$$

such that $j^{\alpha}_{(1)}(\omega = 0) = \sigma_0^{\alpha\beta} E_{\beta}$ as normal.

If we then assume that the effective mass tensor can be described by a scalar, i.e $m_*^{-1} = \frac{1}{d} \delta_{\alpha\beta} (m_*^{-1})^{\alpha\beta}$, we recover the well known DC Drude conductivity.

$$\sigma_0 = \frac{ne^2 \tau}{m_*} \tag{36}$$

If we now consider the AC case, i.e $\omega \neq 0$, we get that the current density is of the form

$$j^{\alpha}_{(1)} = \frac{e^2}{\hbar} \frac{E_{\beta}}{1/\tau - i\omega} \int [d\boldsymbol{k}] f_0 \frac{\partial v^{\alpha}}{\partial k_{\beta}}. \tag{37}$$

This we can simply compare to the static case, such that we we write this current density as

$$j^{\alpha}_{(1)} = \frac{\sigma_0^{\alpha\beta}}{1 - i\omega\tau} E_{\beta} \tag{38}$$

For which we once again recognise the conductivity as the well known AC conductivity for the Drude model

$$\sigma^{\alpha\beta}_{AC} = \frac{\sigma_0^{\alpha\beta}}{1 - i\omega\tau}. \tag{39}$$

6 Electric transport for a free electron model

Using what I found to describe the current, I will now analyse the physics in the use of a free electron model, for which we have the valence electrons of each atom in the material flying freely around inside the material. To describe this model I will make use of the energy formula for this type of model

$$\epsilon = \frac{\hbar^2 \boldsymbol{k}^2}{2m} = \sum_{\alpha'} \frac{\hbar^2 k^2_{\alpha'}}{2m} \tag{40}$$

From what we found earlier we know that to find the currents, we first need to calculate the different derivatives of this energy.
So starting with the first and second derivatives we get

$$\frac{\partial \epsilon}{\partial k_{\alpha}} = \frac{\hbar^2 k^{\alpha}}{m} \tag{41}$$

$$\frac{\partial^2 \epsilon}{\partial k_{\alpha} \partial k_{\beta}} = \delta^{\alpha\beta} \frac{\hbar^2}{m} \tag{42}$$

We see immediately that for derivatives of more than two times we have 0, for this type of electron model.

$$\frac{\partial^n \epsilon}{\partial k_{\alpha_1} \ldots \partial k_{\alpha_n}} = 0 \quad \text{for n > 2} \tag{43}$$

Using this together with equation (31) for the current densities, we see that for the first order we get

$$j^{\alpha}_{(1)} = \frac{e^2}{m}\frac{2}{(2\pi)^d}\frac{E_\beta}{(1/\tau - i\omega)}\oint_{C_F} d^{d-1}\boldsymbol{k}\frac{k^\alpha k^\beta}{\sqrt{\sum_{\alpha'} k^2_{\alpha'}}}. \tag{44}$$

By defining that for the 3D case, the x, y and z components can be described in the k-space, by 2 different angles θ and ϕ, we can write

$$k^\alpha = \begin{cases} k_F(\theta,\phi,\mu)\sin(\theta)\cos(\phi) & \text{for } \alpha = x \\ k_F(\theta,\phi,\mu)\sin(\theta)\sin(\phi) & \text{for } \alpha = y \\ k_F(\theta,\phi,\mu)\cos(\theta) & \text{for } \alpha = z \end{cases} \tag{45}$$

Here we have the azimuthal angle $\theta \in [0,\pi]$ and the polar angle $\phi \in [0, 2\pi[$.And the Fermi wave vector k_F is given by the formula $\epsilon(k_F) = \epsilon_F = \mu$, where μ is the usual chemical potential.
This in turn lets us write that the conductivity tensor for 3D space is

$$\sigma^{\alpha\beta} = \frac{e^2}{m}\frac{2}{(2\pi)^3}\frac{1}{(1/\tau - i\omega)}\int_0^\pi d\theta\int_0^{2\pi} d\phi k_F(\theta,\phi,\mu)\sin(\theta)k^\alpha k^\beta \tag{46}$$

$$= \frac{e^2}{m}\frac{2}{(2\pi)^3}\frac{1}{1/\tau - i\omega}k_F^3(\mu)\int_0^\pi d\theta\int_0^{2\pi} d\phi\sin(\theta)\frac{k^\alpha k^\beta}{k_F^2} \tag{47}$$

$$= \begin{cases} \frac{e^2}{m}\frac{2}{(2\pi)^3}\frac{1}{1/\tau - i\omega}k_F^3(\mu)\frac{4\pi}{3} & \text{for } \alpha = \beta \\ 0 & \text{otherwise} \end{cases} \tag{48}$$

I have in the second step made use of the fact that the Fermi wave vector is a constant with respect to the angles in this model. And I have in step three made use of the parities of k^α and k^β.
If we now use that for the 3D case, we have that the number of states for this type of model, is know from statistical mechanics by the formula $N = 2\frac{4\pi}{3}k_F^3\frac{L^3}{(2\pi)^3}$. We can get the electron density $n = \frac{N}{L^3} = \frac{2}{(2\pi)^3}\frac{4\pi}{3}k_F^3$.

This, not surprisingly, once again gives us back the AC Drude model, but here we observe by the form of our energy that the effective mass is exactly the electron mass, as expected.

$$\sigma^{\alpha\beta} = \frac{ne^2\tau}{m}\frac{\delta^{\alpha\beta}}{1 - i\omega\tau} = \frac{\sigma_0}{1 - i\omega\tau}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{49}$$

For higher orders we see directly from equation (27) that all orders of n > 1 involves differntials of orders 3 or higher, which according to equation (43) means that it all gives

0. And since all orders of n > 1 is zero we can simply write the full current density of the free electron model as

$$j^{\alpha} = \frac{\sigma_0}{1 - i\omega\tau} E^{\alpha} \tag{50}$$

7 The tight binding model

Since the simple free electron model did not have any terms with orders of n > 1, I will move on to a more physical model. I will make use of the tight binding model, where the valence electrons of atoms are restricted to only be able to jump between the nearest neighbors. To describe the nearest neighbor position it is normal to introduce the lattice vectors in normal space $\boldsymbol{a}_i$, such that we can describe crystalline materials, with repeating cells of atoms. By doing so we can write that the energy must be on the form [2]

$$\epsilon = \epsilon_0 - t \sum_i e^{i\boldsymbol{k}\cdot\boldsymbol{a}_i}, \tag{51}$$

where t is the energy term describing the movement from one atom to the neighbor, the so called hopping term, I have here assumed that the energy is the same for all of the nearest neighbors, but this does of course not need to be the case in general.

8 Electric transport for a simple cubic tight binding model

I will here make use of the tight binding model, on a material with a simple cubic crystal structure. I could as well work with the orthorhombic crystal structure, which is a generalization of the cubic structure. But as a start I will use the simple cubic model, for which I can describe the system using the lattice vectors $\boldsymbol{a}_i \in \{(\pm a, 0, 0), (0, \pm a, 0), (0, 0, \pm a)\}$, which gives the well known energy

$$\epsilon = \epsilon_0 - 2t \sum_{\alpha'} \cos\left(a k_{\alpha'}\right) \tag{52}$$

8.1 First order

Again I will start the analysis for this model by determining the derivatives of the energy.
So for the first derivative of the energy we get that it is

$$\frac{\partial \epsilon}{\partial k_\alpha} = 2at \sin\left(a k^{\alpha}\right). \tag{53}$$

Then simply using equation (31), we see that the first order current density can be written as

$$j^{\alpha}_{(1)} = \frac{e^2}{\hbar^2} \frac{4at}{(2\pi)^d} \frac{E_\beta}{1/\tau - i\omega} \oint_{C_F} d^{d-1}\boldsymbol{k} \frac{\sin\left(a k^{\alpha}\right)\sin\left(a k^{\beta}\right)}{\sqrt{\sum_{\alpha'} \sin^2\left(a k_{\alpha'}\right)}}. \tag{54}$$

Then by comparing to equation (32), we see that we can define a static conductivity of the form

$$\sigma_0^{\alpha\beta} = \frac{e^2\tau}{\hbar^2}\frac{4at}{(2\pi)^d}\oint_{C_F} d^{d-1}\boldsymbol{k}\frac{\sin(ak^\alpha)\sin\left(ak^\beta\right)}{\sqrt{\sum_{\alpha'}\sin^2(ak_{\alpha'})}}. \tag{55}$$

And then by comparing this to the equation for the conductivity tensor in (35), as a function of the effective mass tensor, it is clear that

$$\frac{n}{m_*^{\alpha\beta}} = \frac{4at}{\hbar^2(2\pi)^d}\oint_{C_F} d^{d-1}\boldsymbol{k}\frac{\sin(ak^\alpha)\sin\left(ak^\beta\right)}{\sqrt{\sum_{\alpha'}\sin^2(ak_{\alpha'})}}. \tag{56}$$

If we work in 3D, we have that the conductivity is then given by the formula

$$\sigma_0^{\alpha\beta} = \frac{e^2\tau}{\hbar^2}\frac{at}{2\pi^3}\int_0^\pi d\theta\int_0^{2\pi} d\phi\, k_F^2(\theta,\phi,\mu)\sin(\theta)\frac{\sin(ak^\alpha)\sin\left(ak^\beta\right)}{\sqrt{\sin^2(ak_x)+\sin^2(ak_y)+\sin^2(ak_z)}} \tag{57}$$

To find out how the conductivity tensor is structured, I have analysed the parity of the different terms inside of the integral. These parities I have summed up in table 1.
From that we see see that if $\alpha \neq \beta$ the parities mean that the integral becomes 0. And as we might expect we get for all $\alpha = \beta$ the same value. To see that they all have the same value, I have chosen to make a graph of the integral, which is shown in figure 1.

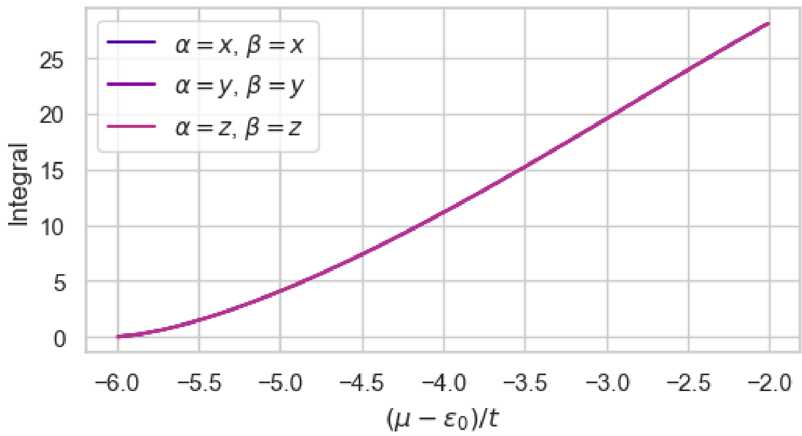

Figure 1: The integral from equation (57) with a=1. All three integrals are equal and therefore the lines coincide.

8.2 Second order

For the second order current density I need to once again find a derivative, which this time is the second

$$\frac{\partial^2 \epsilon}{\partial k_\alpha \partial k_\beta} = \delta^{\alpha\beta} 2a^2 t \cos\big(ak^\alpha\big) \qquad \text{(No summation over } \alpha\text{)} \tag{58}$$

Please note that for the rest of the calculations, where I will be using these second and higher order derivatives, I will omit the comments that there should not be summed over α.

Now to find the actual second order current density, I will again use equation (31) to see that it becomes

$$j^\alpha_{(2)} = \frac{-e^3}{\hbar^3} \frac{4a^2 t}{(2\pi)^d} \frac{E_\beta E_\gamma \delta^{\alpha\gamma}}{(1/\tau - i\omega)(1/\tau - 2i\omega)} \oint_{C_F} d^{d-1}\boldsymbol{k} \frac{\sin\left(ak^\beta\right)\cos\big(ak^\alpha\big)}{\sqrt{\sum_{\alpha'} \sin^2(ak_{\alpha'})}} \tag{59}$$

By then once again looking in table 1, we see that now by the parities, for all α and β the integral becomes 0, which of course means that $j^\alpha_{(2)} = 0$.

	Expression	About $\phi = \pi$	About $\phi = \frac{3}{2}\pi$	About $\theta = \frac{\pi}{2}$
(1)	k_F	even	even	even
(2)	$\cos(a_x\, k_F \sin(\theta)\cos(\phi))$	even	even	even
(3)	$\sin(a_x\, k_F \sin(\theta)\cos(\phi))$	even	odd	even
(4)	$\cos\left(a_y\, k_F \sin(\theta)\sin(\phi)\right)$	even	even	even
(5)	$\sin\left(a_y\, k_F \sin(\theta)\sin(\phi)\right)$	odd	even	even
(6)	$\cos(a_z\, k_F \cos(\theta))$	even	even	even
(7)	$\sin(a_z\, k_F \cos(\theta))$	even	even	odd
(8)	$\sqrt{\sin^2(a_x k_x) + \sin^2(a_y k_y) + \sin^2(a_z k_z)}$	even	even	even
(9)	$\sin(\theta)$	even	even	even

Table 1: Table of parities

8.3 Generalizing to n'th order

Now that we have some examples for the first two orders, the procedure is relatively simple, for the n'th order term we need to find the n'th derivative of the energy and use this to write a current. So I will start by finding the n'th derivative, which here is simple because sine and cosine transform into each other under differentiation.

$$\frac{\partial^n}{\partial k_{\alpha_1} \dots \partial k_{\alpha_n}} \epsilon(\boldsymbol{k}) = \begin{cases} (-1)^{\frac{n-1}{2}} 2a^n t \delta^{\alpha_1 \alpha_2} \dots \delta^{\alpha_1 \alpha_n} \sin\left(ak^{\alpha_1}\right) & \text{for n odd} \\ (-1)^{\frac{n+2}{2}} 2a^n t \delta^{\alpha_1 \alpha_2} \dots \delta^{\alpha_1 \alpha_n} \cos\left(ak^{\alpha_1}\right) & \text{for n even} \end{cases} \tag{60}$$

Again note that there is supposed to be no summation over α. By once again inserting into the general formula for the current density (31), we see that we can write the current density for the simple cubic tight binding model as

$$j^{\alpha}_{(n)} = \begin{cases} \frac{(-1)^{\frac{n-1}{2}} e^{n+1}}{\hbar^{n+1}} \frac{4a^n t}{(2\pi)^d} \frac{E_{\alpha_1} \dots E_{\alpha_n} \delta^{\alpha\alpha_2} \dots \delta^{\alpha\alpha_n}}{\prod_{m=1}^{n} (1/\tau - mi\omega)} \oint_{C_F} d^{d-1}\boldsymbol{k} \frac{\sin\left(ak^{\alpha_1}\right) \sin\left(ak^{\alpha}\right)}{\sqrt{\sum_{\alpha'} \sin^2(ak_{\alpha'})}} & \text{for n odd} \\ \frac{(-1)^{\frac{n}{2}} e^{n+1}}{\hbar^{n+1}} \frac{4a^n t}{(2\pi)^d} \frac{E_{\alpha_1} \dots E_{\alpha_n} \delta^{\alpha\alpha_2} \dots \delta^{\alpha\alpha_n}}{\prod_{m=1}^{n} (1/\tau - mi\omega)} \oint_{C_F} d^{d-1}\boldsymbol{k} \frac{\sin\left(ak^{\alpha_1}\right) \cos\left(ak^{\alpha}\right)}{\sqrt{\sum_{\alpha'} \sin^2(ak_{\alpha'})}} & \text{for n even} \end{cases} \tag{61}$$

We immediately notice that the integral for all of the even orders are the same, which means they are all zero, from what we found for the second order. And from what we found for the first order we see that if $\alpha \neq \alpha_1$ the integral becomes zero here as well, meaning that the overall current can be determined by the conductivity tensors

$$\sigma^{\alpha\alpha_1 \dots \alpha_n} = \begin{cases} \frac{(-1)^{\frac{n-1}{2}} e^{n+1}}{\hbar^{n+1}} \frac{4a^n t}{(2\pi)^d} \frac{1}{\prod_{m=1}^{n} (1/\tau - mi\omega)} \oint_{C_F} d^{d-1}\boldsymbol{k} \frac{\sin\left(ak^{\alpha_1}\right) \sin\left(ak^{\alpha}\right)}{\sqrt{\sum_{\alpha'} \sin^2(ak_{\alpha'})}} & \text{for n odd and } \alpha = \alpha_i \forall i \\ 0 & \text{otherwise} \end{cases} \tag{62}$$

By reintroducing the static conductivity we can find that the n'th order conductivity is given by

$$\sigma^{\alpha\alpha_1 \dots \alpha_n} = \begin{cases} (-1)^{\frac{n-1}{2}} \left(\frac{ea\tau}{\hbar}\right)^{n-1} \frac{\sigma_0^{\alpha\alpha}}{\prod_{m=1}^{n} (1 - mi\tau\omega)} & \text{for n odd and } \alpha = \alpha_i \forall i \\ 0 & \text{otherwise} \end{cases} \tag{63}$$

We see that if we define that $\sigma_{(n)} \equiv \sigma^{\alpha\alpha_1 \dots \alpha_n}$ with $\alpha = \alpha_i \forall i$, then the scaling factor between the odd orders is.

$$\frac{\sigma_{(n+2)}}{\sigma_{(n)}} = -\left(\frac{ea\tau}{\hbar}\right)^2 \frac{1}{(1 - (n+1)i\tau\omega)(1 - (n+2)i\tau\omega)} \tag{64}$$

From this ratio we see that it is highly dependent on the factor $\frac{ea\tau}{\hbar}$. I have chosen to plot the first three odd orders of the conductivity in figure 2, with the relatively large ratio of 0.5 $\left[\frac{m}{V}\right]$.

Going on we can see that we simply can write the total current as

$$j^{\alpha} = \sum_{k=0}^{\infty} (-1)^k \left(\frac{eaE^{\alpha}\tau}{\hbar}\right)^{2k} \frac{\sigma_0^{\alpha\alpha}}{\prod_{m=1}^{2k+1} (1 - mi\omega\tau)} E^{\alpha} \tag{65}$$

Moving all the constants outside we see that the sum is

$$j^{\alpha} = \sigma_0^{\alpha\alpha} E^{\alpha} \sum_{k=0}^{\infty} (-1)^k \left(\frac{eaE^{\alpha}\tau}{\hbar}\right)^{2k} \frac{1}{\prod_{m=1}^{2k+1} (1 - mi\omega\tau)} \tag{66}$$

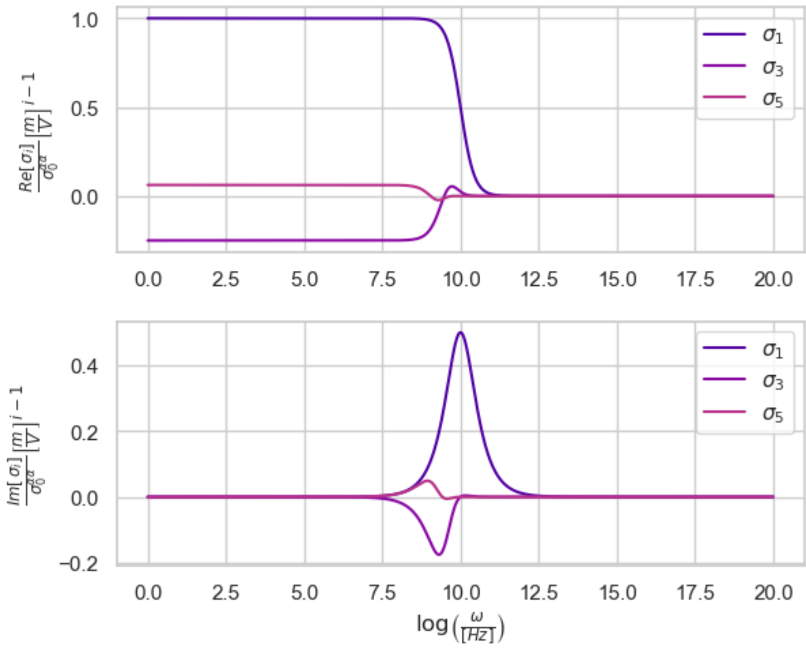

Figure 2: The odd order conductivities from equation (63) as a function of the angular frequency ω, with the scaling factor $\frac{ea\tau}{\hbar} = 0.5\left[\frac{m}{V}\right]$, and $\tau = 10^{-10}s$

We see that this sum of course involves the usual first order term, but that all higher order terms depend on the factor $\frac{eaE^{\alpha}\tau}{\hbar}$. And since the denominator of the fraction has the factors that it has. We see that if the factor of $\frac{eaE^{\alpha}\tau}{\hbar}$>1 the sum diverges towards infinity. Which tells us, that for large E-fields our model must break. Either because of the semi classical Boltzmann equation not working for these strong fields, or because the tight binding model no longer hold.
I have plotted the current in figure 3, for different factors, with the first order current as a reference.

I will now try to analyze this formula for the current density in the case where $\omega\tau >> 1$. Here the current density must be

$$j^{\alpha} = i\frac{\sigma_0^{\alpha\alpha}\hbar}{ea\tau}\sum_{k=0}^{\infty}\frac{1}{(2k+1)!}\left(\frac{eaE^{\alpha}}{\hbar\omega}\right)^{2k+1} \tag{67}$$

$$= i\frac{\sigma_0^{\alpha\alpha}\hbar}{ea\tau}\sinh\left(\frac{eaE^{\alpha}}{\hbar\omega}\right). \tag{68}$$

I will of course also analyze the completely opposite case where $\omega\tau << 1$, for which

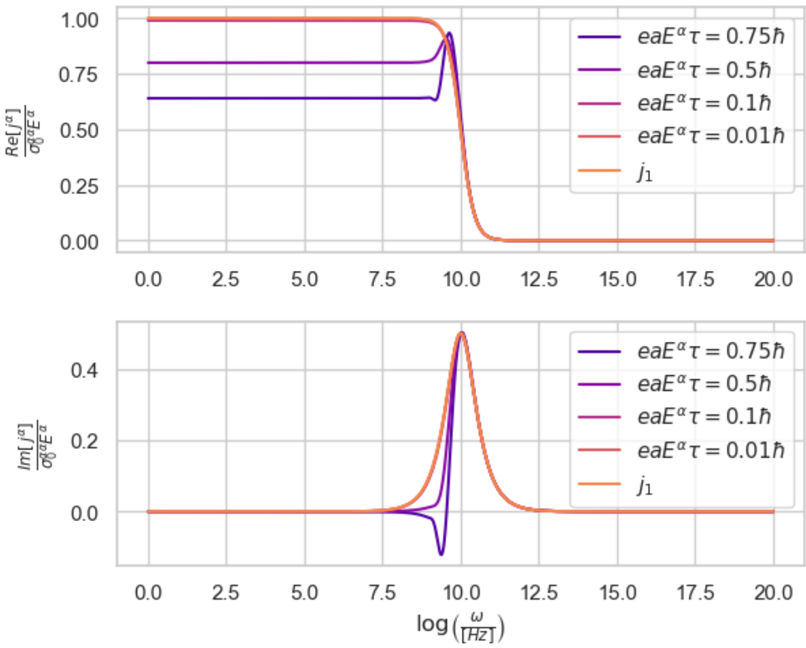

Figure 3: The current from equation (66) summed for the first 200 terms, for the time t=0, with $\tau = 10^{-10}s$, and different scaling factors, with the first order current as a reference. It is clear that if the scaling factors are small, the graphs almost coincide.

the current density is given by

$$j^\alpha = \sigma_0^{\alpha\alpha} E^\alpha \sum_{k=0}^{\infty} \left(- \left(\frac{eaE^\alpha\tau}{\hbar} \right)^2 \right)^k . \tag{69}$$

This is a geometric series, and this only converge if the value inside of the power series is less than 1, i.e if $\left(\frac{eaE^\alpha\tau}{\hbar}\right)^2 < 1$, in which case it becomes

$$j^\alpha = \sigma_0^{\alpha\alpha} E^\alpha \frac{1}{1 + \left(\frac{eaE^\alpha\tau}{\hbar}\right)^2}. \tag{70}$$

8.4 Simple orthorhombic lattice

As a quick side note of our analysis of the simple cubic lattice. We can clearly see from our formulae, that if we use the lattice vectors of the simple orthorhombic lattice $\boldsymbol{a}_i \in \left\{ (\pm a_x, 0, 0), (0, \pm a_y, 0), (0, 0, \pm a_z) \right\}$ instead. All that changes in all of the formulae is that $a \to a^\alpha$.

So then all in all the current density would be

$$j^{\alpha}_{(ortho)} = \sigma_0^{\alpha\alpha} E^{\alpha} \sum_{k=0}^{\infty} (-1)^k \left(\frac{ea^{\alpha} E^{\alpha} \tau}{\hbar} \right)^{2k} \frac{1}{\prod_{m=1}^{2k+1} (1 - mi\omega\tau)}. \tag{71}$$

9 Electric transport for a face centered cubic tight binding model

Since most materials in nature have a more complicated structure than the simple cubic, I will move on to the more common face centered cubic (FCC) lattice structure in 3D. Here the lattice vectors are $\boldsymbol{a}_i \in \left\{ (\pm\frac{a}{2}, \pm\frac{a}{2}, 0), (\pm\frac{a}{2}, 0, \pm\frac{a}{2}), (0, \pm\frac{a}{2}, \pm\frac{a}{2}) \right\}$, where the $\pm$'s are all independent.
This in turn gives us back an energy of the form

$$\epsilon = \epsilon_0 - 2t \left[\sum_{\alpha' \neq \beta'} \cos\left(\frac{ak'_{\alpha}}{2} \right) \cos\left(\frac{ak_{\beta'}}{2} \right) \right] \tag{72}$$

$$= \epsilon_0 - 4t \left[\cos\left(\frac{ak_x}{2} \right) \cos\left(\frac{ak_y}{2} \right) + \cos\left(\frac{ak_x}{2} \right) \cos\left(\frac{ak_z}{2} \right) + \cos\left(\frac{ak_y}{2} \right) \cos\left(\frac{ak_z}{2} \right) \right] \tag{73}$$

9.1 First order

Once again we will need the derivatives, so I will start by taking the first derivative of the energy

$$\frac{\partial \epsilon}{\partial k_{\alpha}} = 4t\frac{a}{2} \left[\sum_{\alpha' \neq \alpha} \sin\left(\frac{ak^{\alpha}}{2} \right) \cos\left(\frac{ak^{\alpha'}}{2} \right) \right]. \tag{74}$$

I will immediately move on to the second derivative, where we see two cases, one for $\alpha = \beta$ and one for $\alpha \neq \beta$

$$\frac{\partial^2 \epsilon}{\partial k_{\alpha} \partial k_{\beta}} = \begin{cases} 4t \left(\frac{a}{2}\right)^2 \left[\sum_{\alpha' \neq \alpha} \cos\left(\frac{ak^{\alpha}}{2} \right) \cos\left(\frac{ak^{\alpha'}}{2} \right) \right] & \text{for } \alpha = \beta \\ -4t \left(\frac{a}{2}\right)^2 \sin\left(\frac{ak^{\alpha}}{2} \right) \sin\left(\frac{ak^{\beta}}{2} \right) & \text{for } \alpha \neq \beta \end{cases} \tag{75}$$

Since it is not yet clear what the pattern will be, I will find the third derivative

$$\frac{\partial^3 \epsilon}{\partial k_{\alpha} \partial k_{\beta} \partial k_{\gamma}} = \begin{cases} -4t \left(\frac{a}{2}\right)^3 \left[\sum_{\alpha' \neq \alpha} \sin\left(\frac{ak^{\alpha}}{2} \right) \cos\left(\frac{ak^{\alpha'}}{2} \right) \right] & \text{for } \alpha = \beta = \gamma \\ -4t \left(\frac{a}{2}\right)^3 \cos\left(\frac{ak^{\alpha}}{2} \right) \sin\left(\frac{ak^{\gamma}}{2} \right) & \text{for } \alpha = \beta \neq \gamma \\ 0 & \text{for } \alpha \neq \beta \neq \gamma \ \ \& \ \ \alpha \neq \gamma \end{cases} \tag{76}$$

Notice I have only written 3 of the cases, since we know that we can obtain the others by simply interchanging indices, since the partial derivatives commute. We also note that if the energy is differentiated with respect to the three directions we get 0.

Now that we have up to the third derivative, we can generalize the derivatives. I have chosen to find the general formula, using indices $\alpha, \beta, \gamma \in \{x, y, z\}$, with $\alpha \neq \beta$, $\alpha \neq \gamma$ and $\beta \neq \gamma$

$$\frac{\partial^n \epsilon}{\partial k_\alpha^{n_\alpha} \partial k_\beta^{n_\beta} \partial k_\gamma^{n_\gamma}} = \begin{cases} (-1)^{\frac{n+2}{2}} 4t \left(\frac{a}{2}\right)^n \left[\sum_{\alpha' \neq \alpha} \cos\left(\frac{ak^\alpha}{2}\right) \cos\left(\frac{ak^{\alpha'}}{2}\right)\right] & \text{for n even \& } n = n_\alpha \\ (-1)^{\frac{n-1}{2}} 4t \left(\frac{a}{2}\right)^n \left[\sum_{\alpha' \neq \alpha} \sin\left(\frac{ak^\alpha}{2}\right) \cos\left(\frac{ak^{\alpha'}}{2}\right)\right] & \text{for n odd \& } n = n_\alpha \\ (-1)^{\frac{n+2}{2}} 4t \left(\frac{a}{2}\right)^n \sin\left(\frac{ak^\alpha}{2}\right) \sin\left(\frac{ak^\beta}{2}\right) & \text{for n even \& } n_\alpha, n_\beta \geq 1 \text{ \& } n_\gamma = 0 \\ (-1)^n 4t \left(\frac{a}{2}\right)^n \cos\left(\frac{ak^\alpha}{2}\right) \sin\left(\frac{ak^\beta}{2}\right) & \text{for n odd \& } n_\alpha \text{ even \& } n_\alpha, n_\beta \geq 1 \text{ \& } n_\gamma = 0 \\ 0 & \text{for } n_\alpha, n_\beta, n_\gamma \geq 1 \end{cases} \tag{77}$$

Since we now have all of the derivatives of the energy, we can then once again determine the n'th order current density using (31).

$$j_{(n)}^\alpha = \frac{(-1)^{n-1} e^{n+1}}{\hbar^{n+1}} \frac{2}{(2\pi)^3} \prod_{m=1}^{n} \left(\frac{E_{\alpha_m}}{(1/\tau - mi\omega)}\right) \cdot \oint_{C_F} d^3\boldsymbol{k} \frac{\sum_{\alpha' \neq \alpha_1} \sin\left(\frac{ak^{\alpha_1}}{2}\right) \cos\left(\frac{ak^{\alpha'}}{2}\right)}{\sqrt{\sum_{\alpha'} \sin^2\left(\frac{ak^{\alpha'}}{2}\right) \left[\sum_{\alpha'' \neq \alpha'} \cos\left(\frac{ak^{\alpha''}}{2}\right)\right]^2}} \frac{\partial^n \epsilon}{\partial k_\alpha \partial k_{\alpha_2} \dots \partial k_{\alpha_n}} \tag{78}$$

I will of course start by defining what the static conductivity is for this current density

$$\sigma_0^{\alpha\beta} = \frac{e^2 \tau}{\hbar^2} \frac{4at}{(2\pi)^3} \oint_{C_F} d^3\boldsymbol{k} \frac{\left[\sum_{\alpha' \neq \beta} \sin\left(\frac{ak^\beta}{2}\right) \cos\left(\frac{ak^{\alpha'}}{2}\right)\right] \left[\sum_{\alpha' \neq \alpha} \sin\left(\frac{ak^\alpha}{2}\right) \cos\left(\frac{ak^{\alpha'}}{2}\right)\right]}{\sqrt{\sum_{\alpha'} \sin^2\left(\frac{ak^{\alpha'}}{2}\right) \left[\sum_{\alpha'' \neq \alpha'} \cos\left(\frac{ak^{\alpha''}}{2}\right)\right]^2}}, \tag{79}$$

We see again by the parity argument, that the integral reduces to 0 if $\alpha \neq \beta$, i.e we can write the static conductivity on the form $\sigma_0^{\alpha\beta} = \delta^{\alpha\beta} \sigma_0$.

9.2 Second order

If we look at the second order conductivity, we surprisingly once again see that by the parity, all the terms equal 0, no matter which α , β & γ one chooses.

$$\sigma^{\alpha\beta\gamma} = \frac{-e^3}{\hbar^3}\frac{2}{(2\pi)^3}\frac{1}{\prod_{m=1}^{2}(1/\tau - mi\omega)} \cdot \oint_{C_F} d^3\boldsymbol{k}\frac{\sum_{\alpha'\neq\beta}\sin\left(\frac{ak^{\beta}}{2}\right)\cos\left(\frac{ak^{\alpha'}}{2}\right)}{\sqrt{\sum_{\alpha'}\sin^2\left(\frac{ak^{\alpha'}}{2}\right)\left[\sum_{\alpha''\neq\alpha'}\cos\left(\frac{ak^{\alpha''}}{2}\right)\right]^2}}\frac{\partial^2\epsilon}{\partial k_\alpha \partial k_\gamma} \tag{80}$$

And by the general equation for the derivatives (77), we once again see the quite remarkable result, that not only does this second order integrate to zero, but *all* even orders integrates to zero, no matter our choice of directions.

9.3 Third order

Moving on to the third order we see that the conductivity is described by

$$\sigma^{\alpha\alpha_1\alpha_2\alpha_3} = \frac{e^4}{\hbar^4}\frac{2}{(2\pi)^3}\frac{1}{\prod_{m=1}^{3}(1/\tau - mi\omega)} \cdot \oint_{C_F} d^3\boldsymbol{k}\frac{\sum_{\alpha'\neq\alpha_1}\sin\left(\frac{ak^{\alpha_1}}{2}\right)\cos\left(\frac{ak^{\alpha'}}{2}\right)}{\sqrt{\sum_{\alpha'}\sin^2\left(\frac{ak^{\alpha'}}{2}\right)\left[\sum_{\alpha''\neq\alpha'}\cos\left(\frac{ak^{\alpha''}}{2}\right)\right]^2}}\frac{\partial^3\epsilon}{\partial k_\alpha \partial k_{\alpha_2}\partial k_{\alpha_3}} \tag{81}$$

To work with this, I will examine the different cases for directions. Starting with all indices being the same, then the conductivity is

$$\sigma^{\alpha\alpha\alpha\alpha} = -\left(\frac{ae\tau}{2\hbar}\right)^2 \frac{\sigma_0^{\alpha\alpha}}{\prod_{m=1}^{3}(1 - mi\tau\omega)} \tag{82}$$

But compared to the simple cubic case this is not the only non-zero term. All the terms with only two different directions, and an even number α indices also have non-zero integrals. Because the conductivity is symmetric in the indices I will simply find one of these.

$$\sigma^{\alpha\beta\alpha\beta} = -4t\left(\frac{a}{2}\right)^3\frac{e^4}{\hbar^4}\frac{2}{(2\pi)^3}\frac{1}{\prod_{m=1}^{3}(1/\tau - mi\omega)} \cdot \oint_{C_F} d^3\boldsymbol{k}\frac{\sum_{\alpha'\neq\beta}\sin^2\left(\frac{ak^{\beta}}{2}\right)\cos\left(\frac{ak^{\alpha'}}{2}\right)\cos\left(\frac{ak^{\alpha}}{2}\right)}{\sqrt{\sum_{\alpha'}\sin^2\left(\frac{ak^{\alpha'}}{2}\right)\left[\sum_{\alpha''\neq\alpha'}\cos\left(\frac{ak^{\alpha''}}{2}\right)\right]^2}} \tag{83}$$

One can show that the sum inside of the integral will integrate to half of that from equation (79), however I will not do that here. But in figure 4 I show numerically that this is indeed the case, for different chemical potentials μ. This in turn means that the conductivity, can be described by the static conductivity

$$\sigma^{\alpha\beta\alpha\beta} = -\frac{1}{2}\left(\frac{ae\tau}{2\hbar}\right)^2 \frac{\sigma_0^{\alpha\alpha}}{\prod_{m=1}^{3}(1 - mi\tau\omega)} \tag{84}$$

This means that for the third order, the conductivity must be given as

$$\sigma^{\alpha\alpha_1\alpha_2\alpha_3} = \begin{cases} -\left(\frac{ae\tau}{2\hbar}\right)^2 \frac{\sigma_0^{\alpha\alpha}}{\prod_{m=1}^{3}(1-mi\tau\omega)} & \text{for } \alpha_i = \alpha \forall i \\ -\frac{1}{2}\left(\frac{ae\tau}{2\hbar}\right)^2 \frac{\sigma_0^{\alpha\alpha}}{\prod_{m=1}^{3}(1-mi\tau\omega)} & \text{for } n_\alpha \text{ even \& } n_\beta \text{ even} \\ 0 & \text{otherwise} \end{cases} \tag{85}$$

Here I have said that n_α is the number of indices in the conductivity which is in the α direction, and n_β is the number of indices in the conductivity in some other direction different from α, i.e if α is x, then β is either y or z, and so on.

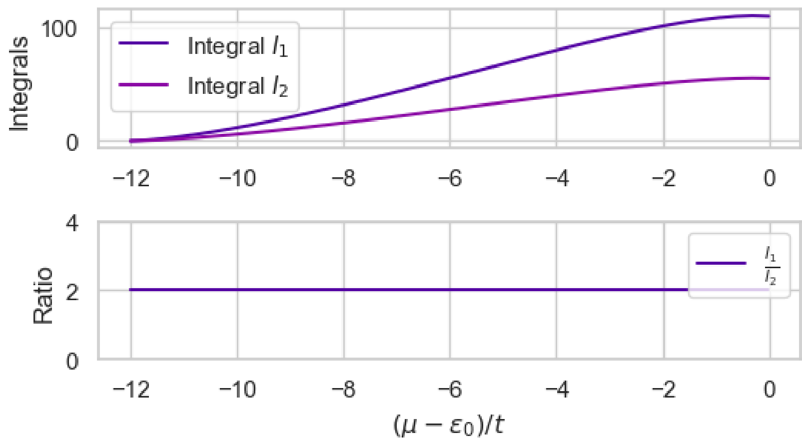

Figure 4: The integrals from equations (79) and (83), which I have named I_1 and I_2 respectively, with a=1.

9.4 Generalizing to the n'th order

Given what we have just found for the first, second and third order conductivities, it is not too difficult to see that because of the derivatives in (77), the pattern is as follows

$$\sigma^{\alpha\alpha_1\alpha_2\ldots\alpha_n} = \begin{cases} (-1)^{\frac{n-1}{2}}\left(\frac{ae\tau}{2\hbar}\right)^{n-1} \frac{\sigma_0^{\alpha\alpha}}{\prod_{m=1}^{n}(1-mi\tau\omega)} & \text{for n odd \& } \alpha_i = \alpha \forall i \\ (-1)^{\frac{n-1}{2}}\frac{1}{2}\left(\frac{ae\tau}{2\hbar}\right)^{n-1} \frac{\sigma_0^{\alpha\alpha}}{\prod_{m=1}^{n}(1-mi\tau\omega)} & \text{for n odd \& } n_\alpha \text{ even \& } n_\beta \text{ even} \\ 0 & \text{otherwise} \end{cases} \tag{86}$$

From this we can see that the current density, must be of the form

$$j^\alpha = \sigma^{\alpha\alpha} E^\alpha + \sigma^{\alpha\alpha\alpha\alpha}(E^\alpha)^3 + 3\sigma^{\alpha\alpha\beta\beta}(E^\beta)^2 E^\alpha + 3\sigma^{\alpha\alpha\gamma\gamma}(E^\gamma)^2 E^\alpha + \dots \tag{87}$$

where $\alpha, \beta, \gamma \in \{x, y, z\}$, but $\alpha \neq \beta$, $\alpha \neq \gamma$ and $\beta \neq \gamma$. By then using the static conductivity, we construct a more useful formula

$$\begin{aligned} j^\alpha = &\frac{\sigma_0^{\alpha\alpha} E^\alpha}{1 - i\tau\omega} - \left(\frac{ae\tau E^\alpha}{2\hbar}\right)^2 \frac{\sigma_0^{\alpha\alpha}}{\prod_{m=1}^{3}(1 - mi\tau\omega)} E^\alpha \\ &- \frac{3}{2}\left(\frac{ae\tau E^\beta}{2\hbar}\right)^2 \frac{\sigma_0^{\alpha\alpha}}{\prod_{m=1}^{3}(1 - mi\tau\omega)} E^\alpha - \frac{3}{2}\left(\frac{ae\tau E^\gamma}{2\hbar}\right)^2 \frac{\sigma_0^{\alpha\alpha}}{\prod_{m=1}^{3}(1 - mi\tau\omega)} E^\alpha + \dots \end{aligned} \tag{88}$$

By spotting the pattern from what we know from equation (86), of the general conductivities for this model (giving a sum of even orders), and that the conductivities are symmetric in their indices (giving a combinatorial term). The full sum can then be written on the form

$$\begin{aligned} j^\alpha = \sigma_0^{\alpha\alpha} E^\alpha \sum_{k=0}^{\infty} (-1)^k \left(\frac{ae\tau}{2\hbar}\right)^{2k} \frac{1}{\prod_{m=1}^{2k+1}(1 - mi\tau\omega)} \Bigg[&\left(E^\alpha\right)^{2k} \\ &+ \frac{1}{2}\sum_{l=1}^{k} \binom{2k+1}{2l} \left(E^\alpha\right)^{2(k-l)} \left(\left(E^\beta\right)^{2l} + \left(E^\gamma\right)^{2l}\right) \Bigg]. \end{aligned} \tag{89}$$

10 Conclusion

Throughout this thesis I have found the current densities and conductivities of different types materials with the use of two different models in the semi classical approach. For the first model, the free electron model, I found that the conductivity was simply given by a single first order conductivity and that all higher orders vanished. This, I assume, is because of the simplicity of the model, and I therefore proceeded to a more physical model, the tight binding model, which take into account the nearest neighbors for each atom. For this model I found that for a simple cubic, an orthorhombic and a face centered cubic lattice structure all odd orders of the conductivity vanish. This, however, might once again be caused by the simple model in use, one might check what would happen if we tried another type of model, since we know that we have observed second and other even order responses for different materials experimentally.
All of this work lays a solid foundation for further exploration of other nonlinear optical properties, for different types of materials.

I have also, throughout the thesis, ignored the influence of the magnetic field. This causes no great error for small electric fields but if large E-fields from light are considered, they will, of course, be accompanied by sizable magnetic fields as well which needs to be accommodated for.

For further work one could examine how the current density and therefore also the conductivities change when we allow for the anomalous velocity which is included in Weyl semi-metals due to the so called Berry curvature. This means one would have to include an extra term for the current densities which might change the vanishing terms for the conductivities which I have calculated.

However all of this work is done within the framework of the semi-classical approximation. For a full analysis of the conductivities one might want to change the models to proper quantum mechanical ones which allows for many other effects to be taken into consideration.

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