Quantum Theory for Dielectric Properties of Conductors
A. Response to Optical Electric Field Only

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Summary

The complex and frequency-dependent dielectric function $\epsilon(\omega)$ describes how light interacts when propagating through matter. It determines the propagation speed, dispersion effects, absorption, and more esoteric phenomena such as Faraday rotation when a DC magnetic field is present. Of particular interest here is the description of $\epsilon(\omega)$ in conductors using quantum mechanics, so that intrinsically quantum mechanical systems can be described. The goal is an appropriate understanding of the contributions from band-to-band transitions, such as in metals and semiconductors, with or without an applied DC magnetic field present.

Part A discusses the general theory of $\epsilon(\omega)$ for a medium only in the presence of the optical electric field. The approach is to find how this electric field modifies the density matrix. It is applied to band-to-band transitions in the absence of an applied magnetic field.

In Part B, the effect of a DC magnetic field is discussed generally, with respect to how it causes Faraday rotation. For free electrons, it causes quantized Landau levels for the electrons; the dielectric function is found for that problem, and related problems are discussed.

In Part C, the important problem is how to include the effect of a DC magnetic field on the band-to-band transitions, such as those in metals and semiconductors. Results are found for 1D and 3D band models, with and without a phenomenolgical damping.

Taken together, these theories should be complete enough to describe Faraday rotation effects in gold, whose dielectric function is strongly dependent on band-to-band transitions for wavelengths below 600 nm.

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Contents

1 Electric polarization and dielectrics

Here I want to consider the basic theory for induced electric dipoles in matter, and how that leads to the electric permittivity $\epsilon(\omega)$. In optical systems, it is clear that the response of a medium to the radiation fields, i.e., photons, induces electric dipoles, and those in turn could react back on the radiation. The theory is related to that just discussed for using time-dependent perturbation theory applied to absorption and emission of photons.

An optical medium has a dielectric response due primarily to its charge carriers of charge e, and their dipole moments induced by applied fields.[2] I will consider this as a quantum problem, because I will include the effects of both the electric and magnetic fields, especially, what happens when a DC magnetic field is applied (Faraday effect).

Start from the simplest problem, the Drude model, where the optical medium is composed just from a gas of free (noninteracting) electrons, moving between fixed nuclei. Classically the problem is quite simple: the electric field in the radiation field at frequency ω displaces the electrons from their original positions, at the frequency of the radiation. Then it is easy to find the induced dipoles and do the necessary electrodynamics to get $\epsilon(\omega)$. The only possible difficulty: the gas oscillates as a whole, leading to plasma oscillations. But we aren't really considering this kind of collective mode, only the averaged response of individual charges. An individual charge e with bare mass m_e follows Newton's Law, in the net field surrounding it, $\mathbf{E} = \mathbf{E}_0 e^{-i\omega t}$,

$$m_e \ddot{\mathbf{r}} = e\mathbf{E}_0 e^{-i\omega t}, \implies \mathbf{r}(t) = \frac{-e\mathbf{E}_0}{m_e \omega^2} e^{-i\omega t} = \frac{-e}{m_e \omega^2}\mathbf{E} \tag{1.1}$$

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[2]For simplicity I use the symbol e to be the charge, it could be a negative number as for electrons.

The charge oscillates at the same frequency as the radiation, and its displacements of amplitude $-e\mathbf{E}_0/m_e\omega^2$ about its original position are proportional to the strength of the radiation. Note that the amplitude of the displacement is extremely tiny. For an electric field strength of $E_0 = 1.0\,\mathrm{MV/m}$, and optical wavelength of $\lambda = 500\,\mathrm{nm}$, the frequency is $\omega = 2\pi c/\lambda = 3.77 \times 10^{15}\,\mathrm{rad/s}$, and

$$|\mathbf{r}| \approx \frac{(1.602 \times 10^{-19}\,\mathrm{C})(1.0 \times 10^6\,\mathrm{V/m})}{(9.11 \times 10^{-31}\,\mathrm{kg})(3.77 \times 10^{15}\,\mathrm{rad/s})^2} = 1.23 \times 10^{-14}\,\mathrm{m}. \tag{1.2}$$

It seems incredible that such small displacements can have such a great importance in physics.

The charge's induced electric dipole moment is $\mathbf{d} = e\mathbf{r}$. If there are N charges in a volume V, or a volume density of $n = N/V$, then the net dipole moment per unit volume is the electric polarization,

$$\mathbf{P} = n\mathbf{d} = ne\mathbf{r} = -\frac{ne^2}{m_e\omega^2}\mathbf{E} \tag{1.3}$$

The total electric displacement can then be found (CGS units) to get the dielectric function,

$$\mathbf{D} = \epsilon\mathbf{E} = \mathbf{E} + 4\pi\mathbf{P} = \left(1 - 4\pi\frac{ne^2}{m_e\omega^2}\right)\mathbf{E} \quad\Longrightarrow\quad \epsilon(\omega) = 1 - 4\pi\frac{ne^2}{m_e\omega^2} \tag{1.4}$$

One can see the large oscillations and response will occur if $\epsilon \to 0$, which takes place at the plasma frequency,

$$\omega_p = \sqrt{\frac{4\pi ne^2}{m_e}} \tag{1.5}$$

Then it is usual to write the dielectric function for this simplest case as

$$\epsilon(\omega) = 1 - 4\pi\frac{ne^2}{m_e\omega^2} = 1 - \frac{\omega_p^2}{\omega^2} \tag{1.6}$$

Note that to convert the formula to SI units, just recall that the charge must be re-scaled by the relation

$$q_{\mathrm{CGS}}^2 \to \frac{q_{\mathrm{SI}}^2}{4\pi\epsilon_0}; \qquad \omega_p = \sqrt{\frac{ne^2}{m_e\epsilon_0}} \quad \text{(SI units)} \tag{1.7}$$

where $\epsilon_0 = 8.854\,\mathrm{pF/m}$ is the permittivity of vacuum.

The dielectric function determines the index of refraction of the medium, (together with the corresponding magnetic permeability μ, which we take to be fixed at 1).

$$n(\omega) = \sqrt{\mu\epsilon(\omega)} = n_r + in_i \tag{1.8}$$

The waves propagate through a medium according to their wave vector $\mathbf{q}$, which depends on the frequency of the light and the refractive index. The electric field is a wave like

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}, \qquad q(\omega) = \frac{\omega}{c}\sqrt{\mu\epsilon(\omega)} = \frac{\omega}{c}n(\omega). \tag{1.9}$$

This shows why the dielectric function is so important. It determines how light propagates through a medium.

When low-frequency light ($\omega < \omega_p$) is incident on a metal, $\epsilon < 0$ and the refractive index becomes imaginary! These waves do not transmit through the metal, but instead are just reflected. For high-frequency light, ϵ will remain positive and the index of refraction remains real; the light travels through the metal. Conclusion: a metal is transparent only to light waves oscillating faster than its natural plasmon resonance frequency. When the light oscillates too fast, the electrons have trouble to follow that motion, they can't adjust themselves to eliminate the electric fields, and the light is let through. For low-frequency light, the electrons have time to move around until they can zero out the electric fields inside the metal, just like in "electrostatics", and the light is transmitted a very limited distance.
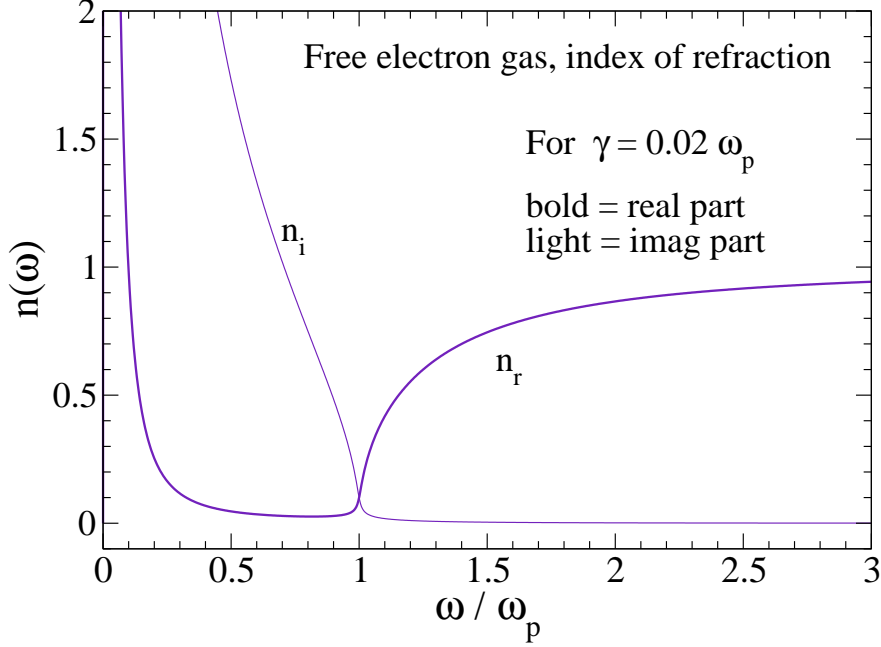
Figure 1: Plot of the real and imaginary parts of the index of refraction $n(\omega) = \sqrt{\epsilon(\omega)}$ for a slightly damped free electron gas with the dielectric function in (1.13). Note that since the imaginary part gets very large for frequencies below the plasma frequency, it is impossible for light at those frequencies to propagate through this medium.

As a modification, one can consider partially bound electrons with damped motion–it removes the sudden transition at the plasma frequency. In addition to the force of the electric field, add a spring force and a damping force that acts against the velocity:

$$m_e \ddot{\mathbf{r}} = e\mathbf{E}_0 e^{-i\omega t} - m_e \omega_0^2 \mathbf{r} - m_e \gamma \dot{\mathbf{r}}, \implies \mathbf{r}(t) = \frac{-e\mathbf{E}}{m_e(\omega^2 - \omega_0^2 + i\gamma\omega)} \tag{1.10}$$

The resulting polarization is

$$\mathbf{P} = ne\mathbf{r} = \frac{-ne^2\mathbf{E}}{m_e(\omega^2 - \omega_0^2 + i\gamma\omega)} \tag{1.11}$$

and then the prediction for the dielectric function is

$$\epsilon(\omega) = 1 - 4\pi \frac{ne^2}{m_e(\omega^2 - \omega_0^2 + i\gamma\omega)} = 1 - \frac{\omega_p^2}{\omega^2 - \omega_0^2 + i\gamma\omega} \tag{1.12}$$

This could represent the dielectric response of bound electrons in a nonconductor, such as ordinary insulating dielectrics. Sometimes, it is generalized to include more than one resonance frequency ω_0, due to the contributions of different electrons with different local atomic environments in the material.

Of particular interest is a gas of electrons that are not bound ($\omega_0 = 0$) but nevertheless have some damping:

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \tag{1.13}$$

This could represent, for example, the nearly free electron gas in a metal, that are not bound to ion cores, but still have their motion impeded in the solid. Then, the dielectric function does not vanish at $\omega = \omega_p$, that singular point is smoothed out due to the damping. The typical dependence of $n(\omega) = \sqrt{\epsilon(\omega)}$ that results is shown in Fig. 1. This makes for a more realistic although emperical

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description of real materials with a simple classical model. It also shows that, in general, both the real and imaginary parts of the index of refraction depend on the light frequency (effects commonly called *dispersion*). Even the real part has a strong dependence on frequency, especially when ω is near ω_p.

1.1 Currents and the dielectric function

Dielectric effects take place in media because the applied EM fields produce induced currents and charges. If in a model we can determine how charges move in response to **E** and **B** then in principle one can calculate or estimate $\epsilon(\omega)$.

Above we used the electric displacement and induced electric dipoles as the basis for finding the permittivity. To me, that is really the physically most fundamental approach and easiest to visualize. But there is another way to look at it, perhaps slightly more technical. Consider one of Maxwell's equations, Ampere's Law (in CGS units), with the displacement current included:

$$\nabla \times \mathbf{H} = \frac{4\pi}{c}\mathbf{J} + \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} \tag{1.14}$$

There are various ways to re-express this. But consider a simple one with a simple interpretation. Suppose that the second term on RHS is the contribution due to vacuum alone, and the first term on RHS is all of the contribution due to the matter. The current density **J** is due to any type of real physical movement of charges. The vacuum contribution is Maxwell's displacement current, it is always there, and so we separate it out. Now we suppose that the entire RHS is just the time-derivative of a total electric displacement, **D**. That is, for practical purposes, **D** represents effects due to both the vacuum and the matter. Then we have

$$\nabla \times \mathbf{H} = \frac{4\pi}{c}\mathbf{J} + \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} = \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t} \tag{1.15}$$

Without worrying about a lot of details, it is usual to take $\mathbf{D} = \tilde{\epsilon} \cdot \mathbf{E}$ to hold in frequency space, with all fields varying as $e^{-i\omega t}$. So we have instead for the electric parts of the equation,

$$\frac{4\pi}{c}\mathbf{J} + \frac{-i\omega}{c}\mathbf{E} = \frac{-i\omega}{c}\,\tilde{\epsilon}\cdot\mathbf{E} \tag{1.16}$$

This leads directly to a macroscopic definition for the dielectric function:

$$-i\omega[\tilde{\epsilon}(\omega) - \mathbf{1}]\cdot\mathbf{E} = 4\pi\mathbf{J} \tag{1.17}$$

The reason the equation is written this way, and not "solved" for $\tilde{\epsilon}$, is that $\tilde{\epsilon}$ is really a tensor or matrix. When **E** is applied, the currents are generated, and really, this relation via $\tilde{\epsilon}$ determines the strength of that response. If $\tilde{\epsilon}$ were unity (as a matrix **1**), the only current induced would be the vacuum displacement current, which is NOT included in **J**. It is important to remember that in this expression, **J** is only the current density due to real charges moving around, some authors would call it $\mathbf{J}^{\text{ind}}$ to emphasize that it contains only the induced currents in the matter.

The permittivity might alternatively be described in terms of the electric susceptibility tensor $\tilde{\chi}$, defined via

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}, \quad \mathbf{P} = \tilde{\chi}\cdot\mathbf{E}, \quad \Longrightarrow \tilde{\epsilon}(\omega) = 1 + 4\pi\tilde{\chi}(\omega) \tag{1.18}$$

Then the equation for determining the susceptibility from the induced currents is even simpler,

$$-i\omega\tilde{\chi}(\omega)\cdot\mathbf{E} = \mathbf{J} \tag{1.19}$$

For a given electric field in applied light waves at frequency ω, if the induced currents can be found in a QM calculation, then the dielectric response can be found.

1.2 Quantum Drude model?

What about the QM problem for the Drude model? The free electrons can be assumed to be in eigenstates of momentum, i.e, their unperturbed Hamiltonian only has kinetic energy:

$$\hat{H}_e = \frac{\hat{\mathbf{p}}^2}{2m_e} \tag{1.20}$$

The eigenstates can be normalized plane waves:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{1.21}$$

First I'll consider a zero temperature problem. One needs to know the effects on an individual electron and its interaction with the quantized radiation fields in the Coulomb gauge. Take the interaction due to single-photon processes, as discussed in other notes:

$$\hat{H}_1 = -\frac{e}{m_e c} \hat{\mathbf{A}} \cdot \hat{\mathbf{p}} \tag{1.22}$$

The perturbation should cause the electron to make transitions between the plane wave states. Let's see what happens. We know the expression for the radiation vector potential, so

$$\hat{H}_1 = \frac{-e}{m_e} \sqrt{\frac{h}{V}} \sum_{\mathbf{k}} \frac{1}{\sqrt{\omega_{\mathbf{k}}}} \left[\hat{\epsilon}_{\mathbf{k}\alpha} a_{\mathbf{k}\alpha} e^{i\mathbf{k}\cdot\mathbf{r}} + \hat{\epsilon}_{\mathbf{k}\alpha}^{\dagger} a_{\mathbf{k}\alpha}^{\dagger} e^{-i\mathbf{k}\cdot\mathbf{r}} \right] \cdot \hat{\mathbf{p}} \tag{1.23}$$

Now we don't necessarily need to know transition rates for this problem, we only want to know the expectation value of the electric dipole moment operator, $\mathbf{d} = e\mathbf{r}$, in the presence of the light field. Unfortunately, we see right away, that for whatever state of the electron we might pick, this expectation will be zero in first order perturbation theory, because of the photon operators. If the photon number does not change, the photon matrix elements will give zero. Thus I suspect we need to look at this problem with second order perturbation theory. Further, we need to be clearer about what is the actual state of the photons being considered. However, that could be fairly simple, say, a state with n identical photons (a very large number) at the frequency for which we need to know $\epsilon(\omega)$. Even for this state, first order PT will not give an induced dipole moment.

Because the way to attack this here is a litlte unclear, instead proceed to a different approach that accounts for a state of equilibrium.

1.3 Quantum Charge Motion

Now I follow an approach by Stephen Adler, Phys, Rev. **126**, p. 413 (1962), "Quantum theory of the dielectric constant in real solids," for how to find $\tilde{\epsilon}$. It is based on using a set of states in which electrons can be found, and determining how the AC optical field modifies the population of those states, in some sense. The modification of their population is represented by using the density matrix approach, because really, this is a statistical problem, and we have a many electron problem so the QM state is not the state of a single particle, but is an averaged state. The current density is found as an appropriate average of the density operator. Then that allows identification of the dielectric function.

Electrons in bands are supposed to behave according to a one-electron Hamiltonian

$$\hat{H} = \frac{1}{2m_e} \left[\hat{\mathbf{p}} - \frac{e}{c} \hat{\mathbf{A}}(\hat{\mathbf{r}}, t) \right]^2 + e\hat{\phi}(\hat{\mathbf{r}}, t) + \hat{U}(\hat{\mathbf{r}}) \tag{1.24}$$

where the charge is $+e$, $\hat{\phi}$ and $\hat{\mathbf{A}}$ are the scalar and vector potentials of the EM fields, and $\hat{U}$ is the periodic potential of the lattice.[3] The optical field is treated as a classical non-quantized field, that

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[3] Quantum operators will be denoted with carets, like $\hat{\mathbf{p}}$ to be distinguished from their expecation values, without carets, $\mathbf{p}$.

oscillates as $e^{-i\omega t}$. This means there are no photons directly considered, but only a continuum field. It is written as an operator because it depends on the position operator. The canonical momentum operator for the electron is $\hat{\mathbf{p}} = -i\hbar\tilde{\nabla}$. Note, however, that the more physical momentum is the kinetic mometum operator,

$$\vec{\pi} = \hat{\mathbf{p}} - \frac{e}{c}\hat{\mathbf{A}}, \tag{1.25}$$

because it is the square of this operator that determines the energy.

The electron bands, unperturbed by fields, come from solution with just the simple KE and the lattice periodic potential,

$$\left[\frac{\hat{\mathbf{p}}^2}{2m_e} + U(\mathbf{r})\right]|l,\mathbf{k}\rangle = E_{l,\mathbf{k}}|l,\mathbf{k}\rangle \tag{1.26}$$

The bands are labelled by index l and the states of wave vector $\mathbf{k}$ have wave functions

$$|l,\mathbf{k}\rangle = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}}u_{l,\mathbf{k}}. \tag{1.27}$$

These can be considered the original states of an unperturbed problem. The optical field is the perturbation.

1.4 Averaging with the density matrix approach

Statistically, these states are populated according to a Fermi-Dirac distribution for the given temperature, when the system is in equilibrium. The density operator $\hat{\rho}$ is a way to introduce this population into the QM problem and provide for mixed states as opposed to pure states. Of course, once the optical field is turned on, a new equilibrium can be established and the density operator (and its matrix) can change. Its basic definition for an equilibrium situation, in terms of the state probabilities w_i is

$$\hat{\rho} = \sum_i w_i|\psi_i\rangle\langle\psi_i| \tag{1.28}$$

Note the time derivative follows from using the Schrödinger equation for each state:

$$\begin{aligned}
\frac{\partial\hat{\rho}}{\partial t} &= \sum_i w_i\left\{(\frac{\partial}{\partial t}|\psi_i\rangle)\langle\psi_i| + |\psi_i\rangle(\frac{\partial}{\partial t}\langle\psi_i|)\right\} \\
&= \sum_i w_i\left\{(\frac{1}{i\hbar}\hat{H}|\psi_i\rangle)\langle\psi_i| + |\psi_i\rangle(\langle\psi_i|\hat{H}\frac{-1}{i\hbar})\right\} = \frac{1}{i\hbar}[\hat{H},\hat{\rho}]
\end{aligned} \tag{1.29}$$

This is known as the quantum Liouville equation. It is analogous to the Liouville equation for the evolution of probability in classical statistical mechanics.

Any basis can be used in the definition of $\hat{\rho}$, so we use the unperturbed band states. But their evolution, when the full Hamiltonian is turned on, causes the density matrix to evolve into something else. That is what we want to find. Further, the kind of expectation value needed is that for the physical current, which can be found from a trace:

$$\langle\hat{\mathbf{J}}\rangle = \text{Tr}\{\hat{\rho}\hat{\mathbf{J}}\} = \sum_j\langle\psi_j|(\sum_i w_i|\psi_i\rangle\langle\psi_i|)\hat{\mathbf{J}}|\psi_j\rangle = \sum_i w_i\langle\psi_i|\hat{\mathbf{J}}|\psi_i\rangle \tag{1.30}$$

1.5 Quantum operators for charge and current densities

The main question still, what is the operator for the current density? But that should not be too difficult, because the charge current is associated with the (quantum) motion of the charge. We need the effective velocity operator $\hat{\mathbf{v}}$ and current density operator $\hat{\mathbf{j}}$ for one quantum particle. The electric charge density $\rho_e(\mathbf{r})$ (not to be confused with the density matrix $\hat{\rho}$) and it associated current

density $\mathbf{j}(\mathbf{r})$, for an individual electron, as expectation values, needs to satisfy a continuity equation that ensures conservation of charge,

$$\frac{\partial}{\partial t}\rho_e(\mathbf{r}) + \tilde{\nabla} \cdot \mathbf{j}(\mathbf{r}) = 0, \quad \text{or} \quad \vec{\nabla} \cdot \mathbf{j}(\mathbf{r}) = -\dot{\rho}_e(\mathbf{r}). \tag{1.31}$$

Note that these quantities are associated with a single electron inside some normalization volume V. To get the physical charge and current densities as per volume quantities, scale them by the number of electrons, N, (this is a noninteracting electron model)

$$\rho_{Ne}(\mathbf{r}) = N\,\rho_e(\mathbf{r}), \qquad \mathbf{J} = N\,\mathbf{j}(\mathbf{r}). \tag{1.32}$$

In the absence of the EM fields, a wave function satisfies a Schrödinger equation, $i\hbar\dot{\psi} = \hat{H}\psi$, and its complex conjugate satisfies $-i\hbar\dot{\psi}^* = \hat{H}^*\psi^*$. The squared wave function gives the probability density, so $\rho_e = e|\psi|^2$. Get the current by looking at its changes with time,

$$\frac{\partial}{\partial t}\psi^*\psi = \dot{\psi}^*\psi + \psi^*\dot{\psi} = \frac{1}{-i\hbar}(\hat{H}^*\psi^*)\psi + \frac{1}{i\hbar}\psi^*(\hat{H}\psi) \tag{1.33}$$

When the Hamiltonian has a nonrelativistic form like $\hat{H} = \vec{\pi}^2/2m_e + U(\hat{\mathbf{r}})$, where the potential is real, there results two obvious contributions to the current. For simplicity of notation, let

$$\vec{\pi} = -i\hbar(\vec{\nabla} - i\vec{\alpha}), \quad \text{where} \quad \vec{\alpha} = \frac{e}{\hbar c}\hat{\mathbf{A}}(\hat{\mathbf{r}}, t). \tag{1.34}$$

The vector potential is considered a real function of space and time. There results

$$-\vec{\nabla} \cdot \mathbf{j}(\mathbf{r}) = e\frac{\partial}{\partial t}\psi^*\psi = \frac{e}{i\hbar}\frac{(-i\hbar)^2}{2m_e}\left[\psi^*(\vec{\pi}^2\psi) - (\vec{\pi}^2\psi)^*\psi\right] \tag{1.35}$$

When the kinetic momentum is inserted and squared out, the terms depending on $\vec{\alpha}^2$ cancel out. The terms depending on ∇^2 give the "momentum current"

$$-\vec{\nabla} \cdot \mathbf{j}_p(\mathbf{r}) = \frac{e}{i\hbar}\frac{(-i\hbar)^2}{2m_e}\left[\psi^*(\nabla^2\psi) - (\nabla^2\psi)^*\psi\right] = \vec{\nabla} \cdot \left\{\frac{ie\hbar}{2m_e}\left[\psi^*(\vec{\nabla}\psi) - (\vec{\nabla}\psi^*)\psi\right]\right\} \tag{1.36}$$

Solving, the momentum current contribution is

$$\mathbf{j}_p(\mathbf{r}) = \frac{-i\hbar e}{2m_e}\left[\psi^*(\vec{\nabla}\psi) - (\vec{\nabla}\psi^*)\psi\right] = \frac{e}{2m_e}\left[\psi^*(\hat{\mathbf{p}}\psi) + (\hat{\mathbf{p}}\psi)^*\psi\right] = \frac{e}{m_e}\text{Re}\{\psi^*(\hat{\mathbf{p}}\psi)\} \tag{1.37}$$

This is the action on a wave function $\psi(\mathbf{r}) = \langle\mathbf{r}|\psi\rangle$. One sees this depends on an operator $e\hat{\mathbf{p}}/m$. However, to apply this formula, the indicated product must be formed, and then the real part must be taken. There should be a slightly different (and more complicated) method to invent an individual operator whose effect between ψ^* and ψ does not require the real part operation. That is described in the paragraphs that follow.

The cross terms between $\vec{\nabla}$ and $\vec{\alpha}$ give the "gauge current density"

$$-\vec{\nabla} \cdot \mathbf{j}_A(\mathbf{r}) = \frac{ie\hbar}{2m_e}(-i)\left\{\psi^*\left[\vec{\nabla} \cdot (\vec{\alpha}\psi) + \vec{\alpha} \cdot (\vec{\nabla}\psi)\right] + \text{c.c.}\right\} \tag{1.38}$$

If we assume the Coulomb gauge, then $\vec{\nabla} \cdot \hat{\mathbf{A}} = 0$ and $\vec{\nabla} \cdot \vec{\alpha} = 0$. The relation $\vec{\nabla} \cdot (\vec{\alpha}\psi) = \vec{\alpha} \cdot \vec{\nabla}\psi$ results, and this simplifies to

$$-\nabla \cdot \mathbf{j}_A(\mathbf{r}) = \frac{e\hbar}{m_e}\left\{\psi^*\vec{\alpha} \cdot \vec{\nabla}\psi + \psi\vec{\alpha} \cdot \vec{\nabla}\psi^*\right\} = \vec{\nabla} \cdot \left[\psi^*\frac{e^2}{m_e c}\hat{\mathbf{A}}(\hat{\mathbf{r}})\psi\right] \tag{1.39}$$

Thus the gauge current is

$$\mathbf{j}_A(\mathbf{r}) = -\frac{e^2}{m_e c}\psi^*\hat{\mathbf{A}}(\mathbf{r})\psi \tag{1.40}$$

and its operator is just $-e^2\hat{\mathbf{A}}(\mathbf{r})/m_e c$. Therefore the total current in a wavefunction $\psi(\mathbf{r})$ is

$$\mathbf{j}(\mathbf{r}) = \mathrm{Re}\left\{\frac{e}{m_e}\psi^*\hat{\mathbf{p}}\psi\right\} - \frac{e^2}{m_e c}\psi^2\hat{\mathbf{A}}\psi = \mathrm{Re}\left\{\frac{e}{m_e}\ \psi^*(\mathbf{r})\left(\hat{\mathbf{p}} - \frac{e}{c}\hat{\mathbf{A}}\right)\psi(\mathbf{r})\right\}. \tag{1.41}$$

One can realize we can write this in terms of a velocity operator; this could make more physical sense:

$$\mathbf{j}(\mathbf{r}) = \mathrm{Re}\left\{e\psi^*(\hat{\mathbf{v}}\psi)\right\}, \qquad \hat{\mathbf{v}} = \frac{\vec{\pi}}{m_e} = \frac{1}{m_e}\left(\hat{\mathbf{p}} - \frac{e}{c}\hat{\mathbf{A}}\right) \tag{1.42}$$

The general velocity operator depends on the total vector potential, that could be due to both AC optical fields and a DC magnetic field. We could have written this based on intuition but it is good to see the mathematical description works within the Schrödinger equation.

Adler has written a current operator, but I think there is something fishy about his expressions, so I am going to avoid them and prefer something well-defined. The $\mathbf{j}(\mathbf{r})$ in (1.41) is not an operator, but only a function that depends on position. In fact, it is an expectation value. There is an operator that is very simple and does not itself depend on position (although the vector potential could have an implicit dependence on position):

$$\hat{\mathbf{j}} = e\hat{\mathbf{v}} = \frac{e}{m_e}\left(\hat{\mathbf{p}} - \frac{e}{c}\hat{\mathbf{A}}\right) \tag{1.43}$$

Similarly, one can make a charge "operator" that is very simple: $\hat{\rho}_e = e$. These can be used together with a density matrix, for example, to produce the space-dependent densities, if desired. However, due to the "offending" operation of taking the real part, it is not as simple as one would like, as seen here: Suppose the density matrix is that for a pure state, $|\psi\rangle$. Then with $\hat{\rho} = |\psi\rangle\langle\psi|$, suppose one writes

$$\langle\mathbf{r}|\hat{\rho}\hat{\rho}_e|\mathbf{r}\rangle = \langle\mathbf{r}|(|\psi\rangle\langle\psi|)e|\mathbf{r}\rangle = e\psi(\mathbf{r})\psi^*(\mathbf{r}) = \rho_e(\mathbf{r}). \tag{1.44}$$

That result is correct for the charge density, because it is already real as an observable should be. Now consider doing the same with the velocity operator,

$$\langle\mathbf{r}|\hat{\rho}e\hat{\mathbf{v}}|\mathbf{r}\rangle = \langle\mathbf{r}|e\hat{\mathbf{v}}(|\psi\rangle\langle\psi|)|\mathbf{r}\rangle = e[\hat{\mathbf{v}}\psi(\mathbf{r})]\psi^*(\mathbf{r}) \neq \mathbf{j}(\mathbf{r}). \tag{1.45}$$

It doesn't work, because the *real* operation is not present! Even for the charge density, this isn't really the correct way to get it.

To get this right, realize that the current density at a point $\mathbf{r}$ is obtained by the following algebra [essentially, rewriting (1.37) and (1.41) in Dirac notation] involving the velocity operator:

$$\mathbf{j}(\mathbf{r}) = \frac{e}{2}\langle\psi|\big(|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}} + \hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}|\big)|\psi\rangle \equiv \langle\psi|\hat{j}(\mathbf{r})|\psi\rangle \tag{1.46}$$

This *is* in the form of an expectation value, and it *is* pure real, where the operator inside (denoted with caret) is quantum current density *operator*,

$$\hat{j}(\mathbf{r}) = \frac{e}{2}\left\{|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}} + \hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}|\right\}. \tag{1.47}$$

This operator does have a position argument. When sandwiched within any state, it will give the current density in that state, at the requested position. It is this operator that needs to be applied within the density matrix formalism. Due to its construction, no "real part" operation is needed afterwards. Similarly, the correct way to define a charge density "operator" (denoted with a caret on top) that gives the charge density at a requested point $\mathbf{r}$, is

$$\hat{\rho}_e(\mathbf{r}) = e|\mathbf{r}\rangle\langle\mathbf{r}|. \tag{1.48}$$

Now for a pure state described with a density operator $\hat{\rho} = |\psi\rangle\langle\psi|$, check that expectation values (denoted without carets) work out correctly. For the charge density the result is

$$\rho_e(\mathbf{r}) = \mathrm{Tr}\left\{\hat{\rho}\hat{\rho}_e(\mathbf{r})\right\} = \sum_i \langle\psi_i|\psi\rangle\langle\psi|e|\mathbf{r}\rangle\langle\mathbf{r}|\psi_i\rangle \tag{1.49}$$

If the states used to do the sum are eigenstates at positions $\mathbf{x}_i$, then the last factor is $\langle \mathbf{r}|\psi_i \rangle = \langle \mathbf{r}|\mathbf{x}_i \rangle = \delta(\mathbf{r} - \mathbf{x}_i)$ and the sum ends up having only the one term where $\mathbf{x}_i = \mathbf{r}$:

$$\rho_e(\mathbf{r}) = \langle \mathbf{r}|\psi \rangle \langle \psi|e|\mathbf{r} \rangle = \psi(\mathbf{r})e\psi^*(\mathbf{r}) = e|\psi(\mathbf{r})|^2 \tag{1.50}$$

which is the expected result. For the current density, by its design the average must work out, i.e.,

$$\mathbf{j}(\mathbf{r}) = \mathrm{Tr}\left\{ \hat{\rho}\hat{j}(\mathbf{r}) \right\} = \frac{e}{2} \sum_i \langle \psi_i|\psi \rangle \langle \psi| \left(|\mathbf{r}\rangle\langle\mathbf{r}|e\hat{\mathbf{v}} + e\hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}| \right) |\psi_i \rangle \tag{1.51}$$

Using arbitrary eigenstates ψ_i, this can be re-arranged so the ψ_i form identity operators,

$$
\begin{aligned}
\mathbf{j}(\mathbf{r}) &= \frac{e}{2} \sum_i \left\{ \langle\psi|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}|\psi_i\rangle\langle\psi_i|\psi\rangle + \langle\psi|\hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}|\psi_i\rangle\langle\psi_i|\psi\rangle \right\} \\
&= \frac{e}{2}\left\{ \langle\psi|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}|\psi\rangle + \langle\psi|\hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}|\psi\rangle \right\} = \mathrm{Re}\left\{ \langle\psi|\mathbf{r}\rangle\langle\mathbf{r}|e\hat{\mathbf{v}}|\psi\rangle \right\} = \mathrm{Re}\left\{ \psi^*(\mathbf{r}) \left[e\hat{\mathbf{v}}\psi(\mathbf{r}) \right] \right\} \tag{1.52}
\end{aligned}
$$

Again, it is the correct result. Similar results will hold if the state is a (diagonal) mixed state, say, using $\hat{\rho} = a|1\rangle\langle1| + b|2\rangle\langle2|$, then there will result for the charge density

$$\rho_e(\mathbf{r}) = \mathrm{Tr}\left\{ \hat{\rho}\hat{\rho}_e \right\} = a|\psi_1(\mathbf{r})|^2 + b|\psi_2(\mathbf{r})|^2 = a\rho_{e1}(\mathbf{r}) + b\rho_{e2}(\mathbf{r}), \tag{1.53}$$

and for the current density,

$$\mathbf{j}(\mathbf{r}) = \mathrm{Tr}\left\{ \hat{\rho}\hat{j}(\mathbf{r}) \right\} = a\,\mathrm{Re}\left\{ \psi_1^*(\mathbf{r})\left[e\mathbf{v}\psi_1(\mathbf{r}) \right] \right\} + b\,\mathrm{Re}\left\{ \psi_2^*(\mathbf{r})\left[e\mathbf{v}\psi_2(\mathbf{r}) \right] \right\} \tag{1.54}$$

where there is a term for each of the states in the mixture.

For application to the dielectric problem, the operator to be averaged is the one-electron current scaled by the number of electrons N,

$$\hat{J}(\mathbf{r}) = N\hat{j}(\mathbf{r}) = Ne\left\{ |\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}} + \hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}| \right\} \tag{1.55}$$

The expectation of this current operator, $\mathbf{J}(\mathbf{r}) = \mathrm{Tr}\{\hat{\rho}\hat{J}\}$, can be used in (1.17) to figure out the dielectric function. This, however, will require some averaging of the current density over position, or if desired, some sort of Fourier analysis. If applied this way, there is no need to to a real part operation. That is what we wanted! The result will be real automatically. At some point in the calculation, there will be a division or normalization by the system volume V, hence the net result will depend on the volume density of electrons, $n = N/V$.

1.5.1 Volume averages of charge and current densities?

So far, expectation values of the operators $\hat{\rho}_e(\mathbf{r})$ and $\hat{J}(\mathbf{r})$ give the densities $\rho_e(\mathbf{r})$ and $\mathbf{J}(\mathbf{r})$ at a desired point in the system. But at the end of a calculation, at times one only wants to know some result averaged over the entire volume. Knowing how to do this helps in summarizing the calculations with these densities. It turns out to be very simple.

I am denoting an average over volume with a bar, like $\overline{\rho_e}$. (Further, it does not have a position argument.) Consider the charge density, and its average over the system volume (in a pure state):

$$\overline{\rho_e} = \frac{1}{V} \int d^3r\, e|\psi(\mathbf{r})|^2 = \frac{1}{V} \int d^3r\, e\langle\psi|\mathbf{r}\rangle\langle\mathbf{r}|\psi\rangle = \frac{e}{V}\langle\psi|\psi\rangle = \frac{e}{V}. \tag{1.56}$$

The integration is the identity operator (and as well, the wave function is unit normalized). This gives the obviously correct result. What if it was a mixed state? Using the example above,

$$\overline{\rho_e} = \frac{1}{V} \int d^3r\, e \sum_i p_i \langle\psi_i|\mathbf{r}\rangle\langle\mathbf{r}|\psi_i\rangle = \frac{e}{V} \sum_i w_i \langle\psi_i|\psi_i\rangle = \frac{e}{V} \sum_i w_i = \frac{e}{V}. \tag{1.57}$$

Again this works because the states used are assumed to be unit normalized, and the probabilities must sum to one. But this could have been written with the integration over $\mathbf{r}$ as a trace:

$$\overline{\rho_e} = \frac{1}{V} \int d^3r \, \langle \mathbf{r}| \Big(e \sum_i w_i |\psi_i\rangle\langle\psi_i| \Big) |\mathbf{r}\rangle = \frac{1}{V} \text{Tr}\,\{\hat{\rho}\,e\} \tag{1.58}$$

It is just the expectation value of e (a constant) divided by the systmem volume. The "operator" to be averaged is just $\hat{\rho}_e \equiv e$, so that $\overline{\rho_e} = \langle\hat{\rho}_e\rangle/V$. No position variables are needed, in fact. The net charge density due to N electrons is

$$\overline{\rho_{Ne}} = (N/V)\langle\hat{\rho}_e\rangle = n\langle\hat{\rho}_e\rangle. \tag{1.59}$$

Consider the volume averaged current density. In a (diagonal) mixed state, the above example showed that the current density at position $\mathbf{r}$ is

$$\mathbf{j}(\mathbf{r}) = \sum_i w_i \,\text{Re}\,\{\psi_i^*(\mathbf{r})\,[e\hat{\mathbf{v}}\psi_i(\mathbf{r})]\} = \frac{e}{2}\sum_i w_i \left(\langle\psi_i|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}|\psi_i\rangle + \langle\psi_i|\hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}|\psi_i\rangle \right) \tag{1.60}$$

Now do its average over the volume, however, the integration over position vectors will lead to identity operators, and both terms become identical, so its volume average is

$$\bar{\mathbf{j}} = \frac{e}{2}\sum_i p_i \,\langle\psi_i|\hat{\mathbf{v}}|\psi_i\rangle \times 2 = \sum_i p_i \,\langle\psi_i|e\hat{\mathbf{v}}|\psi_i\rangle \tag{1.61}$$

While that form is indeed true, also look at it before removing the $\mathbf{r}$ variables–they give a trace operation:

$$\begin{aligned} \bar{\mathbf{j}} &= \frac{1}{V} \int d^3r \, \frac{e}{2}\sum_i p_i \,\{\langle\mathbf{r}|\hat{\mathbf{v}}|\psi_i\rangle\langle\psi_i|\mathbf{r}\rangle + \langle\mathbf{r}|\psi_i\rangle\langle\psi_i|\hat{\mathbf{v}}|\mathbf{r}\rangle\} \\ &= \frac{1}{V} \int d^3r \, \langle\mathbf{r}| \left[\frac{e}{2}\sum_i p_i \left(\hat{\mathbf{v}}|\psi_i\rangle\langle\psi_i| + |\psi_i\rangle\langle\psi_i|\hat{\mathbf{v}} \right) \right] |\mathbf{r}\rangle \end{aligned} \tag{1.62}$$

This has two terms, one proportional to $\text{Tr}\{\hat{\mathbf{v}}\hat{\rho}\}$ and the other $\text{Tr}\{\hat{\rho}\hat{\mathbf{v}}\}$. But this is a cyclic permutation within the trace, that does not change the result. So the two terms are the same. So the result is very simple,

$$\bar{\mathbf{j}} = \frac{1}{V}\text{Tr}\{\hat{\rho}e\hat{\mathbf{v}}\} = \frac{1}{V}\text{Tr}\{\hat{\rho}\hat{\mathbf{j}}\}, \qquad \hat{\mathbf{j}} \equiv e\hat{\mathbf{v}}. \tag{1.63}$$

Obviously, for N electrons, get the net current density,

$$\overline{\mathbf{J}} = N\bar{\mathbf{j}} = n\text{Tr}\left\{\hat{\rho}\hat{\mathbf{j}}\right\} = \text{Tr}\left\{\hat{\rho}\hat{\mathbf{J}}\right\}, \qquad \hat{\mathbf{J}} \equiv ne\hat{\mathbf{v}}. \tag{1.64}$$

That was a lot of work to come to a very simple and intuitive result. The conclusion is: If one is only averaging $\hat{\rho}_{Ne} = ne$ or $\hat{\mathbf{J}} = ne\hat{\mathbf{v}}$, the quantum expectation value is the average of that density over the system volume. The information about variations in space is lost. This, however, is very convenient, because in many problems, all we really want is the volume average. Furthermore, these volume averages will be relatively easy to calculate, because there really isn't any explicit integration over space! If the traces can be found, using whichever complete set of states is most convenient, then the volume averages are found easily.

1.5.2   Finding the quantum electric polarization

I realize there is an alternative approach for finding the dielectric function: Find the averaged electric polarization that is produced in response to the applied AC field. Polarization is just the electric dipole moment per unit volume. First calculate the electric dipole moment (density) associated with a single electron. The operator can be made in analogy with the charge density operator:

$$\hat{\mathbf{d}}(\mathbf{r}) = e\hat{\mathbf{r}}|\mathbf{r}\rangle\langle\mathbf{r}| \tag{1.65}$$

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Even better, is to just go ahead and formulate the operator whose expectation value (when divided by system volume) gives the volume averaged electric dipole moment,

$$\hat{\mathbf{d}} = e\hat{\mathbf{r}} \tag{1.66}$$

There are N electrons in the system, so the polarization is dipole moment per unit volume,

$$\mathbf{P} = \frac{N}{V}\langle\hat{\mathbf{d}}\rangle = n\,\mathrm{Tr}\left\{\hat{\rho}\hat{\mathbf{d}}\right\} \tag{1.67}$$

This is per unit volume, and depends on the number density of electrons, $n = N/V$. One point to be careful: Take only the part of the polarization that is oscillating at the same frequency as the applied AC optical field.

The polarization and current density are closely related. When the velocity is affected, so is the electron position. If the velocity operator is given as in (1.42) and averaged correctly (i.e., over the system volume), then the averaged position operator is its time integral

$$\langle\hat{\mathbf{r}}\rangle = \int dt\,\langle\hat{\mathbf{v}}\rangle = -\frac{1}{i\omega}\langle\hat{\mathbf{v}}\rangle \tag{1.68}$$

The last step follows from the assumption of $e^{-i\omega t}$ dependences (for the response of the entire quantum system as a whole). Then the polarization can be written

$$\mathbf{P} = \langle ne\hat{\mathbf{r}}\rangle = -\frac{1}{i\omega}\langle ne\hat{\mathbf{v}}\rangle = -\frac{1}{i\omega}\overline{\mathbf{J}} \tag{1.69}$$

This is a simple relationship

$$-i\omega\mathbf{P} = \dot{\mathbf{P}} = \overline{\mathbf{J}}. \tag{1.70}$$

Then the dielectric function in terms of polarization would be given by

$$[\tilde{\epsilon}(\omega) - \mathbf{1}]\cdot\mathbf{E} = 4\pi\mathbf{P} \tag{1.71}$$

Unfortunately, there is only one annoying problem in finding dielectric properties using the polarization. It is difficult to get the correct time-dependent polarization, while much easier to get the current density. The reason is, that the vector potential, which is the perturbation due to the optical field, is already contained in the definition of $\hat{\mathbf{J}}$, but it does not appear in the unperturbed states nor in the operator for $\mathbf{P}$. Thus, by doing the perturbation theory and finding expectation values of $\hat{\mathbf{J}}$ gives a better approximation than that using $\mathbf{P}$. In fact, one needs to do the calculations using the currents, so that the plasmon response of the whole electron gas is correctly determined.

1.6 Time-dependent perturbation and the density matrix

For a material in thermal equilibrium, the system cannot be supposed to be a a pure quantum state; that is typically impossible to prepare for a macroscopic system. Even if you could prepare an individual pure state, then it is not the appropriate state to use for averaging usually. We expect a system near thermal equilibrium, and only slightly perturbed from there by the application of the optical field. So the density matrix approach is a good way to do the correct averaging of physical quantities. Otherwise, in what state or states would you find expectation values, and how would you combine those values to get a physically relevant average that would be measured in experiments?

Suppose the (single-particle) Hamiltonian is initially just some unperturbed part that does not include the AC optical field, like

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m_e} + \hat{U}(\hat{\mathbf{r}}) \tag{1.72}$$

For simplicity, denote its eigenstates as $|i\rangle$ with eigenvalues E_i. In thermal equilibrium, the mixed state density operator (for one electron that can occupy different single particle states) is

$$\hat{\rho}_0 = \sum_i w_i|i\rangle\langle i| \tag{1.73}$$

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Each w_i is the probability of the chosen single-particle state being occupied. For one single-particle state, the partition function can be written in terms of the chemical potential μ as

$$Z_i = \sum_{n=0,1} e^{-\beta(E_i-\mu)n} = 1 + e^{-\beta(E_i-\mu)} \tag{1.74}$$

Since the state can hold either 0 or 1 fermion particle, the probability to be occupied is the same as the average number of particles it holds,

$$w_i = \langle n \rangle = \frac{0 * e^0 + 1 * e^{-\beta(E_i-\mu)}}{1 + e^{-\beta(E_i-\mu)}} = \frac{1}{e^{\beta(E_i-\mu)} + 1} \equiv f_0(E_i) \tag{1.75}$$

The last is the Fermi-Dirac distribution function. I'm not totally happy with this normalization, because it does not give a unit normalized density matrix, i.e., $\mathrm{Tr}\{\rho_0\} = N$, where N is the total number of electrons. But this seems to be what people have used for the w_i, I need to clarify this. For the multi-electron problem we are really wanting to solve, it does make sense. But only if we suppose as usual these states will be filled up by many electrons, starting from the lowest energies, until N electrons are place into states (up to the Fermi level). Still, it seems we should need a normalization factor of N to make the w_i into probabilities.

Another way to write the density operator is simply with $w_i = e^{-\beta(E_i-\mu n_i)}/Z$,

$$\hat{\rho}_0 = \frac{1}{Z} \sum_i e^{-\beta(E_i-\mu n_i)} |i\rangle\langle i| = \frac{1}{Z} e^{-\beta(H-\mu N)} \tag{1.76}$$

where the total particle number operator counts up particles in each state,

$$\hat{N} = \sum_i n_i |i\rangle\langle i|. \tag{1.77}$$

Correct normalization requires $Z = \mathrm{Tr}\{e^{-\beta(\hat{H}-\mu\hat{N})}\}$.

Now for the perturbation problem. Let the interaction with the optical field be turned on. It corresponds to an additional term in the Hamiltonian, initially supposed to be an oscillation at frequency ω,

$$\hat{H}_1 = \hat{V}(\hat{\mathbf{r}}) e^{-i\omega t} \tag{1.78}$$

This leads to induced currents and time-dependent electric dipoles. They are then the cause of the dielectric response. Further, its effect also takes place in the density matrix, by adding an additional part. The original unperturbed density matrix is $\hat{\rho}_0$, and this extra induced part is $\hat{\rho}_1$. (Now normalization seems more of a problem, unless $\hat{\rho}_1$ is traceless?) Then we write $\hat{\rho} = \hat{\rho}_0 + \hat{\rho}_1$ and $\hat{H} = \hat{H}_0 + \hat{H}_1$, and solve the QM Liouville equation,

$$i\hbar \frac{\partial\hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}] \tag{1.79}$$

But by its definition, $\hat{\rho}_0$ is independent of time and $[\hat{H}_0, \hat{\rho}_0] = 0$. This leaves only

$$i\hbar \frac{\partial\hat{\rho}_1}{\partial t} = [\hat{H}_0, \hat{\rho}_1] + [\hat{H}_1, \hat{\rho}_0] + [\hat{H}_1, \hat{\rho}_1] \tag{1.80}$$

In order to have a way to solve this, it is supposed that the perturbation $\hat{\rho}_1$ is small and also oscillates as $e^{-i\omega t}$. Then the last term here on the RHS is both smaller still, and oscillating as $e^{-2i\omega t}$, so it can be neglected as a nonlinear correction. To evaluate these kept terms, assume expansions of $\hat{H}_1$ and of $\hat{\rho}_1$ in the unperturbed basis states, using identity operators,

$$\hat{H}_1 = \sum_{fi} |f\rangle\langle f|\hat{H}_1|i\rangle\langle i|, \qquad \hat{\rho}_1 = \sum_{fi} c_{fi} |f\rangle\langle i|. \tag{1.81}$$

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Note that written this way, the constants $c_{fi} = \langle f|\rho_1|i\rangle$ are just the matrix elements of $\hat{\rho}_1$, in the H_0 basis states. Then we can see some results needed for the commutation relations, based on orthogonality relations $\langle i|j\rangle = \delta_{ij}$:

$$\hat{H}_1\rho_0 = \left(\sum_{fi}|f\rangle\langle f|\hat{H}_1|i\rangle\langle i|\right)\left(\sum_j w_j|j\rangle\langle j|\right) = \sum_{fi}|f\rangle\langle f|\hat{H}_1|i\rangle\langle i|w_i \tag{1.82}$$

$$\hat{\rho}_0\hat{H}_1 = \left(\sum_j w_j|j\rangle\langle j|\right)\left(\sum_{fi}|f\rangle\langle f|\hat{H}_1|i\rangle\langle i|\right) = \sum_{fi} w_f|f\rangle\langle f|\hat{H}_1|i\rangle\langle i| \tag{1.83}$$

Then this commutator is

$$[\hat{H}_1,\hat{\rho}_0] = \sum_{fi}(w_i - w_f)|f\rangle\langle f|\hat{H}_1|i\rangle\langle i| \tag{1.84}$$

Do similar algebra for the other commutator,

$$\hat{H}_0\hat{\rho}_1 = \hat{H}_0\left(\sum_{fi} c_{fi}|f\rangle\langle i|\right) = \sum_{fi} c_{fi}E_f|f\rangle\langle i| \tag{1.85}$$

$$\hat{\rho}_1\hat{H}_0 = \left(\sum_{fi} c_{fi}|f\rangle\langle i|\right) H_0 = \sum_{fi} c_{fi}|f\rangle\langle i|E_i \tag{1.86}$$

Then this commutator is

$$[\hat{H}_0,\hat{\rho}_1] = \sum_{fi}(E_f - E_i)c_{fi}|f\rangle\langle i| \tag{1.87}$$

With the assumption that $\hat{\rho}_1 \sim e^{-i\omega t}$, the differential equation is simplified to an algebraic one,

$$\hbar\omega\hat{\rho}_1 = [\hat{H}_0,\hat{\rho}_1] + [\hat{H}_1,\hat{\rho}_0] \tag{1.88}$$

This is now expressed as

$$\sum_{fi}\hbar\omega\, c_{fi}\,|f\rangle\langle i| = \sum_{fi}\left[(E_f - E_i)c_{fi} + (w_i - w_f)\langle f|\hat{H}_1|i\rangle\right]|f\rangle\langle i| \tag{1.89}$$

The factor on $|f\rangle\langle i|$ on both sides must be the same, which gives

$$(\hbar\omega + E_i - E_f)\,c_{fi} = (w_i - w_f)\langle f|\hat{H}_1|i\rangle \tag{1.90}$$

and so the solution for the matrix elements is

$$(\hat{\rho}_1)_{fi} = c_{fi} = \frac{(w_i - w_f)\langle f|\hat{H}_1|i\rangle}{\hbar\omega + (E_i - E_f) + i\gamma} \tag{1.91}$$

A small imaginary part is added to the frequency to effect the turning on of the perturbation. To make the similar expression for the actual density operator,

$$\hat{\rho}_1 = \sum_{fi}\frac{(w_i - w_f)|f\rangle\langle f|\hat{H}_1|i\rangle\langle i|}{\hbar\omega + (E_i - E_f) + i\gamma} \tag{1.92}$$

This agrees with Adler's expression, although my notation follows a thesis of M. Prange where there were various errors. The other authors' expressions, however, used the Fermi-Dirac occupation $f_0(E_i)$ in place of the probabilities w_i. I would say this expression here is absolutely correct. Note that you must use a unit normalized set of w_i if you want to get correct expectation values with it.

I used the notation with i and f to suggest initial and final states in processes that contribute. This expression (1.92) has a large contribution to its sum when $E_f = E_i + \hbar\omega$. That would be a term corresponding to absorption of a photon of energy $\hbar\omega$. But we would expect also to have emission terms. The reason they are not there, is that we cut them out by assuming only $e^{-i\omega t}$ dependence. The perturbation potential should be real and therefore have both negative and positive frequency terms. Thus we can try instead assuming

$$\hat{H}_1 = \hat{V}(\hat{\mathbf{r}})\cos\omega t \rightarrow \hat{V}_1(\hat{\mathbf{r}})e^{-i\omega t} + \hat{V}_1^{\dagger}(\hat{\mathbf{r}})e^{+i\omega t} \tag{1.93}$$

Then to leading order, the positive and negative frequency terms do not interfere and their contributions to $\hat{\rho}_1$ add linearly. The emission term corresponds to the complex conjugate of the absorption term and changing $\omega \rightarrow -\omega$. So the net result for the correction to the density matrix (at frequency ω) is their sum,

$$\hat{\rho}_1 = \sum_{fi}(w_i - w_f)\left\{\frac{\langle f|\hat{V}_1|i\rangle e^{-i\omega t}}{\hbar\omega + (E_i - E_f) + i\gamma} + \frac{\langle f|\hat{V}_1^{\dagger}|i\rangle e^{+i\omega t}}{-\hbar\omega + (E_i - E_f) - i\gamma}\right\}|f\rangle\langle i| \tag{1.94}$$

The Hermitian conjugate is needed for the general case, especially in the case of circular polarization where the polarization vectors of the electric field are complex. Now clearly the second term contributes strongly when $E_f = E_i - \hbar\omega$, which is an emission process. Now, however, it looks more difficult to decide what is the contribution to response functions at a frequency ω.

1.7 Expectation value of Polarization and response to optical field

Try to decide what averaging is simplest for determining the dielectric response. That would seem to be the electric polarization. I noted that there is a problem in doing it this way, but for the record, let's see what comes out.

The dipole operator is just the position (times charge). We can look at a single (positive) frequency and see what we get. The statistically averaged oscillating dipole moment for one electron has one contribution varying with the changes in the density matrix:

$$\langle\hat{\mathbf{d}}\rangle = \langle e\hat{\mathbf{r}}\rangle = \text{Tr}\{e\hat{\mathbf{r}}\hat{\rho}_1\} \tag{1.95}$$

Consider this algebra.

$$\langle\hat{\mathbf{r}}\rangle = \text{Tr}\{\hat{\mathbf{r}}\sum_{fi}c_{fi}|f\rangle\langle i|\} = \sum_m\langle m|\mathbf{r}\left(\sum_{fi}c_{fi}|f\rangle\langle i|\right)|m\rangle = \sum_{fi}c_{fi}\langle i|\hat{\mathbf{r}}|f\rangle = \sum_{fi}c_{fi}\hat{\mathbf{r}}_{if} \tag{1.96}$$

Obviously it is just the matrix product and then summed along the diagonal. To proceed further it seems the actual perturbation should be inserted. But, we can do some interesting rewriting in terms of the velocity operator, if desired. For the unperturbed system, which are the matrix elements needed here, we have for the velocity operator as defined,

$$i\hbar\dot{\hat{\mathbf{r}}} = i\hbar\hat{\mathbf{v}} = [\hat{\mathbf{r}}, \hat{H}_0] \tag{1.97}$$

Then the matrix elements can be found for both sides,

$$i\hbar\langle i|\hat{\mathbf{v}}|f\rangle = \langle i|(\hat{\mathbf{r}}\hat{H}_0 - \hat{H}_0\hat{\mathbf{r}})|f\rangle = \langle i|\hat{\mathbf{r}}E_f|f\rangle - \langle i|E_i\hat{\mathbf{r}}|f\rangle = (E_f - E_i)\langle i|\hat{\mathbf{r}}|f\rangle \tag{1.98}$$

Then the velocity matrix elements can be written

$$\langle i|\hat{\mathbf{v}}|f\rangle = i\omega_{if}\langle i|\hat{\mathbf{r}}|f\rangle, \qquad \omega_{if} \equiv (E_i - E_f)/\hbar. \tag{1.99}$$

Now the physical perturbation is

$$\hat{H}_1 = -\frac{e}{m_e c}\hat{\mathbf{A}}\cdot\hat{\mathbf{p}} \rightarrow -\frac{e}{c}\hat{\mathbf{A}}\cdot\hat{\mathbf{v}} \tag{1.100}$$

(The latter form is exactly correct even if $\hat{H}_0$ includes a magnetic field.) If we assume a uniform plane wave propagating along $\hat{z}$, linearly polarized along $\hat{\epsilon}$, take $\hat{\mathbf{A}} = A\hat{\epsilon}\, e^{i(\mathbf{q}\cdot\mathbf{r}-(\omega+i\gamma)t)}$ for a wave vector $\mathbf{q}$ with $\omega = qc$. The factor of γ is a phenomenological way to include damping in the quantum calculations. It represents, as well, the turning on of the perturbation for negative times. The radiation field in the radiation gauge or Coulomb gauge has electric field $\mathbf{E} = (-1/c)(\partial\mathbf{A}/\partial t) = i[(\omega + i\gamma)/c]\mathbf{A}$. Then the perturbation for the single positive frequency can be expressed

$$\hat{H}_1 = -\frac{e}{c}\left(\frac{c}{i(\omega+i\gamma)}\hat{\mathbf{E}}\right)\cdot\hat{\mathbf{v}} = \frac{-e}{i(\omega+i\gamma)}\hat{\mathbf{E}}\cdot\hat{\mathbf{v}} \tag{1.101}$$

(Note that e is the charge of the particle.) Note that this perturbation varies with $e^{-i\omega t}$ by design. Using this velocity form, can get the needed matrix element for $\hat{\rho}_1$, including the damping,

$$\langle f|\hat{H}_1|i\rangle = \frac{-e}{i(\omega+i\gamma)}\langle f|\hat{\mathbf{E}}\cdot\hat{\mathbf{v}}|i\rangle = \frac{-e}{i(\omega+i\gamma)}\langle f|\left(E_x\hat{v}_x + E_y\hat{v}_y\right)e^{i\mathbf{q}\cdot\hat{\mathbf{r}}}|i\rangle \tag{1.102}$$

This resulted, supposing that E_x and E_y vary as $e^{-i\omega t}$ and determine the polarization and magnitude of the electric wave. For simplicity, in the dipole approximation we'll assume $e^{i\mathbf{q}\cdot\mathbf{r}} \approx 1$. Then this just involves velocity matrix elements. So we can use the density matrix and find the averaged dipole of one electron:

$$\langle\hat{\mathbf{d}}\rangle = e\mathrm{Tr}\{\hat{\mathbf{r}}\hat{\rho}_1\} = e\sum_{fi}c_{fi}\hat{\mathbf{r}}_{if} = e\sum_{fi}\frac{(w_i - w_f)\langle f|\hat{H}_1|i\rangle}{\hbar\omega + (E_i - E_f) + i\gamma}\langle i|\hat{\mathbf{r}}|f\rangle \tag{1.103}$$

Write all in terms of the velocity matrix elements,

$$\langle\hat{\mathbf{d}}\rangle = e\sum_{fi}\frac{(w_i - w_f)}{\hbar\omega + (E_i - E_f) + i\gamma}\left(\frac{-e}{i(\omega+i\gamma)}\right)[E_x\langle f|\hat{v}_x|i\rangle + E_y\langle f|\hat{v}_y|i\rangle]\;\frac{i\hbar}{(E_f - E_i)}\langle i|\hat{\mathbf{v}}|f\rangle \tag{1.104}$$

This needs to be divided by the system volume V to get the dielectric polarization (dipole moment per unit volume), then with the electric fields "removed" to get components of the susceptibility tensor. I said it applies to a single electron, but really, because of the occupation probabilities and sums over all possible states, it really does give the response of the full N-electron system. In its simplest application, I will take the occupations to be $w_i = 1$ for the occupied "initial" states and $w_f = 0$ for the unoccupied "final" states. That means if the calculation is done for N electrons, the N occupied states will be filled up to the Fermi level for that electron density, N/V.

Here, change notation slightly on the electronic states ($i \rightarrow k$, $f \rightarrow k'$), and drop some of the operator symbols for simplicity. We can see, for example, the x-component of polarization that results due to the applied field along x:

$$P_{x,x} = \frac{e^2}{\hbar(\omega+i\gamma)V}\sum_{kk'}\frac{(w_k - w_{k'})\langle k|v_x|k'\rangle\langle k'|v_x|k\rangle}{\omega_{kk'}(\omega + \omega_{kk'} + i\gamma)}E_x \tag{1.105}$$

We can also see the x-component of polarization due to applied field along y:

$$P_{x,y} = \frac{e^2}{\hbar(\omega+i\gamma)V}\sum_{kk'}\frac{(w_k - w_{k'})\langle k|v_x|k'\rangle\langle k'|v_y|k\rangle}{\omega_{kk'}(\omega + \omega_{kk'} + i\gamma)}E_y \tag{1.106}$$

Then the general cartesian component of the susceptibility tensor that results is

$$\chi_{i,j} = \frac{e^2}{\hbar(\omega+i\gamma)V}\sum_{kk'}\frac{(w_k - w_{k'})\langle k|v_i|k'\rangle\langle k'|v_j|k\rangle}{\omega_{kk'}(\omega + \omega_{kk'} + i\gamma)} \tag{1.107}$$

Now we just have a couple more details to clear up: (1) This expression only includes the positive frequency response or the absorption processes–emission needs to be included, too. (2) The effect of the infinitesimal $i\gamma$ for convergence needs to be described. (3) The plasmon response of a free electron gas is missing! The calculation based on polarization has this annoying defect. I'll re-do the calculation below by finding the averaged current density; there the plasmon response does appear.

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1.7.1 Virtual emission and absorption terms?

Consider (1). The physical optical field $\mathbf{E}$ has to be real. Yet the calculation of $\epsilon(\omega)$ requires a complex perturbation varying as $Ve^{-i\omega t}$. So there is a dilemma. Writing here something like $\mathbf{E} = (E_x\hat{x} + E_y\hat{y})e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}$, for example, usually means that we imagine taking the real part of this expression and later results that follow from it. But this doesn't work here. Instead, avoiding using the result (1.94), I follow Adler's approach, and suppose we really only use the $e^{-i\omega t}$ perturbation. The result (1.107) for susceptibility has unrestricted sums over k and k', so it means which is "initial" and which is "final" is arbitrary. We can take that expression and write out explicitly one term where k is an occupied state (o) with k' unoccupied (u), and, another term where k is unoccupied and k' is occupied. Assuming transtions start in occupied states and end in unoccupied states, these will correspond to absorption and emission, respectively.

$$\chi_{i,j} = \frac{e^2}{\hbar(\omega+i\gamma)V}\left\{\sum_k^o\sum_{k'}^u \frac{(w_k-w_{k'})\langle k|v_i|k'\rangle\langle k'|v_j|k\rangle}{\omega_{kk'}(\omega+\omega_{kk'}+i\gamma)} + \sum_k^u\sum_{k'}^o \frac{(w_k-w_{k'})\langle k|v_i|k'\rangle\langle k'|v_j|k\rangle}{\omega_{kk'}(\omega+\omega_{kk'}+i\gamma)}\right\}$$
(1.108)

The k and k' labels can be swapped on the second term, as they are dummy indeces. Then the terms can be combined into one sum:

$$\chi_{i,j} = \frac{e^2}{\hbar(\omega+i\gamma)V}\sum_k^o\sum_{k'}^u\left\{\frac{(w_k-w_{k'})\langle k|v_i|k'\rangle\langle k'|v_j|k\rangle}{\omega_{kk'}(\omega+\omega_{kk'}+i\gamma)} + \frac{(w_{k'}-w_k)\langle k'|v_i|k\rangle\langle k|v_j|k'\rangle}{\omega_{k'k}(\omega+\omega_{k'k}+i\gamma)}\right\}$$
(1.109)

Now with $\omega_{k'k} = -\omega_{kk'}$ and a few other simple manipulations on the 2nd term,

$$\chi_{i,j} = \frac{e^2}{\hbar(\omega+i\gamma)V}\sum_k^o\sum_{k'}^u \frac{(w_k-w_{k'})}{\omega_{kk'}}\left\{\frac{\langle k|v_i|k'\rangle\langle k'|v_j|k\rangle}{(\omega+\omega_{kk'}+i\gamma)} + \frac{\langle k|v_j|k'\rangle\langle k'|v_i|k\rangle}{(\omega-\omega_{kk'}+i\gamma)}\right\}$$
(1.110)

This resembles an expression in Boswarva, Howard and Lidiard (1962), however, some signs seem to be different there, although I do not see any mistakes that I made. In BWL the factor of volume is missing. Everywhere they have $\omega_{k'k}$, I have $\omega_{kk'}$. But they don't show their derivation.

I refered to the terms as absorption and emission, but probably these are really just virtual processes, and when looking at the combination of matrix elements, they might be considered to resturn to their original occupied states.

1.7.2 Resonant absorption?

Now point (2). The infinitesimal $i\gamma$ in the denominators was added in an ad hoc way. One can see, however, that when ω matches a transition ω_{fi}, something singular will happen and there should be strong real (not virtual) absorption in a material. In order to avoid a catastrophe and exploding solution, the real world would have an actual physical damping that would limit the response. This a linearized model and does not include such damping, but we can put in a term to regulate this divergence, and later let it go to zero in some limit.

Go back to the differential equation which was solved to get an element of the density matrix. Check some algebra. That equation is

$$i\hbar\frac{d}{dt}(\rho_1)_{fi} = \hbar\omega_{fi}(\rho_1)_{fi} + \alpha H_{fi}(t)$$
(1.111)

or re-arranged and simplified

$$\left(i\frac{d}{dt} - \omega_{fi}\right)\rho(t) = a\,e^{-i\omega t}$$
(1.112)

To solve this, one way is to first find the Green's function for the operator on the LHS; the RHS is a source term, and we change it to a delta function just to get the Green's function. Furthermore, I am going to add a damping to get, in particular, the retarded GF. We have right now, with a source $f(t)$:

$$i\dot{G} - \omega_{fi}G = f, \qquad \text{or} \quad \ddot{G} = -i\dot{f} - \omega_{fi}^2 G$$
(1.113)

The 2nd form is just a forced harmonic oscillator whose coordinate is G. A damping would be an extra term $-\gamma \dot{G}$ on the RHS (a force opposing the velocity). Adding that term and re-arranging,

$$\ddot{G} + \gamma \dot{G} + \omega_{fi}^2 G = \frac{d}{dt}\left[\dot{G} + (\gamma + i\omega_{fi})G\right] = -i\frac{d}{dt}\left[i\dot{G} + (i\gamma - \omega_{fi})G\right] = -i\dot{f} \qquad (1.114)$$

Now putting the delta function source, solve

$$i\dot{G} + (i\gamma - \omega_{fi})G = \delta(t) \qquad (1.115)$$

This can be solved by Fourier transforms:

$$G(z) = \int_{-\infty}^{\infty} dt\ G(t)e^{izt}, \qquad G(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dz\ G(z)e^{-izt}, \qquad (1.116)$$

Here I used z as the frequency parameter within these transforms, because ω is used as the frequency of the optical field. Doing the transform of the ODE gives

$$\int dt\ e^{izt}\left(i\frac{d}{dt} - \omega_{fi} + i\gamma\right)G(t) = \int dt\ e^{izt}\delta(t) \qquad (1.117)$$

Integrating by parts on the LHS, and using the delta on RHS,

$$\left[-i(iz) - \omega_{fi} + i\gamma\right]G(z) = 1 \implies G(z) = \frac{1}{z - \omega_{fi} + i\gamma} \qquad (1.118)$$

It's very simple in the frequency space. To get back the time dependence, invert the FT:

$$G(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dz\ \frac{e^{-izt}}{z - \omega_{fi} + i\gamma} \qquad (1.119)$$

When you look at the integral in the complex z-plane, there is a pole at $z = \omega_{fi} - i\gamma$, in the lower half-plane. Due to the argument in the exponential, the contour should be closed in the upper half-plane for $t < 0$ and in the lower half-plane [with a (-) sign] for $t > 0$. So only for $t > 0$ is there a nonzero result, and taking the integral to be $-2\pi i$ times the residue at the pole, there results,

$$G(t) = -iH(t)e^{-i(\omega_{fi} - i\gamma)t} \qquad (1.120)$$

The step function $H(t)$ insures only a result for $t > 0$, as expected for a retarded GF. Now we can easily solve for a component of the density matrix, using the source $f(t) = ae^{-i\omega t}$.

$$\rho(t) = \int_{-\infty}^{\infty} dt'\ G(t-t')f(t') = \int_{-\infty}^{t} dt'\ (-ie^{-i(\omega_{fi}-i\gamma)(t-t')})\ ae^{-i\omega t'} \qquad (1.121)$$

The integration is simple and gives an exact simple result we could have expected:

$$\rho(t) = \frac{ae^{-i\omega t}}{\omega + i\gamma - \omega_{fi}} \qquad (1.122)$$

This is the steady state solution when the source has been turned on for a long time, and we want to see the response at the current time t. Even though there *is* damping in this calculation, it does not appear in the argument of the exponential. But there is a phase shift between the source and the response, due to the damping appearing in the denominator. Incredibly, you could get this in one line by really believing that everything just oscillates at a single frequency like the source.

   This solution just confirms what was found earlier. One curiosity is that if you do the solution using the advanced GF, the only change will be in the sign of the damping. But the difficulty here is how to let the damping go to zero. I have not found a physically enlightening way to do that. The above does not apply to $\gamma = 0$, because it was found with a pole off of the real axis. The limit would put that pole onto the real axis, and different mathematics needs to be applied. The mathematical

problem really *is* singular at $\gamma \to 0^+$, because the modes that would absorb real energy when $\omega = \omega_{fi}$ are not included in our system (the energy would go to heating of the material, to phonons, etc., rather than an ever increasing electron energy).

It is interesting to imagine that the source was only turned on at time $= 0$. Then the lower limit in (1.121) is now 0, and gives a transient term:

$$\rho(t) = \frac{ae^{-i\omega t} - e^{-\gamma t}e^{-i\omega_{fi}t}}{\omega + i\gamma - \omega_{fi}} \tag{1.123}$$

Now when the damping becomes weak and the driving frequency is near ω_{fi} we have, for short times,

$$\rho(t) = a\frac{1 - e^{i(\omega - \omega_{fi} + i\gamma)t}}{\omega - \omega_{fi} + i\gamma}e^{-i\omega t} \approx -iat\, e^{-i\omega t} \tag{1.124}$$

This is similar to an absorption at a constant rate, until an equilibrium is reached.

After all this, I don't have a very satisfactory explation of what to do with the $i\gamma$ in the expressions, but here is what is usually done. Eventually, the system may be exposed to a spectrum of light rather than a single frequency. Thus, the response will involve some integration over that spectrum. Or alternatively, the sums over states will be transformed into integrals oer k-space, for example. It means that in those integrations we can use the Sokchatsky-Weierstrass theorem for taking the limit of zero damping parameter, which states

$$\lim_{\gamma \to 0^+} \int_{-\infty}^{\infty} dx\, \frac{f(x)}{x + i\gamma} = \lim_{\gamma \to 0^+} \int_{|x|>\gamma} dx\, \frac{f(x)}{x} - i\pi f(0) \tag{1.125}$$

The integral on the RHS is a Cauchy principal valued integral. The second term is as if there was a delta function in the integrand. Sometimes this is stated in symbolic form,

$$\lim_{\gamma \to 0^+} \frac{1}{x + i\gamma} = \text{p.v.}\left(\frac{1}{x}\right) - i\pi\delta(x) \tag{1.126}$$

This is applied as the interpretation of the damping terms that have been added to the expressions for ρ_1 and hence the response tensors.

Interestingly, the proof of the SW theorem is surprisingly simple. Do some algebra.

$$\frac{1}{x + i\gamma} = \frac{1}{x + i\gamma} \cdot \frac{x - i\gamma}{x - i\gamma} = \left(\frac{x^2}{x^2 + \gamma^2}\right)\frac{1}{x} - i\pi\left(\frac{\gamma}{\pi(x^2 + \gamma^2)}\right). \tag{1.127}$$

When placed inside an integral, the first factor in parenthesis goes to 1 for $x^2 \gg \gamma^2$ and goes to zero for $x^2 \ll \gamma^2$. Thus as $\gamma \to 0$ it produces the Cauchy principal value. The second factor in parenthesis gives a representation of the delta function $\delta(x)$ as $\gamma \to 0^+$. It's integral over the entire axis gives 1 for any value of $\gamma > 0$, and it becomes peaked around the origin as $\gamma \to 0^+$. Thus, the theorem is proved. If the sign of γ is reversed, then the sign on the delta function also is reversed.

The SW theorem is applied to the expressions for χ as follows. Where an integration over the source spectrum occurs, the terms where $i\gamma$ appear are presumed to be substituted by their SW expressions. Specifically, in the expression for χ there are terms

$$\frac{1}{\omega + \omega_{kk'} + i\gamma} \longrightarrow \text{p.v.}\left(\frac{1}{\omega + \omega_{kk'}}\right) - i\pi\delta(\omega + \omega_{kk'}) \tag{1.128}$$

$$\frac{-1}{-\omega + \omega_{kk'} - i\gamma} \longrightarrow \text{p.v.}\left(\frac{-1}{-\omega + \omega_{kk'}}\right) - i\pi\delta(-\omega + \omega_{kk'}) \tag{1.129}$$

Then the signs on the two delta function terms are the same, and these terms should correspond to energy absorption by the matter.

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1.8 Expectation value of Current Density: The plasmon term in χ

The previous subsection described how to get the response proportional to the change in the density matrix, using averaging of the polarization. But amazingly, that misses a very important term in the susceptibility, namely, the plasmonic oscillations.

Instead, consider here finding the susceptibility from the (volume) averaged current density. We need to do the full averaging with the whole density matrix. The volume averaged current density is

$$\langle \mathbf{J} \rangle = \langle ne\mathbf{v} \rangle = \text{Tr}\{ne\mathbf{v}(\rho_0 + \rho_1)\} = ne\left(\text{Tr}\{\mathbf{v}\rho_0\} + \text{Tr}\{\mathbf{v}\rho_1\}\right) \tag{1.130}$$

The electron velocity operator is $\mathbf{v} = [\mathbf{p} - (e/c)\mathbf{A}]/m_e$. Its averaging using the unperturbed density matrix (1st term above) gives

$$\text{Tr}\{\mathbf{v}\rho_0\} = \frac{1}{m_e}\text{Tr}\{\mathbf{p}\rho_0\} - \frac{e}{m_e c}\text{Tr}\{\mathbf{A}\rho_0\} \tag{1.131}$$

The averaged momentum in the unperturbed state is zero:

$$\langle \mathbf{p} \rangle_0 = \text{Tr}\{\mathbf{p}\rho_0\} = \sum_k \langle k|\mathbf{p}\left(\sum_{k'} w_{k'}|k'\rangle\langle k'|\right)|k\rangle = \sum_k w_k \langle k|\mathbf{p}|k\rangle = \sum_k w_k \mathbf{p}_k = 0 \tag{1.132}$$

The sum is zero because for every state with a positive momentum, there will be another state at the same energy and probability with the opposite momentum (using $H_0 = \mathbf{p}^2/2m_e + U(\mathbf{r})$ only). For the vector potential, we assume waves

$$\mathbf{A}(\mathbf{r}, t) = \tilde{\mathbf{A}}e^{i(\mathbf{q}\cdot\mathbf{r} - \omega t)} \tag{1.133}$$

The averaged vector potential is then

$$\langle \mathbf{A} \rangle_0 = \text{Tr}\{\mathbf{A}\rho_0\} = \tilde{\mathbf{A}}e^{-i\omega t}\,\text{Tr}\{e^{i\mathbf{q}\cdot\mathbf{r}}\rho_0\} = \tilde{\mathbf{A}}e^{-i\omega t}\sum_k w_k \langle k|e^{i\mathbf{q}\cdot\mathbf{r}}|k\rangle = \tilde{\mathbf{A}}e^{-i\omega t}\langle e^{i\mathbf{q}\cdot\mathbf{r}} \rangle_0 \tag{1.134}$$

Here use either momentum or position eigenstates for the matrix elements, and apply the fact that the trace of ρ_0 is unity. But then this last term produces a current! The value is

$$\begin{aligned}
\mathbf{J}_0 &= ne\langle \mathbf{v} \rangle_0 = ne\text{Tr}\{\mathbf{v}\rho_0\} = -\frac{ne^2}{m_e c}\langle \mathbf{A} \rangle_0 \\
&= -\frac{ne^2}{m_e c}\tilde{\mathbf{A}}\,\langle e^{i\mathbf{q}\cdot\mathbf{r}} \rangle_0\,e^{-i(\omega + i\gamma)t} = -\frac{ne^2}{i(\omega + i\gamma)m_e}\tilde{\mathbf{E}}\,\langle e^{i\mathbf{q}\cdot\mathbf{r}} \rangle_0\,e^{-i(\omega + i\gamma)t}
\end{aligned} \tag{1.135}$$

In the last step I used $\tilde{\mathbf{E}} = [i(\omega + i\gamma)/c]\tilde{\mathbf{A}}$ for the amplitudes. Based on using (1.19), its contribution to the susceptibility is diagonal,

$$\chi_{ij}^{(A)}(\omega) = -\frac{ne^2}{m_e\omega(\omega + i\gamma)}\delta_{ij} \tag{1.136}$$

It is the same as the classical model calculation–which explains why the damping had to be included the way it was.

Note that there is some technical detail about requiring the average $\langle e^{i\mathbf{q}\cdot\mathbf{r}} \rangle_0 \to 1$; it seems to require $\mathbf{q} = \mathbf{0}$ to give a factor of 1. But this is what we do in the dipole approximation, so I'll assume that there is no great error in this here. In fact, one needs to assume that the averaging volume is small compared to the wavelength of the light. Then this term leads to the usual plasmon frequency term in $\epsilon(\omega)$, for free electrons.

1.9 The current from the perturbation term in the density matrix

Check now the contribution from the second term in the current density,

$$\mathbf{J}_1 = ne\langle\mathbf{v}\rangle_1 = ne\text{Tr}\{\mathbf{v}\rho_1\} = ne\sum_{kk'}\mathbf{v}_{kk'}\,(\rho_1)_{k'k} \tag{1.137}$$

Using the unrestricted sums over the states, and the expression (1.91) for the density matrix, as well as (1.102), there results

$$
\begin{aligned}
\mathbf{J}_1 &= \frac{e}{V}\sum_{kk'}\hat{\mathbf{v}}_{kk'}\frac{(w_k - w_{k'})\langle k'|\hat{H}_1|k\rangle}{\hbar\omega + (E_k - E_{k'}) + i\gamma}\\
&= \frac{e}{V}\sum_{kk'}\hat{\mathbf{v}}_{kk'}\frac{(w_k - w_{k'})}{\hbar\omega + (E_k - E_{k'}) + i\gamma}\left(\frac{-e}{i(\omega + i\gamma)}\right)\langle k'|\left(E_x\hat{v}_x + E_y\hat{v}_y\right)e^{i\mathbf{q}\cdot\mathbf{r}}|k\rangle \quad (1.138)
\end{aligned}
$$

(Since the sums are effectively over all N electrons, I adjusted the normalization.) The current along x when the electric field is along x is

$$(J_1)_{x,x} = -\frac{e^2}{i(\omega + i\gamma)V}\sum_{kk'}\frac{(w_k - w_{k'})\langle k|\hat{v}_x|k'\rangle\langle k'|\hat{v}_x|k\rangle}{\hbar\omega + (E_k - E_{k'}) + i\gamma}E_x \tag{1.139}$$

Similarly, the current along x when the electric field is along y is

$$(J_1)_{x,y} = -\frac{e^2}{i(\omega + i\gamma)V}\sum_{kk'}\frac{(w_k - w_{k'})\langle k|\hat{v}_x|k'\rangle\langle k'|\hat{v}_y|k\rangle}{\hbar\omega + (E_k - E_{k'}) + i\gamma}E_y \tag{1.140}$$

In both of these I used the dipole approximation, $e^{i\mathbf{q}\cdot\mathbf{r}} \approx 1$. Dividing by $-i\omega$ [like integration w.r.t time, see (1.19)] and taking out the factors of electric field gives the general susceptibility component,

$$\chi_{ij}^{(B)}(\omega) = -\frac{e^2}{\hbar\omega(\omega + i\gamma)V}\sum_{kk'}\frac{(w_k - w_{k'})\langle k|v_i|k'\rangle\langle k'|v_j|k\rangle}{\omega + \omega_{kk'} + i\gamma} \tag{1.141}$$

This is different than that obtained by from the polarization, Eqn. (1.107), however, it agrees with the calculations of Adler. Especially, it has the extra factor of source frequency ω in the denominator, where the polarization calculation had $-\omega_{kk'}$. How to consolidate this? Overall, this last calculation was simpler and more believable. One factor of ω came from switching $\mathbf{A}$ into $\mathbf{E}$; the other factor came from doing the classical E&M theory for $\tilde{\epsilon}(\omega)$, it is hard to see an error there. But the polarization and current results are *approximately* the same. The denominator forces the largest contributions to come when $\omega + \omega_{kk'} \approx 0$, and this would then imply changing $\omega_{kk'} \to -\omega$ in the other factor in the denominator of Eqn. (1.107). That makes the expressions almost agree, but they are not identical.

Combining with the gauge current term, this approach gives the total susceptibility,

$$\chi_{ij}(\omega) = -\frac{ne^2}{m\omega(\omega + i\gamma)}\delta_{ij} - \frac{e^2}{\hbar\omega(\omega + i\gamma)V}\sum_{kk'}\frac{(w_k - w_{k'})\langle k|v_i|k'\rangle\langle k'|v_j|k\rangle}{\omega + \omega_{kk'} + i\gamma} \tag{1.142}$$

The resulting dielectric function is obtained from $\epsilon = 1 + 4\pi\chi$,

$$\epsilon_{ij}(\omega) = \delta_{ij} - \frac{4\pi ne^2}{m\omega(\omega + i\gamma)}\delta_{ij} - \frac{4\pi e^2}{\hbar\omega(\omega + i\gamma)V}\sum_{kk'}\frac{(w_k - w_{k'})\langle k|v_i|k'\rangle\langle k'|v_j|k\rangle}{\omega + \omega_{kk'} + i\gamma} \tag{1.143}$$

Adler says in a material of cubic symmetry, this gives an isotropic function, i.e., the dielectrc function is diagonal. Would need to insert momentum states and do some special averages to see that.

I want to see the result in terms of occupied and unoccupied states. Letting k be occupied and k' unoccupied, and then vice versa, we have

$$\chi_{ij}^{(B)} = \frac{-e^2}{\hbar\omega(\omega + i\gamma)V}\left\{\sum_{k}^{o}\sum_{k'}^{u}\frac{(w_k - w_{k'})\langle k|v_i|k'\rangle\langle k'|v_j|k\rangle}{\omega + \omega_{kk'} + i\gamma} + \sum_{k}^{u}\sum_{k'}^{o}\frac{(w_k - w_{k'})\langle k|v_i|k'\rangle\langle k'|v_j|k\rangle}{\omega + \omega_{kk'} + i\gamma}\right\}$$
(1.144)

Switch the names on the 2nd sum:

$$\chi_{ij}^{(B)} = \frac{-e^2}{\hbar\omega(\omega + i\gamma)V}\sum_{k}^{o}\sum_{k'}^{u}\left\{\frac{(w_k - w_{k'})\langle k|v_i|k'\rangle\langle k'|v_j|k\rangle}{\omega + \omega_{kk'} + i\gamma} + \frac{(w_{k'} - w_k)\langle k'|v_i|k\rangle\langle k|v_j|k'\rangle}{\omega + \omega_{k'k} + i\gamma}\right\}$$
(1.145)

Make a few other simple manipulations on the 2nd term,

$$\chi_{ij}^{(B)} = \frac{-e^2}{\hbar\omega(\omega + i\gamma)V}\sum_{k}^{o}\sum_{k'}^{u}(w_k - w_{k'})\left\{\frac{\langle k|v_i|k'\rangle\langle k'|v_j|k\rangle}{\omega + \omega_{kk'} + i\gamma} + \frac{\langle k|v_j|k'\rangle\langle k'|v_i|k\rangle}{-\omega + \omega_{kk'} - i\gamma}\right\}$$
(1.146)

At some point this form could be useful. Putting together with the other parts, and expanding the effect of $i\gamma$, the dielectric function in the limit of zero damping can be expressed as

$$\begin{aligned}
\epsilon_{ij}(\omega) &= \left(1 - \frac{4\pi n e^2}{m_e\omega^2}\right)\delta_{ij} \\
&- \frac{4\pi e^2}{\hbar\omega^2 V}\sum_{k}^{o}\sum_{k'}^{u}\langle k|v_i|k'\rangle\langle k'|v_j|k\rangle\left[\text{p.v.}\left(\frac{1}{\omega + \omega_{kk'}}\right) - i\pi\delta(\omega + \omega_{kk'})\right] \\
&- \frac{4\pi e^2}{\hbar\omega^2 V}\sum_{k}^{o}\sum_{k'}^{u}\langle k|v_j|k'\rangle\langle k'|v_i|k\rangle\left[\text{p.v.}\left(\frac{-1}{\omega - \omega_{kk'}}\right) + i\pi\delta(\omega - \omega_{kk'})\right]
\end{aligned}$$
(1.147)

In the 2nd and 3rd lines I used $(w_k - w_{k'}) = 1$. In this form the two delta functions have opposite signs; not sure about the significace of that, for example, in the diagonal elements of $\tilde{\epsilon}$. For those diagonal elements, the product of matrix elements in these expressions are real, of the form, $|\langle k|v_i|k'\rangle|^2$. Another point: Adler takes the wavevector of the final states to be the same as the wavevector of the initial states (direct band-to-band transitions). This has some further simplifying effects on the matrix elements.

It would be good to see if this can be applied to some simple models for the electrons.

1.10 The plasmon term in χ: From averaged polarization?

I noted the difficulty to get the diagonal plasma response by using the averaging of the electric polarization. It seems that term in χ or ϵ does not come out naively. However, we can force it to come out, by making some reasonable definitions.

The difficulty comes about, because the averaging by $\mathbf{J} = \langle ne\hat{\mathbf{v}}\rangle/(-i\omega)$ has no simple analogue in terms of the position operator average $\mathbf{P} = \langle ne\hat{\mathbf{r}}\rangle$ needed for polarization averaging. But these two ways have to be connected, because we know the basic quantum dynamics is described by equations of motion for $\mathbf{r}$ and $\mathbf{v}$, the latter of which is defined via

$$\hat{\mathbf{v}} = \frac{1}{m_e}\vec{\pi} = \frac{1}{m_e}\left(\hat{\mathbf{p}} - \frac{e}{c}\hat{\mathbf{A}}\right)$$
(1.148)

To make both approaches give this desired plasma term, we can do the following very reasonable definition for a dynamic position operator, *defined from the kinetic momentum*:

$$\hat{\mathbf{r}} = \frac{d}{dt}\hat{\mathbf{v}} \equiv \frac{\hat{\mathbf{v}}}{-i\omega} = \frac{\vec{\pi}}{-i\omega m_e}.$$
(1.149)

It is not the most fundamental definition, because ω is defined from the source field. So what I mean more specifically, is that it applies to the velocity and the position associated with the averages

using $\hat{\rho}_1$, i.e., only with the parts due to the AC perturbation, which comes only from the vector potential. Those are

$$\hat{\mathbf{v}}_1 \equiv -\frac{e}{m_e c}\hat{\mathbf{A}}, \quad \hat{\mathbf{r}}_1 \equiv \frac{\hat{\mathbf{v}}_1}{-i\omega} = \frac{e}{i\omega m_e c}\hat{\mathbf{A}}. \tag{1.150}$$

Then with this definition of a "dynamic position" operator, its thermal average will indeed give back the same plasma term as did the averaging of the current density, by design.

$$\mathbf{P}_1 = \langle ne\hat{\mathbf{r}}_1 \rangle = (ne)\frac{e}{i\omega m_e c}\mathrm{Tr}\left\{\hat{\rho}_1 \hat{\mathbf{A}}\right\} \to \frac{-ne^2}{m_e\omega(\omega + i\gamma)}\mathbf{E}. \tag{1.151}$$

It may not be a very rigorous approach, howver, it seems necessary in the presence of the type of current/motion that is induced by the vector potential term. Essentially, one has to imagine that a quantum electron actually moves back and forth in the direction of $\mathbf{A}$ as it oscillates in time. Otherwise, one does not reproduce this very simple physical effect, of the direct polarization of the electron charge by the applied electric field. This may be a difficulty that appears only because we are using the Coulomb gauge with zero scalar potential ϕ.

2   Applications to some models

The QM theory was seen above to be considerably more difficult than the classical theory for $\tilde{\epsilon}(\omega)$. Some tests of the theory would be a good idea. Especially, it would be good to look at (1) a quantum free electron gas; (2) electrons making band-to-band transitions; (3) an electron gas in a DC magnetic field; (4) the band-to-band transition problem, with the DC magnetic field included.

Except for (1), these problems have no true classical analogue against which the results can be compared. Electron bands are inherently quantum mechanical. Once a magnetic field is applied, electron states are quantized in Landau levels, which have interesting QM properties. They may move similar to cyclotron motions, but that analogy cannot be taken too far in the QM world.

2.1   Quantum free electron gas

We know there should be the plasmon term as in (1.143), but are there contributions due to the kk' sum? The short answer is: NO. Suppose the basis states are taken as plane waves normalized in a volume V, that are eigenstates of momentum:

$$\psi_{\mathbf{k}} = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}} \tag{2.1}$$

The momentum eigenvalues are $\mathbf{p}_k = \hbar\mathbf{k}$. The matrix elements we need are really just diagonal:

$$\langle k'|v_x|k\rangle = \frac{1}{m_e}\langle \mathbf{k}'|\hat{p}_x|\mathbf{k}\rangle = \frac{\hbar k_x}{m_e}\delta_{\mathbf{k},\mathbf{k}'} \tag{2.2}$$

This forces the initial and final states to be the same. But their probabilities are equal, with $w_k - w_{k'} = 0$, so there are no nonzero contributions to the sum. Because the electrons' transitions in this theory do not change wave vector, there is no contribution. So to leading order, the dielectric function is just the typical plasmon response,

$$\epsilon(\omega) \approx 1 - \frac{4\pi ne^2}{m_e\omega^2} \tag{2.3}$$

If we went beyond the dipole approximation, then there would be small changes in momentum in the transitions, according to the momentum in the photons, into states with a slightly different probability. That would lead to some small but nonzero changes in $\tilde{\epsilon}$. In that case, we would want to look for the induced polarization at the wave vector $\mathbf{q}$ of the light field. Further, the light field

wave appears in the perturbation $\hat{H}_1$. So it looks like one can see the main changes here by keeping the factor $e^{i\mathbf{q}\cdot\mathbf{r}}$ in the matrix elements:

$$\langle k'|\hat{\mathbf{v}}e^{i\mathbf{q}\cdot\hat{\mathbf{r}}}|k\rangle = \frac{1}{m_e}\langle \mathbf{k}'|\hat{\mathbf{p}}e^{i\mathbf{q}\cdot\hat{\mathbf{r}}}|\mathbf{k}\rangle = \frac{1}{m_e}\langle \mathbf{k}'|\hat{\mathbf{p}}e^{i\mathbf{q}\cdot\hat{\mathbf{r}}}|\mathbf{k}\rangle\delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}} \tag{2.4}$$

The delta enforces momentum conservation. I have over-simplified it; including these details would lead to corrections to the dielectric function that depend on both the frequency and wave vector.

2.2   Band to band transitions

The free electron gas really has all the electrons living in a single electron band, if you like, whose energy dispersion is just $E = \hbar^2\mathbf{k}^2/2m_e$. For momentum conserving transitions, or in the dipole approximation, the terms in the sums are all zero.

Instead, suppose the electrons live in two (or more) different electron bands. Usually the simplest case is that of a valence band at lower energies and a conduction band at higher energies, with the two possibly separated by some gap E_g (as in a semiconductor). Now there can be inter-band transitions that will indeed contribute to the sum (B) in the expression for χ. It will be supposed that the valence band states are (nearly) filled and the conduction band states are (nearly) empty. So the most important transitions go from the valence band into the conduction band.

As discussed for the free electron gas, use the plane wave states (times basis states $u_{l,\mathbf{k}}(\mathbf{r})$) and only consider (momentum conserving) vertical transitions so that $\mathbf{k}' = \mathbf{k}$. For an isotropic system, let's assume that χ is diagonal. The basic matrix element needed is simple:

$$\langle k'|v_x|k\rangle = \frac{1}{m_e}\langle \mathbf{k}'|\hat{p}_x|\mathbf{k}\rangle = \frac{\hbar k_x}{m_e}M(\mathbf{k})\,\delta_{\mathbf{k}',\mathbf{k}} \tag{2.5}$$

However, this depends on the overlap integral between the states in the two different bands l and l', at the wavevector of interest:

$$M(\mathbf{k}) = \langle u_{l,\mathbf{k}}|u_{l',\mathbf{k}'}\rangle \tag{2.6}$$

The (B) sum for χ, based on the averaging of the polarization, can be expressed as

$$\chi_{xx}^{(B)} = \frac{e^2}{\hbar(\omega+i\gamma)V}\frac{\hbar^2}{m_e^2}\sum_k^o\sum_{k'}^u \frac{(w_k-w_{k'})}{\omega_{kk'}}k_x^2|M(\mathbf{k})|^2\delta_{\mathbf{k}',\mathbf{k}}\left\{\frac{1}{\omega+\omega_{kk'}+i\gamma}+\frac{1}{\omega-\omega_{kk'}+i\gamma}\right\} \tag{2.7}$$

Following Inouye, I am going to keep the infinitesimal damping term and call it γ here. It could be kept finite in the calculation to describe damping, as was done for the classical plasmon analysis. k and k' are states in two different bands. Since k is in the "occupied" band, it is in the valence (or hole quasiparticle) band, while k' is in the conduction (or electron quasiparticle) band. Take the two bands to have parabolic dispersions,

$$E_k = E_h = -\frac{1}{2}E_g - \frac{\hbar^2 k^2}{2m_h^*}, \qquad E_{k'} = E_e = \frac{1}{2}E_g + \frac{\hbar^2 k'^2}{2m_e^*}, \tag{2.8}$$

The zero of energy is taken in the middle of the gap between the bands. The frequency difference for the transitions is

$$\omega_{kk'} = \frac{1}{\hbar}(E_h - E_e) = -\frac{1}{\hbar}\left[E_g + \frac{\hbar^2 k^2}{2m_h^*} + \frac{\hbar^2 k'^2}{2m_e^*}\right] \tag{2.9}$$

But since the wave vectors have the same magnitudes, this difference is

$$\omega_{kk'} = -\frac{1}{\hbar}\left(E_g + \frac{\hbar^2 k^2}{2\tilde{m}}\right) = -\left(\omega_g + \frac{\hbar k^2}{2\tilde{m}}\right), \qquad \frac{1}{\tilde{m}} \equiv \frac{1}{m_h^*} + \frac{1}{m_e^*}, \tag{2.10}$$

where $\tilde{m}$ is the reduced electron/hole mass and $\omega_g = E_g/\hbar$ is the gap frequency.

Only one sum survives, due to the delta, and that sum can be transformed into an integral. Let me leave it as a sum for the moment,

$$\chi_{xx}^{(B)} = \frac{e^2\hbar}{m_e^2(\omega+i\gamma)V} \sum_k^o \frac{(w_k - w_{k'})}{\omega_{kk'}} k_x^2 |M(\mathbf{k})|^2 \left\{ \frac{1}{\omega + \omega_{kk'} + i\gamma} + \frac{1}{\omega - \omega_{kk'} + i\gamma} \right\} \qquad (2.11)$$

and rewrite the summand:

$$\chi_{xx}^{(B)} = \frac{2e^2\hbar}{m_e^2(\omega+i\gamma)V} \sum_k^o F_{kk'} \, k_x^2 \, |M(\mathbf{k})|^2 \left[\frac{(\omega+i\gamma)/\omega_{kk'}}{(\omega+i\gamma)^2 - \omega_{kk'}^2} \right] \qquad (2.12)$$

Although there is no k' left, the transition energy difference is defined above and $F_{kk'} = w_k - w_{k'}$ is the change in occupation probabilities. The expression (2.11) might be used in the limit $\gamma \to 0$ along with the SW theorem. Expression (2.12) is better if we want to keep a finite damping. Even so, to proceed further, we need to know the "dimensionality" of the bands, so the sum can be converted to an integral.

2.3 Three-dimensional bands without damping

First, suppose that the bands we are talking about have their energies expanded around $k = 0$ and they are isotropic 3D bands. This could be the case if somehow the band structure of the material has the two bands centered isotropically around the Γ-point ($k = 0$) in the Brilluoin zone. It is not realistic, however, if the gap occurs somewhere else in the zone.

It is assumed that the sum over $\mathbf{k}$ can be transformed to an integral in the usual way,

$$\sum_{\mathbf{k}} \to \frac{V}{(2\pi)^3} \int d^3k \qquad (2.13)$$

the reason being, of course, that each mode in k-space occupies a volume there of $(\frac{2\pi}{L})^3$. Furthermore, for simplicity take $w_k - w_{k'} = 1$ and suppose that the matrix element M is a constant. I will use the expressions such as (1.110) and (2.11) based on the polarization approach, because that seems to have been used by Inouye and appears to have a better convergence. In the limit of zero damping, Eqn. (2.11) has a principal value part $\chi^{(B_1)}$ and a delta-function part $\chi^{(B_2)}$.

Delta functions: Let's first evaluate the resonant absorption part $\chi^{(B_2)}$ due to the delta-functions. It is

$$\chi_{xx}^{(B_2)} = \frac{e^2\hbar}{m_e^2\omega V} \frac{V}{(2\pi)^3} \int d^3k \, \frac{k_x^2}{\omega_{kk'}} |M(\mathbf{k})|^2 (-i\pi) \left\{ \delta(\omega + \omega_{kk'}) + \delta(\omega - \omega_{kk'}) \right\} \qquad (2.14)$$

Using $k_x = k \sin\theta \cos\phi$, and $d^3k = k^2 \, d\Omega = k^2 \, dk \, d(\cos\theta) \, d\phi$, the angular parts of the integral give

$$\int d\Omega \, k_x^2 = \int_0^{2\pi} d\phi \int_{-1}^{+1} d(\cos\theta) \, (k\sin\theta\cos\phi)^2 = \frac{4\pi}{3} k^2 \qquad (2.15)$$

This gives

$$\chi_{xx}^{(B_2)} = \frac{-i\pi e^2\hbar}{m_e^2\omega} \frac{4\pi/3}{(2\pi)^3} \int dk \, \frac{k^4}{\omega_{kk'}} |M(\mathbf{k})|^2 \left\{ \delta(\omega + \omega_{kk'}) + \delta(\omega - \omega_{kk'}) \right\} \qquad (2.16)$$

The transition frequency $\omega_{kk'}$ is negative. So actually, only the first delta function will give a nonzero result. What remains is

$$\chi_{xx}^{(B_2)} = \frac{-i e^2\hbar}{6\pi m_e^2\omega} \int dk \, \frac{k^4}{\omega_{kk'}} |M(\mathbf{k})|^2 \delta(\omega + \omega_{kk'}) \qquad (2.17)$$

The argument of the delta and the variable of integraton are different. So bring them to be the same. I can solve for the wave vector:

$$k^2 = -\frac{2\tilde{m}}{\hbar}(\omega_g + \omega_{kk'}) = \frac{2\tilde{m}}{\hbar}(x - \omega_g) \qquad (2.18)$$

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Here for convenience $-\omega_{kk'}$ has been renamed x, i.e., $x = \omega_g + \hbar k^2/2\tilde{m}$ is the transition change. Then the integral transforms to

$$\chi_{xx}^{(B_2)} = \frac{ie^2\hbar}{6\pi m_e^2\omega} \int dx \, \frac{\tilde{m}}{\hbar} \frac{1}{x} \left[\frac{2\tilde{m}}{\hbar}(x - \omega_g) \right]^{3/2} |M(\mathbf{k})|^2 \delta(\omega - x) \tag{2.19}$$

Only one point on the k axis contributes, at $k = k_0 = \sqrt{(2\tilde{m}/\hbar)(\omega - \omega_g)}$, due to the delta function forcing $x = \omega$, leaving,

$$\chi_{xx}^{(B_2)} = \frac{ie^2\hbar}{6\pi m_e^2\omega} \frac{\tilde{m}}{\hbar} \frac{1}{\omega} \left[\frac{2\tilde{m}}{\hbar}(\omega - \omega_g) \right]^{3/2} |M(k_0)|^2 \tag{2.20}$$

It can be re-arranged slightly

$$\chi_{xx}^{(B_2)} = \frac{ie^2}{3\pi\hbar c} \frac{\tilde{m}^2}{m_e^2} |M(k_0)|^2 \sqrt{\frac{2\tilde{m}c^2}{\hbar\omega_g}} \sqrt{\frac{\omega_g}{\omega}} \left[\frac{\omega - \omega_g}{\omega} \right]^{3/2} \tag{2.21}$$

Although it is an ugly expression, the main interesting part is the dependence on the frequency of the light (or photon energy $\hbar\omega$). There is no effect until the photon energy surpasses the gap, then the effect rises. Overall, this makes a positive contribution to the imaginary part of $\epsilon(\omega)$. That's the same sign as we saw in the simple classical models with damping, where damping represents real absoption. Hence this term is an absorption in the medium. Can see that this is dimensionless as it should be.

For CGS units we have the fine structure constant, $e^2/\hbar c \approx 1/137$. Consider that the reduced mass is close to the bare electron mass, with $\tilde{m}c^2 \approx 511$ keV, and band gap energies are around 3.0 eV. Then the typical order of magnitude here is

$$\chi_{xx}^{(B_2)} \approx i\frac{1}{3\pi} \frac{1}{137} \sqrt{\frac{2 \times 511 \text{ keV}}{3 \text{ eV}}} |M|^2 \sqrt{\frac{\omega_g}{\omega}} \left[\frac{\omega - \omega_g}{\omega} \right]^{3/2} \approx i\, 0.45\, |M|^2 \sqrt{\frac{\omega_g}{\omega}} \left[\frac{\omega - \omega_g}{\omega} \right]^{3/2} \tag{2.22}$$

This is a moderate effect, unless the matrix element happens to be small. The result could be modified significantly if the reduced mass is not close to the bare electron mass. The last part that depends on ω/ω_g has a maximum value of about 0.32 where $\omega \approx 4\omega_g$. Thus, the largest $\chi_{xx}^{(B_2)}$ can be is about $i0.45 * 0.32|M|^2 \approx i0.15|M|^2$. Then its contribution to the imaginary part of ϵ (via $\epsilon = 1 + 4\pi\chi$) could be at most about $i1.8|M|^2$, which could be quite strong.

Principal Value Integral: Now consider the contribution due to the principal value integral, which should give the real part, $\chi_{xx}^{(B_1)}$. For the three-dimensional band we have

$$\chi_{xx}^{(B_1)} = \frac{e^2\hbar}{m_e^2\omega V} \frac{V}{(2\pi)^3} \text{p.v.} \left\{ \int d^3k \, \frac{k_x^2}{\omega_{kk'}} |M(\mathbf{k})|^2 \left[\frac{1}{\omega + \omega_{kk'}} + \frac{1}{\omega - \omega_{kk'}} \right] \right\} \tag{2.23}$$

The angular integration is the same as before. Really, the p.v. is needed only for the first part, the last term does not have a pole on the real k axis because $\omega_{kk'}$ is negative. Doing the transformation to variable $x = -\omega_{kk'}$, this is

$$\chi_{xx}^{(B_1)} = \frac{-e^2\hbar}{m_e^2\omega} \frac{4\pi/3}{(2\pi)^3} \text{ p.v.} \left\{ \int dx \, \frac{\tilde{m}}{\hbar} \frac{1}{x} \left[\frac{2\tilde{m}}{\hbar}(x - \omega_g) \right]^{3/2} |M(\mathbf{k})|^2 \left[\frac{2\omega}{\omega^2 - x^2} \right] \right\} \tag{2.24}$$

To go further, assume a constant matrix element. The lower limit (from $k = 0$) is $x = \omega_g$. Also, really, the upper limit isn't infinity, because it should be limited by the Fermi wave vector k_F, according to the number of electrons per unit volume. So there is a corresponding upper frequency limit, x_F given by

$$x_F = \omega_g + \frac{\hbar k_F^2}{2\tilde{m}} \tag{2.25}$$

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It could be that the integral is sufficiently convergent (varies as $x^{-3/2}$ at large x) to let the upper limit go to infinity, but that would be another approximation. Now we have

$$\chi_{xx}^{(B_1)} = \frac{-e^2\hbar}{3\pi^2 m_e^2} \frac{\tilde{m}}{\hbar} \left(\frac{2\tilde{m}}{\hbar}\right)^{3/2} |M|^2 \text{ p.v.} \int_{\omega_g}^{x_F} dx \, \frac{(x-\omega_g)^{3/2}}{x(\omega^2-x^2)} \tag{2.26}$$

The integrand has the one pole at $x = \omega$, which is jumped over by doing the principal value.

While the last expression puts the result in a compact form, I find it easier to evaluate the integral if we go to a rescaled wave vector as the variable of integration. Consider the definitions

$$x = \omega_g + \frac{\hbar k^2}{2\tilde{m}} = \omega_g + s^2, \qquad s = \sqrt{\frac{\hbar}{2\tilde{m}}} \, k. \tag{2.27}$$

Then this transforms the susceptibility into

$$\chi_{xx}^{(B_1)} = \frac{-e^2\hbar}{6\pi^2 m_e^2 \omega^2} \left(\frac{2\tilde{m}}{\hbar}\right)^{5/2} |M|^2 \text{ p.v.} \int_0^{s_F} ds \, \frac{s^4}{x} \left(\frac{2\omega^2}{\omega^2-x^2}\right) \tag{2.28}$$

Some partial fraction expansions are very helpful at this point, and we have

$$
\begin{aligned}
\frac{2\omega}{\omega^2-x^2} &= \frac{1}{\omega-x} + \frac{1}{\omega+x}, & \frac{2\omega}{x(\omega^2-x^2)} &= \frac{1}{x(\omega-x)} + \frac{1}{x(\omega+x)} \\
\frac{\omega}{x(\omega-x)} &= \frac{1}{x} + \frac{1}{\omega-x}, & \frac{\omega}{x(\omega+x)} &= \frac{1}{x} - \frac{1}{\omega+x} \\
\frac{2\omega^2}{x(\omega^2-x^2)} &= \frac{2}{x} - \frac{1}{\omega+x} + \frac{1}{\omega-x}
\end{aligned}
\tag{2.29}
$$

After these manipulations, see that there are three different integrals to do, however, only the one with $\omega - x$ in the denominator can be seen to be singular. The p.v. integral is

$$I = \text{p.v.} \int_0^{s_F} ds \, s^4 \left[\frac{2}{\omega_g+s^2} - \frac{1}{\omega+\omega_g+s^2} + \frac{1}{\omega-\omega_g-s^2}\right] = 2I_1 - I_2 + I_3. \tag{2.30}$$

The first two of these are of the same form, just with different parameters. The last one is the singular one, which has a divergence and undefined value at $s = \sqrt{\omega-\omega_g}$. Here initially I assume that $\omega > \omega_g$, otherwise, one would not expect any transitions. However, in the opposite case, $\omega < \omega_g$, all of the integrals have the same form, so still the calculation can be carried out. This would correspond to a photon excitation energy below the gap energy, and even though it would not cause real transitions, the dielectric properties could be affected.

Case 1: Excitations above the gap ($\omega > \omega_g$). Integral I_1 can be found by the transformation, $s = a\tan\theta$, where $a = \sqrt{\omega_g}$. I_2 can be done the same way but with $a = \sqrt{\omega+\omega_g}$. For the indefinite integral this gives

$$I_1 = \int ds \, \frac{s^4}{a^2+s^2} = \int (a\sec^2\theta d\theta) \frac{(a\tan\theta)^4}{a^2(1+\tan^2\theta)} = a^3 \int d\theta \, \tan^4\theta \tag{2.31}$$

Applying identity $1 + \tan^2\theta = \sec^2\theta$, this involves $\int d\theta \, \tan^4\theta$, which is equal to

$$\int d\theta \, [(\sec^2\theta - 1)\tan^2\theta] = \int d\theta \, [\sec^2\theta \tan^2\theta - (\sec^2\theta - 1)] = \frac{1}{3}\tan^3\theta - \tan\theta + \theta \tag{2.32}$$

Then the desired integral is

$$I_1 = a^3 \left[\frac{1}{3}\tan^3\theta - \tan\theta + \theta\right] = \frac{1}{3}s^3 - a^2 s + a^3 \tan^{-1}\left(\frac{s}{a}\right). \tag{2.33}$$

Inserting the specific values, $a = \sqrt{\omega_g}$ for I_1 and $a = \sqrt{\omega + \omega_g}$ for I_2, we have

$$I_1 = \frac{1}{3}s^3 - \omega_g s + \omega_g^{3/2} \tan^{-1} \frac{s}{\sqrt{\omega_g}},$$

$$I_2 = \frac{1}{3}s^3 - (\omega + \omega_g)s + (\omega + \omega_g)^{3/2} \tan^{-1} \frac{s}{\sqrt{\omega + \omega_g}}. \tag{2.34}$$

For I_3, we need different transformations, depending on the size of s relative to $a = \sqrt{\omega - \omega_g}$. First suppose that $s < a$, which will hold in some region because the range of integration starts at $s = 0$. For that region, do the transformation, $s = a \tanh \theta$, with $ds = a \, \mathrm{sech}^2\theta d\theta$, and $1 - \tanh^2 \theta = \mathrm{sech}^2\theta$. So now the integral transforms to

$$I_3 = \int ds \, \frac{s^4}{a^2 - s^2} = \int \mathrm{sech}^2\theta \, d\theta \, \frac{(a \tanh \theta)^4}{a^2(1 - \tanh^2 \theta)} = a^3 \int d\theta \, \tanh^4 \theta \tag{2.35}$$

Again, some simple transformations with $\tanh^2 \theta = 1 - \mathrm{sech}^2\theta$ lead to the result for $\int d\theta \, \tanh^4 \theta$,

$$\int d\theta \, \tanh^2 \theta (1 - \mathrm{sech}^2\theta) = \int d\theta \, [1 - \mathrm{sech}^2\theta - \tanh^2 \theta \, \mathrm{sech}^2\theta] = \theta - \tanh \theta - \frac{1}{3}\tanh^3 \theta \tag{2.36}$$

Then the desired indefinite integral is

$$I_3 = a^3 \left[-\frac{1}{3}\tanh^3 \theta - \tanh \theta + \theta \right] = -\frac{1}{3}s^3 - a^2 s + a^3 \tanh^{-1} \left(\frac{s}{a} \right), \quad \text{for } s < a. \tag{2.37}$$

To deal with the principal value, the result for $s > a$ must also be known, because the integral will have to avoid that point, and I assume the upper limit is above that point. Hyperbolic tangent never gives a result greater than 1. On the other hand, hyperbolic cotangent has magnitude always greater than 1, So for $s > a$, the appropriate transformation to try is $s = a \coth \theta$, with $ds = -a \, \mathrm{csch}^2\theta \, d\theta$. The identity $\coth^2 \theta = 1 + \mathrm{csch}^2\theta$ will be useful. Then the integral transforms as

$$I_3 = \int ds \, \frac{s^4}{a^2 - s^2} = \int -\mathrm{csch}^2\theta \, d\theta \, \frac{(a \coth \theta)^4}{a^2(1 - \coth^2 \theta)} = a^3 \int d\theta \, \coth^4 \theta \tag{2.38}$$

In this case, the integral of $\coth^4 \theta$ becomes

$$\int d\theta \, \coth^2 \theta (1 + \mathrm{csch}^2\theta) = \int d\theta \, [1 + \mathrm{csch}^2\theta + \coth^2 \theta \, \mathrm{csch}^2\theta] = \theta - \coth \theta - \frac{1}{3}\coth^3 \theta \tag{2.39}$$

So now the desired integral is

$$I_3 = a^3 \left[-\frac{1}{3}\coth^3 \theta - \coth \theta + \theta \right] = -\frac{1}{3}s^3 - a^2 s + a^3 \coth^{-1} \left(\frac{s}{a} \right), \quad \text{for } s > a. \tag{2.40}$$

The only change that happened is that inverse hyp tangent turned into inverse hyp cotangent. In a sense, these can be thought of as part of the same function, that we could define over the whole positive range of s. So far, we found the result, for $a^2 = \omega - \omega_g > 0$,

$$I_3 = \int ds \, \frac{s^4}{a^2 - s^2} = \begin{cases} -\frac{1}{3}s^3 - a^2 s + a^3 \tanh^{-1} \left(\frac{s}{a} \right), & \text{for } s < a, \\ -\frac{1}{3}s^3 - a^2 s + a^3 \coth^{-1} \left(\frac{s}{a} \right), & \text{for } s > a. \end{cases} \tag{2.41}$$

This integral can also be evaluated another way, by doing the partial fraction expansion and integrating term by term. The result of that somewhay ugly algebra is

$$I_3 = \int ds \, \frac{s^4}{a^2 - s^2} = -\frac{1}{3}s^3 - a^2 s + \frac{a^3}{2} \ln \left(\frac{|s + a|}{|s - a|} \right) \tag{2.42}$$

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On the other hand, check the definitions of the inverse hyperbolic functions. If we have $x = \tanh\theta = (e^{2\theta} - 1)/(e^{2\theta} + 1) < 1$, then solving gives

$$\theta(x) = \tanh^{-1} x = \frac{1}{2}\ln\left(\frac{1+x}{1-x}\right) = -\frac{1}{2}\ln\left(\frac{1-x}{1+x}\right), \quad \text{for } |x| < 1. \tag{2.43}$$

Do the same for inverse coth, namely, $x = \coth\theta = (\tanh\theta)^{-1} = (e^{2\theta} + 1)/(e^{2\theta} - 1) > 1$, solving gives

$$\theta(x) = \coth^{-1} x = \frac{1}{2}\ln\left(\frac{x+1}{x-1}\right) = -\frac{1}{2}\ln\left(\frac{x-1}{x+1}\right), \quad \text{for } |x| > 1. \tag{2.44}$$

Note that we could have done just $\coth^{-1}(x) = \tanh^{-1}(1/x)$ to get the second result. Then these can be combined into a single function, a generalized inverse hyperbolic tangent, $L(x)$, defined by

$$L(x) = \frac{1}{2}\ln\left(\frac{|1+x|}{|1-x|}\right) = \begin{cases} \tanh^{-1} x & \text{for } |x| < 1, \\ \coth^{-1} x & \text{for } |x| > 1. \end{cases} \tag{2.45}$$

The integral that was desired is then

$$I_3 = \int ds\, \frac{s^4}{a^2 - s^2} = -\frac{1}{3}s^3 - a^2 s + a^3 L\left(\frac{s}{a}\right) \equiv F_3(s) \tag{2.46}$$

which is the same arrived at by expanding and integrating.

Finally with $a = \sqrt{\omega - \omega_g}$ the indefinite integral I_3 can be expressed

$$I_3 = -\frac{1}{3}s^3 - (\omega - \omega_g)s + (\omega - \omega_g)^{3/2} L\left(\frac{s}{\sqrt{\omega - \omega_g}}\right) \tag{2.47}$$

Before combining it with I_1 and I_2, already do the p.v. operation here. The limits of integration are from $s = 0$ to a scaled Fermi wave vector, $s = s_F$. But the point $s = a = \sqrt{\omega - \omega_g}$ must be jumped over. So the evaluation of the p.v. between the limits means

$$\text{p.v.} \int_0^{s_F} ds = \lim_{\gamma \to 0} \left\{ \int_0^{a-\gamma} ds + \int_{a+\gamma}^{s_F} ds \right\} \tag{2.48}$$

At the lower limit, $F_3(0) = 0$. Consider this p.v. operation on the singular term, $L(s/a)$. It gives

$$\text{p.v.} \int_0^{s_F} ds = \lim_{\gamma \to 0} \left\{ L\left(\frac{a-\gamma}{a}\right) - L(0) + L(s_F) - L\left(\frac{a+\gamma}{a}\right) \right\} \tag{2.49}$$

With $L(0) = 0$, and using the definition of $L(x)$, this becomes

$$\begin{aligned}
\text{p.v.} \int_0^{s_F} ds &= \lim_{\gamma \to 0} \left\{ \frac{1}{2}\ln\left[\frac{a + (a-\gamma)}{a - (a-\gamma)}\right] - \frac{1}{2}\ln\left[\frac{(a+\gamma)+a}{(a+\gamma)-a}\right] + L\left(\frac{s_F}{a}\right) \right\} \\
&= \lim_{\gamma \to 0} \left\{ \frac{1}{2}\ln\left[\frac{a + (a-\gamma)}{a - (a-\gamma)} \cdot \frac{(a+\gamma)-a}{(a+\gamma)+a}\right] + L\left(\frac{s_F}{a}\right) \right\} \\
&= \lim_{\gamma \to 0} \left\{ \frac{1}{2}\ln\left[\frac{2a-\gamma}{\gamma} \cdot \frac{\gamma}{2a+\gamma}\right] + L\left(\frac{s_F}{a}\right) \right\} = L\left(\frac{s_F}{a}\right) \tag{2.50}
\end{aligned}$$

So the principal value just removes the singular parts; they cancel each other. In the end, we can ignore the p.v. and just evaluate the indefinite integral at its upper limit!

Therefore, after all this algebra, the total integral to determine χ is

$$\begin{aligned}
I = 2I_1 - I_2 + I_3 &= 2\left[\frac{1}{3}s^3 - \omega_g s + \omega_g^{3/2}\tan^{-1}\frac{s}{\sqrt{\omega_g}}\right] \\
&\quad - \left[\frac{1}{3}s^3 - (\omega + \omega_g)s + (\omega + \omega_g)^{3/2}\tan^{-1}\frac{s}{\sqrt{\omega + \omega_g}}\right] \\
&\quad + \left[-\frac{1}{3}s^3 - (\omega - \omega_g)s + (\omega - \omega_g)^{3/2}L\left(\frac{s}{\sqrt{\omega - \omega_g}}\right)\right] \tag{2.51}
\end{aligned}$$

This is where some magic happens. Amazingly, the terms proportional to s and s^3 all cancel out! Only the inverse tangent parts survive. We only need this evaluated at it upper limit, $s = s_F = \sqrt{\hbar/2\tilde{m}}\, k_F$.

So finally, for the case of excitations above the gap, $\omega > \omega_g$, we have

$$
\begin{aligned}
\chi_{xx}^{(B_1)} &= \frac{-e^2\hbar}{6\pi^2 m_e^2 \omega^2} \left(\frac{2\tilde{m}}{\hbar}\right)^{5/2} |M|^2 \,(2I_1 - I_2 + I_3) \\
&= \frac{-e^2\hbar}{6\pi^2 m_e^2 \omega^2} \left(\frac{2\tilde{m}}{\hbar}\right)^{5/2} |M|^2 \left\{ 2\omega_g^{3/2} \tan^{-1} \frac{s_F}{\sqrt{\omega_g}} \right. \\
&\quad \left. - [\omega + \omega_g]^{3/2} \tan^{-1} \frac{s_F}{\sqrt{\omega + \omega_g}} + [\omega - \omega_g]^{3/2} L\left[\frac{s_F}{\sqrt{\omega - \omega_g}}\right] \right\}
\end{aligned}
\tag{2.52}
$$

The last function $L(x)$ is equivalent to $\coth^{-1}(x)$ for $x > 1$ or $\tanh^{-1}(x)$ for $x < 1$. The result is somewhat complicated, such that it is difficult to see any simple limit, or perhaps an approximation where the argument s_F is very large. This is because there are several different energy scales present.

Case 2: Excitation below the gap, $\omega < \omega_g$: In this case, the I_3 integral is not singular, because $\omega - \omega_g < 0$, and there is no p.v. needed. Also, I_3 takes on the same form as I_1 and I_2. Denote $a^2 = \omega_g - \omega > 0$. Then the I_3 integral is found using the result for I_1,

$$
I_3 = -\int_0^{s_F} ds \, \frac{s^4}{a^2 + s^2} = -\left[\frac{1}{3}s^3 - a^2 s + a^3 \tan^{-1}\left(\frac{s}{a}\right)\right].
\tag{2.53}
$$

Substituting the value for a,

$$
I_3 = -\int_0^{s_F} ds \, \frac{s^4}{a^2 + s^2} = -\frac{1}{3}s^3 + (\omega_g - \omega)s - (\omega_g - \omega)^{3/2} \tan^{-1}\left(\frac{s}{\sqrt{\omega_g - \omega}}\right).
\tag{2.54}
$$

The first two terms are the same as before, and they cancel with terms in I_1 and I_2. Only the inverse tangent term will survive; it is essentially the analytic continuation of the $L(x)$ function. Now it is trivial to find the new value for χ, as there are no changes in the I_1 and I_2 integrals. So for excitations below the gap, $\omega < \omega_g$, we have

$$
\begin{aligned}
\chi_{xx}^{(B_1)} &= \frac{-e^2\hbar}{6\pi^2 m_e^2 \omega^2} \left(\frac{2\tilde{m}}{\hbar}\right)^{5/2} |M|^2 \,(2I_1 - I_2 + I_3) \\
&= \frac{-e^2\hbar}{6\pi^2 m_e^2 \omega^2} \left(\frac{2\tilde{m}}{\hbar}\right)^{5/2} |M|^2 \left\{ 2\omega_g^{3/2} \tan^{-1} \frac{s_F}{\sqrt{\omega_g}} \right. \\
&\quad \left. - [\omega + \omega_g]^{3/2} \tan^{-1} \frac{s_F}{\sqrt{\omega + \omega_g}} - [\omega_g - \omega]^{3/2} \tan^{-1}\left[\frac{s_F}{\sqrt{\omega_g - \omega}}\right] \right\}
\end{aligned}
\tag{2.55}
$$

It is interesting that in this case, although there are no real transitions, there is still a polarization of the medium by the optical field. The imaginary part of $\chi^{(B)}$, however, will be zero because the arguments of the delta functions will not be satisfied. This result will give the contribution to the real part of the dielectric function, when multiplied by 4π according to $\epsilon = 1 + 4\pi\chi$. This is in addition to any plasmon term [in $\chi^{(A)}$].

2.4 Three-dimensional bands with damping

That was a lot of work to take the limit of zero damping. Instead, one can consider keeping the damping $\gamma > 0$ as a phenomenological parameter. In this way, there is no need to evaluate a delta function integral separately from a principal valued integral. There is just one integral for the complex contribution to χ (aside from the plasmon term). Going to the expression that would be obtained using the polarization, we would have the same expression used in the p.v. integral, but with the $i\gamma$ included in the denominators, and no p.v.!

$$
\chi_{xx}^{(B)} = \frac{e^2\hbar}{m_e^2(\omega + i\gamma)V} \frac{V}{(2\pi)^3} \int d^3k \, \frac{k_x^2}{\omega_{kk'}} |M(\mathbf{k})|^2 \left[\frac{1}{\omega + i\gamma + \omega_{kk'}} + \frac{1}{\omega + i\gamma - \omega_{kk'}}\right]
\tag{2.56}
$$

Do the angular integration and transform this in terms of x or in terms of s:

$$\begin{aligned}
\chi_{xx}^{(B)} &= \frac{-e^2\hbar|M|^2}{6\pi^2 m_e^2(\omega + i\gamma)} \int dk \, \frac{k^4}{x}\left[\frac{1}{\omega + i\gamma - x} + \frac{1}{\omega + i\gamma + x}\right] \\
&= \frac{-e^2\hbar|M|^2}{6\pi^2 m_e^2(\omega + i\gamma)}\left(\frac{2\tilde{m}}{\hbar}\right)^{5/2} \int ds \, \frac{s^4}{x}\left[\frac{1}{\omega + i\gamma - x} + \frac{1}{\omega + i\gamma + x}\right] \\
&= \frac{-e^2\hbar|M|^2}{6\pi^2 m_e^2(\omega + i\gamma)}\left(\frac{2\tilde{m}}{\hbar}\right)^{5/2} \int dx \, \frac{(x - \omega_g)^{3/2}}{2x}\left[\frac{1}{\omega + i\gamma - x} + \frac{1}{\omega + i\gamma + x}\right] \quad (2.57)
\end{aligned}$$

Again really I prefer the form in terms of s, as we know how to do these integrals. There would be the same kind of partial fraction expansions,

$$\frac{1}{x(b-x)} = \frac{1}{b}\left[\frac{1}{x} + \frac{1}{b-x}\right], \qquad \frac{1}{x(b+x)} = \frac{1}{b}\left[\frac{1}{x} - \frac{1}{b+x}\right], \quad \text{with } b = \omega + i\gamma \qquad (2.58)$$

This leads to

$$\chi_{xx}^{(B)} = \frac{-e^2\hbar|M|^2(2\tilde{m}/\hbar)^{5/2}}{6\pi^2 m_e^2(\omega + i\gamma)^2} \int ds \, s^4\left[\frac{2}{\omega_g + s^2} - \frac{1}{\omega + i\gamma + \omega_g + s^2} + \frac{1}{\omega + i\gamma - \omega_g - s^2}\right] \qquad (2.59)$$

It has the same integrals $[2I_1 - I_2 + I_3]$ we had earlier for the p.v. integral, but with $\omega + i\gamma$ in place of ω. This is the analytic continuation of the p.v. integral. One interesting thing is the presence of $\omega + i\gamma$ in the factors out front, very much like what appeared in the simple classical damped electron model these notes started with.

One could use the expression already found for $2I_1 - I_2 + I_3$, and claim that that is the result, however, it won't display the real and imaginary parts (although I_1 is the same as before and pure real). Another approach is to already get the integrands into real and imaginary parts, and then integrate. Either way, there will be some ugly algebra and not much interesting physics along the way. I may save that for later.

For example, for I_2 with $a^2 = \omega + \omega_g$, can do the change

$$\frac{1}{\omega + i\gamma + \omega_g + s^2} = \frac{1}{a^2 + i\gamma + s^2} \cdot \frac{a^2 - i\gamma + s^2}{a^2 - i\gamma + s^2} = \frac{a^2 + s^2 - i\gamma}{(a^2 + s^2)^2 + \gamma^2} \qquad (2.60)$$

Then one needs the following real integrals to get $I_2 = I_{2r} + iI_{2i}$:

$$I_{2r} = \int ds \, \frac{s^4(a^2 + s^2)}{(a^2 + s^2)^2 + \gamma^2}, \qquad I_{2i} = \int ds \, \frac{s^4(-\gamma)}{(a^2 + s^2)^2 + \gamma^2}. \qquad (2.61)$$

It could be more of a challenge to find these in closed form analytically.

2.5   One-dimensional bands without damping

The band structure in real materials can be very complicated. The isotropic 3D just discussed probably does not apply to any real solids. But it may be even harder to imagine that a 1D band could apply to a real material. The thing is, this could be the approximate situation where some bands are close to each other, for the electron wave vector along some certain direction. That is the case for gold and some other metals, where two bands are separated by a small gap of around 2 eV width. For gold that happens along the 111 direction at the Fermi surface. Because this happens along a particular direction, a 1D band model is appropriate. Inouye et al even used this model to get the absorption contribution in gold due to the interband transitions. They were able to fit the absorption very well for photon energies above 2 eV up into the ultraviolet, well above the small particle plasmon resonance. Without interband transitions taken into account,it is impossible to get this kind of good fitting. They needed to have an accurate approximation for the real and imaginary parts of ϵ in order to do this.

The main difference from the 3D problem, is that the integration may start out in 3D, but needs to be reduced to the integration only along the active direction of the band, which is taken as the x-axis. We could simply ignore any integration along the other two directions, but somehow the units won't work out in the end. Start from the expression (2.11) obtained with the polarization averaging, and write:

$$\chi_{xx}^{(B)} = \lim_{\gamma \to 0} \frac{e^2 \hbar |M|^2}{m_e^2 (\omega + i\gamma) V} \sum_k^o \frac{k_x^2}{\omega_{kk'}} \left\{ \frac{1}{\omega + \omega_{kk'} + i\gamma} + \frac{1}{\omega - \omega_{kk'} + i\gamma} \right\} \qquad (2.62)$$

The V is needed because we found polarization, which is dipole moment per unit volume. This can't be scaled into just length of the active direction, there would be units of an area missing. Instead, we will convert to a full 3D integral first, but let each axis go over a range sufficient to fill up to the Fermi level. Suppose the usual isotropic Fermi wave vector is k_F, so that the number of (spin-1/2) electrons is counted as

$$N = \sum_k 2 = \frac{V}{(2\pi)^3} \int_0^{k_F} d^3k \; 2 = \frac{2V}{8\pi^3} \times \frac{4\pi k_F^3}{3} = \frac{V k_F^3}{3\pi^2} \implies k_F = (3\pi^2 N/V)^{1/3} = (3\pi^2 n)^{1/3}. \quad (2.63)$$

And then also the Fermi energy, $E_F = (\hbar k_F)^2 / 2m$, is proportional to $n^{2/3}$. Instead of doing this, consider a cubic box in which the system lives, of side L. If we do the same kind of counting, but in Cartesian coordinates, we have

$$N = \sum_k 2 = \left(\frac{L}{2\pi} \right)^3 \int_{-k_F}^{k_F} dk_x \int_{-k_F}^{k_F} dk_y \int_{-k_F}^{k_F} dk_z \; 2 = \frac{2V}{8\pi^3} \times 8k_F^3 = \frac{2V k_F^3}{\pi^3} \qquad (2.64)$$

This gives a slightly different definition for k_F, that is practical for the current calculation,

$$k_F = \left(\frac{\pi^3 n}{2} \right)^{1/3} \qquad (2.65)$$

Now why this is needed, is that we already carry out the integrations in y and z, and leave the integration along k_x of the 1D band. So we let the wave vector sum go over into

$$\sum_k^o \to \frac{2V}{(2\pi)^3} (2k_F)^2 \int_{-k_F}^{k_F} dk_x = \frac{V k_F^2}{\pi^3} \int_{-k_F}^{k_F} dk_x. \qquad (2.66)$$

Here the 2 on the volume counts the spin states at each $\mathbf{k}$, and the factors of $2k_F$ are the transverse integrations that have already been carried out. This way, the integration over wave vector still will give a dimensionless result, and preserve the correct units for χ (that is, it will keep χ dimensionless!).

Now the rest of the calculation is similar to that for 3D. Transform to the scaled wave vector along the band direction, $s = \sqrt{\hbar/2\tilde{m}} \, k_x$.

$$\chi_{xx}^{(B)} = \lim_{\gamma \to 0} \frac{-e^2 \hbar |M|^2}{m_e^2 (\omega + i\gamma) V} \frac{V k_F^2}{\pi^3} \left(\frac{2\tilde{m}}{\hbar} \right)^{3/2} \int_{-s_F}^{s_F} ds \; \frac{s^2}{\omega_g + s^2} \left\{ \frac{1}{\omega + i\gamma + \omega_g + s^2} + \frac{1}{\omega + i\gamma - \omega_g - s^2} \right\} \qquad (2.67)$$

At this form, is essentially what was carried out by Inouye et al, however, without taking γ to zero, and keeping the factor of state probabilities that I have set to 1. But I want to see how this works out first in the limit of no damping. The contribution of the **delta functions** in this limit is proportional to **twice** the following integral (even integrand):

$$I_\delta = (-i\pi) \int_0^{s_F} ds \; \frac{s^2}{\omega_g + s^2} \left\{ \delta(\omega + \omega_g + s^2) + \delta(\omega - \omega_g - s^2) \right\} \qquad (2.68)$$

The variable of integration is different than the arguments in the deltas, so they can be brought together first, by noting $2s \, ds = d(s^2)$ and writing this as

$$I_\delta = \frac{-i\pi}{2} \int_0^{s_F^2} d(s^2) \; \frac{\sqrt{s^2}}{\omega_g + s^2} \left\{ \delta(\omega + \omega_g + s^2) + \delta(\omega - \omega_g - s^2) \right\} \qquad (2.69)$$

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Only the second integral can contribute. The result is trivially found, as only the point $s^2 = \omega - \omega_g$ contributes,

$$I_\delta = \frac{-i\pi}{2} \frac{\sqrt{\omega - \omega_g}}{\omega_g + \omega - \omega_g} = \frac{-i\pi}{2\omega} \sqrt{\omega - \omega_g} \tag{2.70}$$

So the absorption term is

$$\chi_{xx}^{(B_2)} = \frac{-e^2 \hbar |M|^2}{m_e^2 \omega} \frac{k_F^2}{\pi^3} \left(\frac{2\tilde{m}}{\hbar} \right)^{3/2} \left[2 \times \frac{-i\pi}{2\omega} \sqrt{\omega - \omega_g} \right] \tag{2.71}$$

Some simplification gives

$$\chi_{xx}^{(B_2)} = \frac{ie^2 \hbar |M|^2}{\pi^2 m_e^2} k_F^2 \left(\frac{2\tilde{m}}{\hbar} \right)^{3/2} \frac{\sqrt{\omega - \omega_g}}{\omega^2} \tag{2.72}$$

There is some similarity to the 3D result, for example, they both have ω^2 in the denominator. But the dependence on $\sqrt{\omega - \omega_g}$ here reflects the fact that the band is one-dimensional. This factor appears cubed for the 3D problem. The net result is positive, which will produce the correct sign for a physical absorption in the dielectric function. Also can write it so that it can be seen to be dimensionless:

$$\chi_{xx}^{(B_2)} = i \frac{|M|^2}{\pi^2} \frac{e^2}{\hbar c} \left(\frac{\hbar k_F}{m_e c} \right)^2 \left(\frac{2\tilde{m}c^2}{\hbar \omega_g} \right)^{3/2} \left[\frac{\omega_g}{\omega} \right]^{3/2} \sqrt{\frac{\omega - \omega_g}{\omega}} \tag{2.73}$$

Due to the presence of the Fermi momentum $\hbar k_F$, the result depends on the number density of electrons. This is in contrast to the 3D result. Also, the factor depending on reduced mass is cubed here compared to that in 3D, this will have an amplifying effect.

Now for the **principal valued part.** We need **twice** the corresponding integral from (2.67),

$$I_p = \text{p.v.} \int_0^{s_F} ds \frac{s^2}{\omega_g + s^2} \left\{ \frac{1}{\omega + \omega_g + s^2} + \frac{1}{\omega - \omega_g - s^2} \right\} \tag{2.74}$$

Once again, expansion by partial fractions will save the day, and these are ones we already have done. A little algebra (with $x = \omega_g + s^2$) shows the part inside the integrand is just like in 3D,

$$\frac{1}{x(\omega + x)} + \frac{1}{x(\omega - x)} = \frac{1}{\omega} \left[\frac{2}{x} - \frac{1}{\omega + x} + \frac{1}{\omega - x} \right] \tag{2.75}$$

So now we need to find three simple integrals,

$$I_p = \frac{1}{\omega} \text{ p.v.} \int_0^{s_F} ds \left\{ \frac{2s^2}{\omega_g + s^2} - \frac{s^2}{\omega + \omega_g + s^2} + \frac{s^2}{\omega - \omega_g - s^2} \right\} = \frac{1}{\omega} \left[2I_1 - I_2 + I_3 \right] \tag{2.76}$$

Only I_3 is singular and needs the p.v. The first two are done by a transform like $s = a \tan \theta$, or just for different fun, this way:

$$I_1 = \int ds \frac{s^2}{\omega_g + s^2} = \int ds \frac{s^2 + \omega_g - \omega_g}{\omega_g + s^2} = \int ds \left[1 - \frac{\omega_g}{\omega_g + s^2} \right] = s - \sqrt{\omega_g} \tan^{-1} \frac{s}{\sqrt{\omega_g}} \tag{2.77}$$

By analogy,

$$I_2 = \int ds \frac{s^2}{\omega + \omega_g + s^2} = s - \sqrt{\omega + \omega_g} \tan^{-1} \frac{s}{\sqrt{\omega + \omega_g}} \tag{2.78}$$

Assume **excitations above the gap:** $\omega > \omega_g$. The last integral needs different treatment depending whether $s < \omega - \omega_g$ or $s > \omega - \omega_g$. In the first case, try a similar algebra, with $a = \sqrt{\omega - \omega_g}$,

$$I_3 = \int ds \frac{s^2}{\omega - \omega_g - s^2} = \int ds \frac{s^2 - a^2 + a^2}{a^2 - s^2} = \int ds \left[-1 + \frac{a^2}{a^2 - s^2} \right] = -s + a \tanh^{-1} \frac{s}{a} \tag{2.79}$$

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That was the result for $s < a$, but we know the tanh will change into coth for $s > a$, so

$$I_3 = \begin{cases} -s + \sqrt{\omega - \omega_g} \tanh^{-1} \frac{s}{\sqrt{\omega - \omega_g}} & \text{for } s < a, \\ -s + \sqrt{\omega - \omega_g} \coth^{-1} \frac{s}{\sqrt{\omega - \omega_g}} & \text{for } s > a. \end{cases} \tag{2.80}$$

Or, of course, just substitute $\tanh^{-1} / \coth^{-1}$ by the function $L(x)$ defined earlier in (2.45) for the 3D problem.

When the p.v. is applied for evaluating I_3, again because of the logarithmic dependence of $L(x)$, the singular point is just canceled out. Only the values at the outer limits will be needed. The combined indefinite p.v. integral is

$$\begin{aligned} \omega I_p = 2I_1 - I_2 + I_3 &= 2\left[s - \sqrt{\omega_g} \tan^{-1} \frac{s}{\sqrt{\omega_g}} \right] \\ &\quad - \left[s - \sqrt{\omega + \omega_g} \tan^{-1} \frac{s}{\sqrt{\omega + \omega_g}} \right] \\ &\quad + \left[-s + \sqrt{\omega - \omega_g} \coth^{-1} \frac{s}{\sqrt{\omega - \omega_g}} \right] \end{aligned} \tag{2.81}$$

The terms in s cancel out and leave only the inverse functions. Applying the limits gives

$$I_p = \frac{1}{\omega} \left\{ -2\sqrt{\omega_g} \tan^{-1} \frac{s_F}{\sqrt{\omega_g}} + \sqrt{\omega + \omega_g} \tan^{-1} \frac{s_F}{\sqrt{\omega + \omega_g}} + \sqrt{\omega - \omega_g} \coth^{-1} \frac{s_F}{\sqrt{\omega - \omega_g}} \right\} \tag{2.82}$$

This assumes $s_F > \sqrt{\omega - \omega_g}$. If not, switch the $\coth^{-1}$ to $\tanh^{-1}$. Then including the coefficients, for excitations above the gap, $\omega > \omega_g$, the real part of the susceptibility is,

$$\begin{aligned} \chi_{xx}^{(B_1)} &= \frac{-e^2 \hbar |M|^2}{m_e^2 \omega} \frac{k_F^2}{\pi^3} \left(\frac{2\tilde{m}}{\hbar} \right)^{3/2} 2 \times \frac{1}{\omega} (2I_1 - I_2 + I_3) \\ &= \frac{-e^2 \hbar |M|^2}{m_e^2 \omega^2} \frac{k_F^2}{\pi^3} \left(\frac{2\tilde{m}}{\hbar} \right)^{3/2} 2 \left\{ -2\sqrt{\omega_g} \tan^{-1} \frac{s_F}{\sqrt{\omega_g}} \right. \\ &\quad \left. + \sqrt{\omega + \omega_g} \tan^{-1} \frac{s_F}{\sqrt{\omega + \omega_g}} + \sqrt{\omega - \omega_g} \coth^{-1} \frac{s_F}{\sqrt{\omega - \omega_g}} \right\}, \quad \text{for } \omega > \omega_g. \text{ (2.83)} \end{aligned}$$

Can re-arrange to obvious dimensionless form,

$$\begin{aligned} \chi_{xx}^{(B_1)} &= -\frac{2|M|^2}{\pi^3} \frac{e^2}{\hbar c} \left(\frac{\hbar k_F}{m_e c} \right)^2 \left(\frac{2\tilde{m}c^2}{\hbar \omega_g} \right)^{3/2} \frac{\omega_g^{3/2}}{\omega^2} \left\{ -2\sqrt{\omega_g} \tan^{-1} \frac{s_F}{\sqrt{\omega_g}} \right. \\ &\quad \left. + \sqrt{\omega + \omega_g} \tan^{-1} \frac{s_F}{\sqrt{\omega + \omega_g}} + \sqrt{\omega - \omega_g} L \left(\frac{s_F}{\sqrt{\omega - \omega_g}} \right) \right\}, \quad \text{for } \omega > \omega_g. \quad \text{(2.84)} \end{aligned}$$

For the case of **excitations below the gap**, $\omega < \omega_g$, there will be no delta term and hence no imaginary part. But there is still polarization and the p.v. integral. Only the I_3 integral is affected. It becomes, with $a^2 = \omega_g - \omega > 0$,

$$I_3 = \int ds \, \frac{s^2}{\omega - \omega_g - s^2} = \int ds \, \frac{s^2}{-a^2 - s^2} = -\int ds \, \frac{s^2}{a^2 + s^2} = -s + a \tan^{-1} \frac{s}{a} \tag{2.85}$$

Insertng the value of a, it is the analytic continuation of the previous result for above the gap excitation,

$$I_3 = -s + \sqrt{\omega_g - \omega} \tan^{-1} \frac{s}{\sqrt{\omega_g - \omega}} \tag{2.86}$$

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Then the total susceptibility in this case is

$$\chi_{xx}^{(B)} = -\frac{2|M|^2}{\pi^3}\frac{e^2}{\hbar c}\left(\frac{\hbar k_F}{m_e c}\right)^2 \left(\frac{2\tilde{m}c^2}{\hbar\omega_g}\right)^{3/2}\frac{\omega_g^{3/2}}{\omega^2}\left\{-2\sqrt{\omega_g}\tan^{-1}\frac{s_F}{\sqrt{\omega_g}}\right.$$

$$\left. + \sqrt{\omega+\omega_g}\tan^{-1}\frac{s_F}{\sqrt{\omega+\omega_g}} + \sqrt{\omega_g-\omega}\tan^{-1}\frac{s_F}{\sqrt{\omega_g-\omega}}\right\}, \quad \text{for } \omega < \omega_g. \quad (2.87)$$

Once again, without an inputted estimate for the Fermi wave vector, it is difficult to make any simple estimate of this, due to the various different energy scales.

2.6 One-dimensional bands with damping

In this part, I consider the one-dimensional band model already described, but keep the damping parameter $\gamma > 0$. This is what I think was was carried out by Inouye et al to analyze the response of gold particles. (They also were interested in temperature effects, among other things.) They did not obtain and analytic result, partly because they also kept the probability term $F_{kk'}$ different than 1, in order to keep some basic effects of temperature.

So here I try to analyze the expression (2.67) already obtained, but for finite damping,

$$\chi_{xx}^{(B)} = \frac{-e^2\hbar|M|^2}{m_e^2(\omega+i\gamma)}\frac{k_F^2}{\pi^3}\left(\frac{2\tilde{m}}{\hbar}\right)^{3/2}\int_{-s_F}^{s_F}ds\,\frac{s^2}{\omega_g+s^2}\left\{\frac{1}{\omega+i\gamma+\omega_g+s^2}+\frac{1}{\omega+i\gamma-\omega_g-s^2}\right\} \quad (2.88)$$

First, transform to the variable $x = \omega_g + s^2$, to compare whether this agrees with their published expression, in any way. The braces in the integral can be expressed as

$$\frac{1}{\omega+i\gamma+x}+\frac{1}{\omega+i\gamma-x} = \frac{2(\omega+i\gamma)}{(\omega+i\gamma)^2-x^2} = \frac{2(\omega+i\gamma)}{\omega^2-x^2-\gamma^2+2i\omega\gamma} \quad (2.89)$$

They have rationalized the function so as to isolate better the real and imaginary parts.

$$= 2(\omega+i\gamma)\frac{\omega^2-x^2-\gamma^2-2i\omega\gamma}{(\omega^2-x^2-\gamma^2)^2+4\omega^2\gamma^2} \quad (2.90)$$

Including the sign and other factors, this agrees well with the expression of Scaffardi & Tocho (2006), which say they corrected some errors in the expression of Inouye et al (1998). The factor of $\omega+i\gamma$ in the denominator of the basic formula cancels with that in the numerator of the partial fraction expansion! So after changing to x as the variable of integration, I get

$$\chi_{xx}^{(B)} = \frac{e^2\hbar|M|^2}{m_e^2}\frac{k_F^2}{\pi^3}\left(\frac{2\tilde{m}}{\hbar}\right)^{3/2}2\int_{\omega_g}^{x_F}dx\,\frac{\sqrt{x-\omega_g}}{x}\cdot\frac{(x^2-\omega^2+\gamma^2+2i\omega\gamma)}{(x^2-\omega^2+\gamma^2)^2+4\omega^2\gamma^2} \quad (2.91)$$

The 2 immediately preceding the integral symbol is because the integral was symmetric in s, but not in x. The upper limit is $x_F = \omega_g + s_F^2$, where $s_F = \sqrt{\hbar/2\tilde{m}}\,k_F$. The integrand agrees with that of Scaffardi & Tocho (2006), but they include an occupation factor. They also let the upper limit go to infinity. They are considering optical frequencies with $\hbar\omega \sim 2-5$ eV, while it is stated that $\gamma \approx 158$ meV for gold, so these do satisfy $\gamma \ll \hbar\omega$ reasonably well. Then it is not a large error to ignore the factor of $(\omega+i\gamma)/\omega$. They also state that the gap frequency is $\omega_g \approx 2.1$ eV. This expression applies either to above or below the gap excitation. For either case, it has a positive imaginary part, which is the correct sign for absorption.

2.6.1 The I_γ integrals for susceptibility

I think the expression is difficult at best to evaluate. Let me look at another way to express it, since. I prefer integration over s, which is more symmetrical. With partial fraction expansion the integral needed in (2.88) is the same as the extension of I_p (but no p.v.) in the previous section,

$$I_\gamma = \frac{1}{\omega+i\gamma}\int_0^{s_F}ds\,\left\{\frac{2s^2}{\omega_g+s^2}-\frac{s^2}{\omega+i\gamma+\omega_g+s^2}+\frac{s^2}{\omega+i\gamma-\omega_g-s^2}\right\} = \frac{1}{\omega+i\gamma}\left[2I_1-I_2+I_3\right] \quad (2.92)$$

Integral I_1 is already known and in fact, a pure real function with inverse tangent:

$$I_1 = \int_0^{s_F} \frac{ds\, s^2}{\omega_g + s^2} = \int_0^{s_F} ds \left[1 - \frac{\omega_g}{\omega_g + s^2}\right] = s_F - \sqrt{\omega_g}\, \tan^{-1} \frac{s_F}{\sqrt{\omega_g}}. \tag{2.93}$$

The other integrals can also be done exactly, although the algebra isn't too pretty. Indeed, I_2 is analytically the same as I_1 but with a complex factor in the denominator. Consider the parameter $a^2 = \omega + \omega_g + i\gamma$ in I_2 and $a^2 = \omega_g - \omega - i\gamma$ in $-I_3$ (with reversed signs in denominator). Denote this argument generally as $a^2 = \Omega + i\Gamma$, a complex number with an arbitrary real part.

Then all are of the following form, for which we do a little algebra:

$$f(a) = \int ds\, \frac{s^2}{a^2 + s^2} = \int ds\, \frac{s^2 + a^2 - a^2}{s^2 + a^2} = \int ds \left[1 - \frac{a^2}{a^2 + s^2}\right] = s - a\tan^{-1}\left(\frac{s}{a}\right). \tag{2.94}$$

OK, we knew that one already, but now instead, do it by converting to logarithmic integrals via a partial fraction expansion:

$$f(a) = s - \frac{a}{2} \int ds \left[\frac{1}{a + is} + \frac{1}{a - is}\right] = s - \frac{a}{2}\left[-i\ln(a + is) + i\ln(a - is)\right] \tag{2.95}$$

Combining the logs gives

$$f(a) = s - \frac{ia}{2}\ln\left(\frac{a - is}{a + is}\right), \quad \implies \quad \tan^{-1}\left(\frac{s}{a}\right) = \frac{i}{2}\ln\left(\frac{a - is}{a + is}\right). \tag{2.96}$$

The last part is another way to write the inverse tangent, since this must agree with the other result, and they have to match at $s = 0$. Check that it is correct if a and s are real: Note that

$$a - is = \sqrt{a^2 + s^2}\, e^{-i\tan^{-1}(s/a)}, \qquad a + is = \sqrt{a^2 + s^2}\, e^{+i\tan^{-1}(s/a)}, \tag{2.97}$$

Then we go in a circle to recover the inverse tangent:

$$\frac{i}{2}\ln\left(\frac{a - is}{a + is}\right) = \frac{i}{2}\ln\left(\frac{\sqrt{a^2 + s^2}\, e^{-i\tan^{-1}(s/a)}}{\sqrt{a^2 + s^2}\, e^{+i\tan^{-1}(s/a)}}\right) = \frac{i}{2}\left[-2i\tan^{-1}\left(\frac{s}{a}\right)\right] = \tan^{-1}\left(\frac{s}{a}\right). \tag{2.98}$$

OK, but the integration didn't care if they if the parameters are complex, especially a. So the log function works to define the inverse tangent even when $a^2 = \Omega + i\Gamma$. But it works best if we know the real and imaginary parts of a, not of a^2. So we need first to do the complex square root. Use a polar approach:

$$a^2 = \sqrt{\Omega^2 + \Gamma^2}\, e^{i\tan^{-1}(\Gamma/\Omega)} \quad \implies \quad a = \sqrt{\Omega + i\Gamma} = (\Omega^2 + \Gamma^2)^{1/4}\, e^{i\frac{1}{2}\tan^{-1}(\Gamma/\Omega)}. \tag{2.99}$$

If we let the phase angle of a^2 be $\phi = \tan^{-1}(\Gamma/\Omega)$, then also we have $\cos\phi = \Omega/\sqrt{\Omega^2 + \Gamma^2}$ and $\sin\phi = \Gamma/\sqrt{\Omega^2 + \Gamma^2}$. But we want the cosine and sine of half of this angle, which are easily found,

$$\cos\frac{\phi}{2} = \sqrt{\frac{(1 + \cos\phi)}{2}} = \sqrt{\frac{1}{2}\left[1 + \frac{\Omega}{\sqrt{\Omega^2 + \Gamma^2}}\right]}, \quad \sin\frac{\phi}{2} = \sqrt{\frac{(1 - \cos\phi)}{2}}\sqrt{\frac{1}{2}\left[1 - \frac{\Omega}{\sqrt{\Omega^2 + \Gamma^2}}\right]}. \tag{2.100}$$

Then the desired square root is $a = (\Omega^2 + \Gamma^2)^{1/4}[\cos(\phi/2) + i\sin(\phi/2)]$, or

$$a = \sqrt{\Omega + i\Gamma} = \sqrt{\frac{1}{2}\left(\sqrt{\Omega^2 + \Gamma^2} + \Omega\right)} + i\sqrt{\frac{1}{2}\left(\sqrt{\Omega^2 + \Gamma^2} - \Omega\right)} \equiv x + iy. \tag{2.101}$$

Then some more ugly algebra to give $\tan^{-1}(s/a)$,

$$\tan^{-1}\left(\frac{s}{x + iy}\right) = \frac{i}{2}\ln\left[\frac{x + iy - is}{x + iy + is}\right] = \frac{i}{2}\ln\left[\frac{\sqrt{x^2 + (y - s)^2}\, e^{i\tan^{-1}[(y-s)/x]}}{\sqrt{x^2 + (y + s)^2}\, e^{i\tan^{-1}[(y+s)/x]}}\right] \tag{2.102}$$

There are different ways to go from here; the simplest is this symmetric approach. Next we have

$$\tan^{-1}\left(\frac{s}{x+iy}\right) = \frac{i}{2}\left\{i\left[\tan^{-1}\left(\frac{y-s}{x}\right) - \tan^{-1}\left(\frac{y+s}{x}\right)\right] + \frac{1}{2}\ln\left[\frac{x^2+(y-s)^2}{x^2+(y+s)^2}\right]\right\} \qquad (2.103)$$

If desired, the inverse tangents can be combined. Let $\theta_1 = \tan^{-1}[(y-s)/x]$ and $\theta_2 = \tan^{-1}[(y+s)/x]$. The combination wanted is $\theta_1 - \theta_2$. Its tangent is

$$\tan(\theta_1 - \theta_2) = \frac{\tan\theta_1 - \tan\theta_2}{1 + \tan\theta_1\tan\theta_2} = \frac{\frac{y-s}{x} - \frac{y+s}{x}}{1 + \frac{y-s}{x}\frac{y+s}{x}} = \frac{-2sx}{x^2+y^2-s^2}. \qquad (2.104)$$

Then the function we need is expressed more simply,

$$\tan^{-1}\left(\frac{s}{a}\right) = \tan^{-1}\left(\frac{s}{x+iy}\right) = \frac{1}{2}\tan^{-1}\left[\frac{2xs}{x^2+y^2-s^2}\right] + \frac{i}{4}\ln\left[\frac{x^2+(y-s)^2}{x^2+(y+s)^2}\right] \qquad (2.105)$$

To give I_2, this needs to be applied with $\Omega = \omega + \omega_g, \quad \Gamma = \gamma,$

$$I_2 = \int ds \frac{s^2}{\omega + \omega_g + i\gamma + s^2} = f(\omega + \omega_g, \gamma). \qquad (2.106)$$

One way to get I_3, is to use the above algebra, applied with $\Omega = \omega_g - \omega, \quad \Gamma = -\gamma$, that actually would give $-I_3$, so include a minus sign:

$$I_3 = \int ds \frac{s^2}{\omega - \omega_g + i\gamma - s^2} = \int ds \frac{-s^2}{\omega_g - \omega - i\gamma + s^2} = -f(\omega_g - \omega, -\gamma). \qquad (2.107)$$

Another way to get I_3 is to let $\Omega = \omega - \omega_g, \quad \Gamma = \gamma$, and do a variable change, $s = iz$. Then we have a similar form as found for I_2:

$$I_3 = -i\int dz \frac{z^2}{a^2+z^2} = -i\left[z - a\tan^{-1}\left(\frac{z}{a}\right)\right] = -s + ia\tan^{-1}\left(\frac{-is}{a}\right) \qquad (2.108)$$

OK, we know how to get the real and imaginary parts of the inverse tangent here too,

$$i\tan^{-1}\left(\frac{z}{a}\right) = i\frac{i}{2}\ln\left(\frac{a-iz}{a+iz}\right) = -\frac{1}{2}\ln\left(\frac{a-s}{a+s}\right) \qquad (2.109)$$

If a were real, this would be a pure real function, in fact, it is the generalized inverse hyperbolic tangent function, $L(s/a)$. With a complex $a = x + iy$, there results

$$\tan^{-1}\left(\frac{z}{x+iy}\right) = \frac{i}{2}\ln\left[\frac{x+iy-s}{x+iy+s}\right] = \frac{i}{2}\ln\left[\frac{\sqrt{(x-s)^2+y^2}\ e^{i\tan^{-1}[y/(x-s)]}}{\sqrt{(x+s)^2+y^2}\ e^{i\tan^{-1}[y/(x+s)]}}\right] \qquad (2.110)$$

Expanding out the log,

$$\tan^{-1}\left(\frac{z}{x+iy}\right) = \frac{i}{2}\left\{i\left[\tan^{-1}\left(\frac{y}{x-s}\right) - \tan^{-1}\left(\frac{y}{x+s}\right)\right] + \frac{1}{2}\ln\left[\frac{(x-s)^2+y^2}{(x+s)^2+y^2}\right]\right\} \qquad (2.111)$$

Combining the angles the same way as earlier, this is

$$\tan^{-1}\left(\frac{-is}{a}\right) = \tan^{-1}\left(\frac{z}{x+iy}\right) = -\frac{1}{2}\tan^{-1}\left[\frac{2ys}{x^2+y^2-s^2}\right] + \frac{i}{4}\ln\left[\frac{(x-s)^2+y^2}{(x+s)^2+y^2}\right] \qquad (2.112)$$

This seems to be the rotated version of what resulted for I_2.

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2.6.2 The final result for susceptibility in 1D bands with damping

With that, the integral for the band-to-band susceptibility for finite damping is found exactly. The total integral I_γ can be spelled out. The parameters a are square roots of complex frequencies. All the terms linear in s cancel out, leaving only the inverse tangent parts:

$$
\begin{aligned}
(\omega + i\gamma)I_\gamma = 2I_1 - I_2 + I_3 \;=\;& 2\left[s - \sqrt{\omega_g}\,\tan^{-1}\left(\frac{s}{\sqrt{\omega_g}}\right)\right] \\
& - \left[s - \sqrt{\omega + \omega_g + i\gamma}\,\tan^{-1}\left(\frac{s}{\sqrt{\omega + \omega_g + i\gamma}}\right)\right] \\
& + \left[-s + i\sqrt{\omega - \omega_g + i\gamma}\,\tan^{-1}\left(\frac{-is}{\sqrt{\omega - \omega_g + i\gamma}}\right)\right]
\end{aligned} \quad (2.113)
$$

This doesn't display the real and imaginary parts very well; but the $\tan^{-1}$ are defined already, and each square root is defined via functions like

$$
\sqrt{\omega + i\gamma} = x(\omega) + iy(\omega), \quad (2.114)
$$

where

$$
x(\omega) = \sqrt{\frac{1}{2}\left[\sqrt{\omega^2 + \gamma^2} + \omega\right]}, \qquad y(\omega) = \sqrt{\frac{1}{2}\left[\sqrt{\omega^2 + \gamma^2} - \omega\right]}. \quad (2.115)
$$

Also the reciprocal of the complex frequency is very simple,

$$
\frac{1}{\omega + i\gamma} = \frac{\omega - i\gamma}{\omega^2 + \gamma^2} \quad (2.116)
$$

So the real and imaginary parts of I_γ can be computed exactly by computer without doing a numerical integration. I can quote the net result for the susceptibility,

$$
\begin{aligned}
\chi_{xx}^{(B)} \;=\;& \frac{-e^2\hbar|M|^2}{m_e^2(\omega + i\gamma)}\frac{k_F^2}{\pi^3}\left(\frac{2\tilde{m}}{\hbar}\right)^{3/2}\frac{2I_\gamma}{\omega + i\gamma} \quad (2.117) \\
\;=\;& \frac{-2e^2\hbar|M|^2}{m_e^2(\omega + i\gamma)^2}\frac{k_F^2}{\pi^3}\left(\frac{2\tilde{m}}{\hbar}\right)^{3/2}\left\{-2\sqrt{\omega_g}\,\tan^{-1}\left[\frac{s_F}{\sqrt{\omega_g}}\right]\right. \\
& + \left. \sqrt{\omega + \omega_g + i\gamma}\,\tan^{-1}\left[\frac{s_F}{\sqrt{\omega + \omega_g + i\gamma}}\right] + i\sqrt{\omega - \omega_g + i\gamma}\,\tan^{-1}\left[\frac{-is_F}{\sqrt{\omega - \omega_g + i\gamma}}\right]\right\}
\end{aligned}
$$

The evaluation between the limits of $-s_F$ and $+s_F$ led to the overall factor of 2. The first inverse tangent of a complex argument is defined via (2.105), and the second one via (2.112). So this is a closed form solution. Lastly, put the pre-factor into dimensionless form,

$$
\begin{aligned}
\chi_{xx}^{(B)} \;=\;& -\frac{2|M|^2}{\pi^3}\frac{e^2}{\hbar c}\left(\frac{\hbar k_F}{m_e c}\right)^2\left(\frac{2\tilde{m}c^2}{\hbar\omega_g}\right)^{3/2}\frac{\omega_g^{3/2}}{(\omega + i\gamma)^2}\left\{-2\sqrt{\omega_g}\,\tan^{-1}\left[\frac{s_F}{\sqrt{\omega_g}}\right]\right. \\
& + \left. \sqrt{\omega + \omega_g + i\gamma}\,\tan^{-1}\left[\frac{s_F}{\sqrt{\omega + \omega_g + i\gamma}}\right] + i\sqrt{\omega - \omega_g + i\gamma}\,\tan^{-1}\left[\frac{-is_F}{\sqrt{\omega - \omega_g + i\gamma}}\right]\right\}
\end{aligned}
$$

Amazingly (or not), this is just the analytic continuation of the result (2.84) obtained for the principal value integral in the limit of no damping, i.e., that result with ω changed to $\omega + i\gamma$ (even in the first ω of the pre-factor). Personally, it leads me to believe that the limit $\gamma \to 0$ may give some results pretty close to this last one, especially when γ is less than 10% of the other frequency scales in the problem. To test this, I would need to do some numerical evaluations of these diffferent results, maybe later!

2.6.3 Addendum: More about the I_2 integral

Another way to the the algebra for I_2, with a complex $a^2 = (x + iy)^2$, is as follows. The integral can be expanded in partial fractions, and always written with log functions:

$$
\begin{aligned}
I_2(a) &= \int_0^{s_F} \frac{ds\, s^2}{a^2 + s^2} = \int_0^{s_F} ds \left[1 - \frac{a^2}{a^2 + s^2} \right] = s_F - \frac{a}{2i} \int_0^{s_F} ds \left[\frac{1}{s - ia} - \frac{1}{s + ia} \right] \\
&= s_F + \frac{ia}{2} \ln \left[\frac{s - ia}{s + ia} \right]_0^{s_F} = s_F + \frac{ia}{2} \left\{ \ln \left[\frac{s_F - ia}{s_F + ia} \right] - \ln \left[\frac{-ia}{+ia} \right] \right\}.
\end{aligned}
\tag{2.118}
$$

It's important to include the lower limit, which reverses the sign in the log. Then there results

$$
I_2(a) = s_F + \frac{ia}{2} \ln \left[\frac{ia - s_F}{ia + s_F} \right].
\tag{2.119}
$$

The second term we recall is the same as $-a \tan^{-1}(s_F/a)$, or as we had earlier,

$$
\tan^{-1} \left(\frac{s}{a} \right) = \int_0^s \frac{ds\, a}{a^2 + s^2} = -\frac{i}{2} \ln \left[\frac{ia - s}{ia + s} \right] = +\frac{i}{2} \ln \left[\frac{ia + s}{ia - s} \right] = +\frac{i}{2} \ln \left[\frac{a - is}{a + is} \right]
\tag{2.120}
$$

So that is nothing new. But now we suppose we did the square root so we know $a = x + iy$. Another way to do the log algebra is to look separately at the magnitude and phase of its total argument. The argument is

$$
u = \frac{a - is}{a + is} = \frac{(x + iy) - is}{(x + iy) + is} = \frac{x + i(y - s)}{x + i(y + s)}
\tag{2.121}
$$

So far, still nothing new here. Now the new part. One can rationalize it to see the phase:

$$
u = \frac{x + i(y - s)}{x + i(y + s)} \cdot \frac{x - i(y + s)}{x - i(y + s)} = \frac{x^2 + y^2 - s^2 - 2ixs}{x^2 + (y + s)^2}
\tag{2.122}
$$

Then u can be expressed

$$
u = |u| e^{i\theta} = |u| \exp \left\{ i \tan^{-1} \left[\frac{-2xs}{x^2 + y^2 - s^2} \right] \right\}
\tag{2.123}
$$

The magnitude can be obtained in the same symmetrical manner as before,

$$
|u| = \left| \frac{x + i(y - s)}{x + i(y + s)} \right| = \sqrt{\frac{x^2 + (y - s)^2}{x^2 + (y + s)^2}}.
\tag{2.124}
$$

Then this checks out with the previous calculation, giving for the inverse tangent the same result, namely

$$
\tan^{-1} \frac{s}{a} = \tan^{-1} \frac{s}{x + iy} = \frac{i}{2} \ln \left(|u| e^{i\theta} \right) = \frac{i}{2} \left(\ln |u| + i\theta \right)
\tag{2.125}
$$

After some simple arrangments this is

$$
\tan^{-1} \frac{s}{x + iy} = \frac{1}{2} \tan^{-1} \left[\frac{+2xs}{x^2 + y^2 - s^2} \right] + \frac{i}{4} \ln \left[\frac{x^2 + (y - s)^2}{x^2 + (y + s)^2} \right].
\tag{2.126}
$$

Then finally this is used as

$$
I_2(a) = I_2(x, y) = s_F - (x + iy) \tan^{-1} \frac{s_F}{x + iy}.
\tag{2.127}
$$

2.6.4 Addendum: More about the I_3 integral

Can do the I_3 integral as follows:

$$
\begin{aligned}
I_3(a) &= \int_0^{s_F} \frac{ds\, s^2}{a^2 - s^2} = \int_0^{s_F} ds\, \frac{s^2 - a^2 + a^2}{a^2 - s^2} = \int_0^{s_F} ds \left[-1 + \frac{a^2}{a^2 - s^2} \right] \\
&= -s_F + \frac{a}{2} \int_0^{s_F} ds \left[\frac{1}{s + a} - \frac{1}{s - a} \right] = -s_F + \frac{a}{2} \ln \left[\frac{s + a}{s - a} \right]_0^{s_F}.
\end{aligned} \tag{2.128}
$$

Then putting in the limits

$$
I_3(a) = -s_F + \frac{a}{2} \left\{ \ln \left[\frac{s_F + a}{s_F - a} \right] - \ln \left[\frac{+a}{-a} \right] \right\} = -s_F + \frac{a}{2} \ln \left[\frac{a + s_F}{a - s_F} \right]. \tag{2.129}
$$

But the second part is a generalized $\tanh^{-1}$ function, (when $s_F < a$ for real arguments):

$$
g(a) = \int_0^{s_F} \frac{ds\, a^2}{a^2 - s^2}, \qquad \text{put } s = a \tanh u, \quad ds = a \operatorname{sech}^2 u\, du. \tag{2.130}
$$

$$
g(a) = \int_0^{s_F} \frac{a^2\, a \operatorname{sech}^2 u\, du}{a^2 \operatorname{sech}^2 u} = au \big|_0^{s_F} = a \tanh^{-1} \frac{s_F}{a}. \tag{2.131}
$$

So we have the result as obtained much earlier,

$$
I_3(a) = -s_F + a \tanh^{-1} \frac{s_F}{a} \tag{2.132}
$$

where thie inverse hyp function is defined by

$$
\tanh^{-1} \frac{s}{a} = \int_0^s \frac{ds\, a}{a^2 - s^2} = \frac{1}{2} \ln \left[\frac{a + s}{a - s} \right]. \tag{2.133}
$$

I have commented before, that really, it might better be called some other name, because when $s/a > 1$ and real, the usual real $\tanh^{-1}$ is undefined, but $\coth^{-1}$ is OK. These are just names so I don't worry about that too much, and jsut consider its analytic continuation . Further, all this difficulty is because if the parameter a is real, then there is a singularity on the real axis and the integral is not defined. But we want the case with a complex.

Now if we put $a = x + iy$, and expand out the log, we get its argument:

$$
u = \frac{a + s}{a - s} = \frac{x + iy + s}{x + iy - s} = \frac{x + s + iy}{x - s + iy} \tag{2.134}
$$

Rationalize to get the phase:

$$
u = \frac{x + s + iy}{x - s + iy} \cdot \frac{x - s - iy}{x - s - iy} = \frac{x^2 + y^2 - s^2 - 2iys}{(x - s)^2 + y^2}. \tag{2.135}
$$

Get the magnitude symmetrically:

$$
|u| = \left| \frac{x + s + iy}{x - s + iy} \right| = \sqrt{\frac{(x + s)^2 + y^2}{(x - s)^2 + y^2}}. \tag{2.136}
$$

Then

$$
u = |u| e^{i\theta} = \sqrt{\frac{(x + s)^2 + y^2}{(x - s)^2 + y^2}} \exp \left\{ i \tan^{-1} \left[\frac{-2ys}{x^2 + y^2 - s^2} \right] \right\}. \tag{2.137}
$$

Put it all together,

$$
\tanh^{-1} \frac{s}{a} = \tanh^{-1} \frac{s}{x + iy} = \frac{i}{2} \tan^{-1} \left[\frac{-2ys}{x^2 + y^2 - s^2} \right] + \frac{1}{4} \ln \left[\frac{(x + s)^2 + y^2}{(x - s)^2 + y^2} \right]. \tag{2.138}
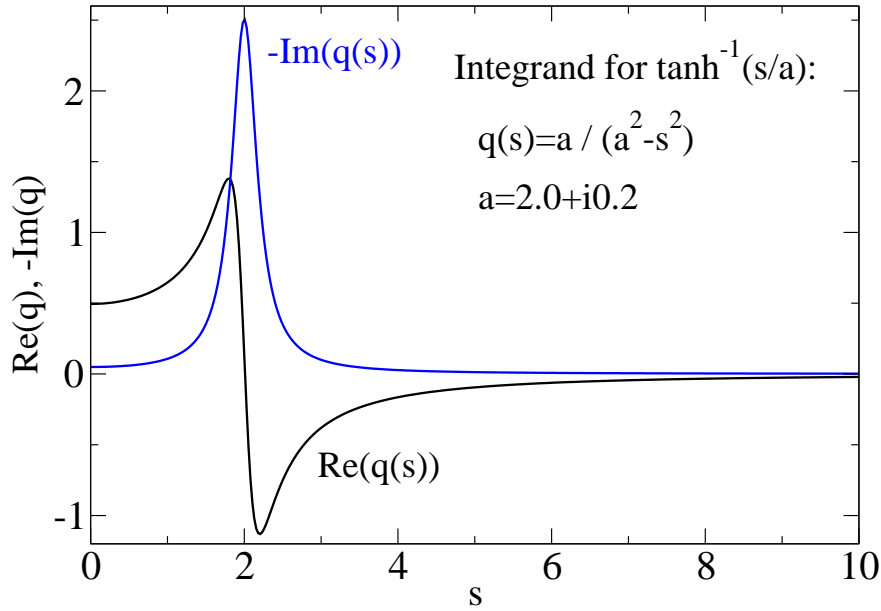$$

Figure 2: Plot of the real and imaginary parts of the integrand that gives inverse hyperbolic tangent, at $\mathrm{Im}\{a\} = 0.2$, a fairly large value.
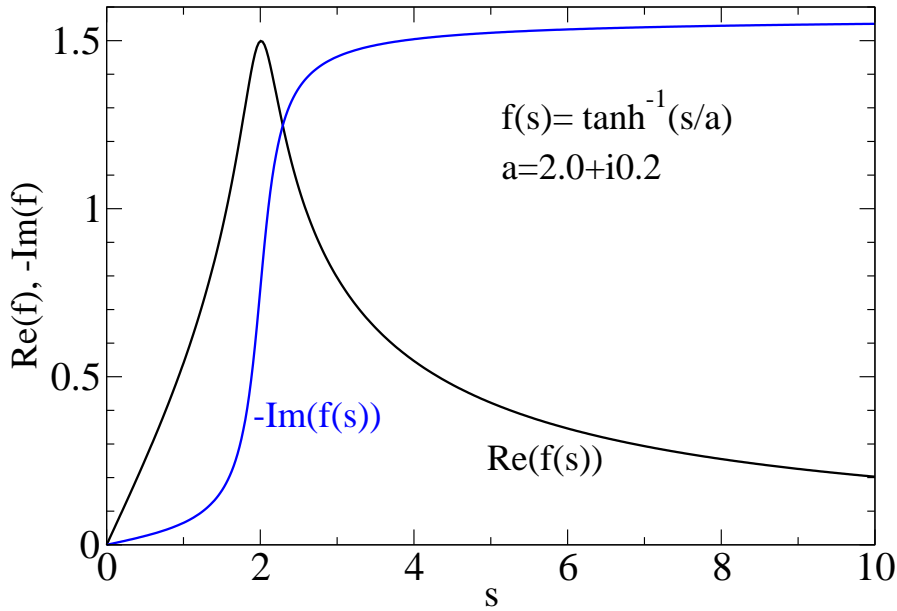

Figure 3: Plot of the real and imaginary parts of the $\tanh^{-1}$ function that is part of the $I_3(a)$ integral. The imaginary part smoothly approaches $-\frac{1}{2}\pi$ for large upper limit in the integral, for points s to the right of the weakly singular point at $s = \mathrm{Re}\{a\}$.
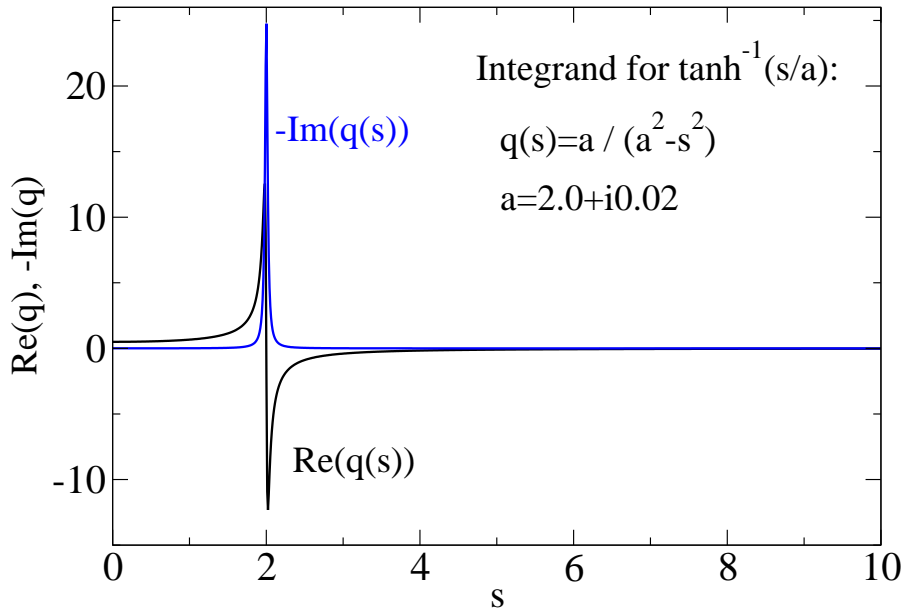
Figure 4: Plot of the real and imaginary parts of the integrand that gives inverse hyperbolic tangent, for a smaller imaginary part of a. Note how the imaginary part is a narrow but high peak, which becomes more accentuated as the imaginary part of a gets smaller. In the limit that $\text{Im}\{a\} \to 0$, the imaginary part becomes a delta function and the real part is the principal value operator.
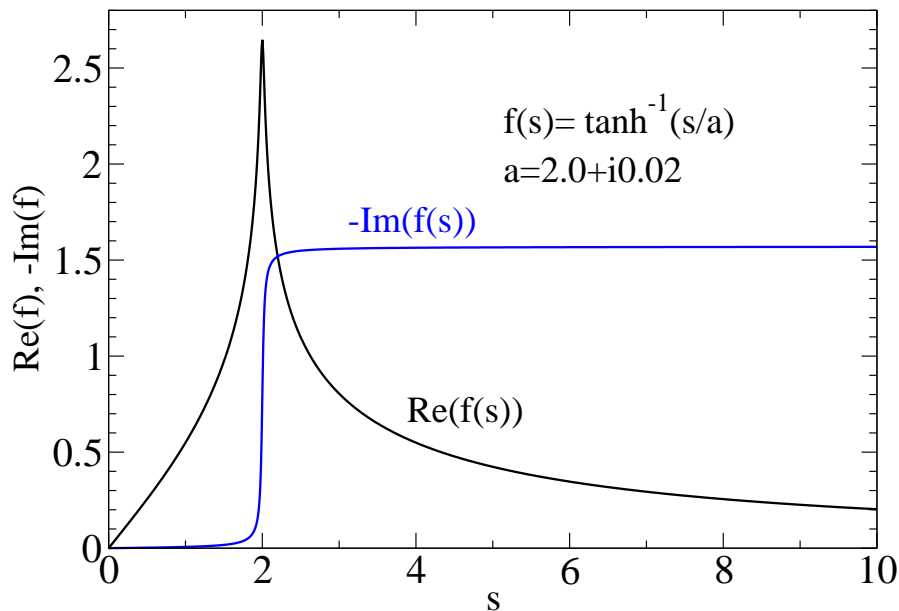

Figure 5: Plot of the real and imaginary parts of the $\tanh^{-1}$ function that is part of the $I_3(a)$ integral, for smaller imaginary part of a. The imaginary part of $\tanh^{-1}$ approaches $-\frac{1}{2}\pi$ for large upper limit in the integral, jumping suddenly like a step function for points s to the right of the more singular point at $s = \text{Re}\{a\}$.

Then this is used as

$$I_3(a) = I_3(x,y) = -s_F + (x+iy)\tanh^{-1}\frac{s_F}{x+iy}. \tag{2.139}$$

Some examples of how the integrations work can be seen in the Figures 2 through 5. At small value of $\text{Im}\{a\} = y$, the behavior is especially interesting. The limit of zero imaginary part produces a delta function and a principal valued integral, see Figs. 2 and 3. One sees that the imaginary part of the inverse hyperbolic tangent becomes like a step function, with the jump in the vicinity of $s = x$. The jump is always by the amount $\frac{1}{2}\pi$. This is due to the delta-function like property of the imaginary part of the integrand, $q(s) = a/(a^2 - s^2)$. On the other hand, the real part passes through zero near $s = x$ and acts as a principal value operation. Further, note Fig. 5, where $y = 0.02$, a small value compared to $x = 2$. The real part of $\tanh^{-1}$ can be seen to have the separate segments: the usual inverse function for $s < x$ and what is actually close to $\coth^{-1}$ for $s > x$. Hence the need to possibly give it a different name.