**Absorption Spectrum**

**Now let’s look at the absorption spectrum of electrons, taking into account the e-e interaction between them. Might compare this to the corresponding file in the Semiconductors folder.**

**Absorption via Plasma Waves**

**So we have (from EM folder, say):**

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And if we plug in our result for σ(ω) that we didn’t calculate then we can not calculate A(ω) as well. There are two ways to calculate the absorptivity though. We can also do

****

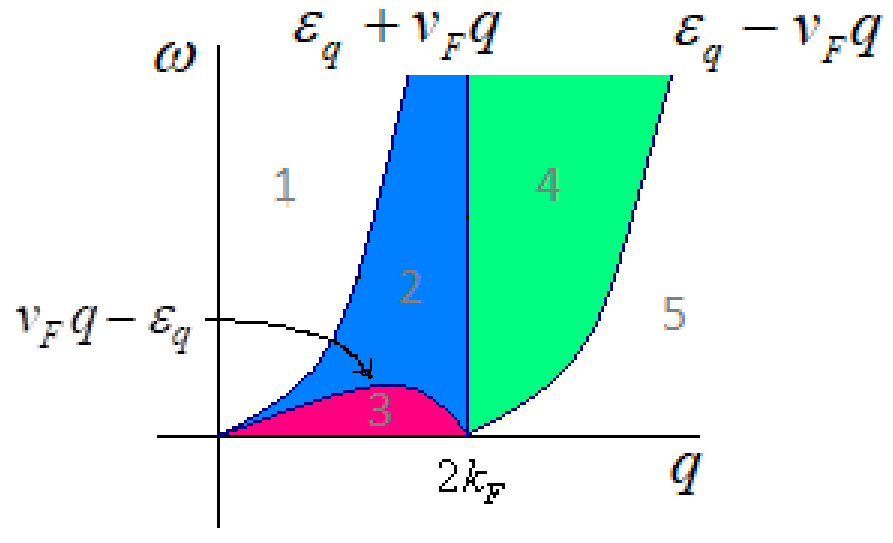
These two formulas should give us the same result as long as we include all effects. In the Electrons + Impurities folder we looked at the contribution of disorder to σ(ω), but not the contribution of the e-e interaction and the concomittant charge density fluctuations it could provoke (we kind of assumed charge density fluctuations were small anyway when we set the electron charge density ρ = ρ0 = opposite the jelly background charge density, in our derivation of the GF expansion of σ(ω), and so might have to revisit the derivation if we don’t make that assumption?). And here, in looking at the GF expansion of ε(ω), we have included the e-e interaction, but have ignored the effect of disorder. FWIW, further down in this folder, we’ll look at calculating σ(ω) including both effects. But for now, we can look at the effect of these charge density waves on the absorptivity through their influence on ε(ω). So recall in the previous file we said,



where V(q) = 4πe2/q. And in the Collective Excitations file, we stated (found/quoted results in the Free Day/Electrons/Nonequilibrium Properties/Susceptibility file):



where the regions are:



The colored regions correspond to the regions delineated above, where ImεRPA(q,ω) exists. So it is zero outside those regions. So filling in our results,



We see we get no absorption in the white regions. Evidently, at these EM frequencies/wavevectors, the Coulomb force between electrons is strong enough to keep the electrons locked into their plasma wave excitation structure. At these frequencies/wavevectors, the electrons will respond to the field like a rope to a person shaking one end of it. The charges will move in phase with the field, and accordingly, their velocities and associated current will move 90o out of phase with the field. Therefore the field will do no net work on them, and we’ll get no absorption. Any energy the EM field imparts to the plasma wave during one half cycle gets put back into the field during the next half cycle (at least in the steady state situation – I guess initially the EM field would have to impart more energy than it receives just to set up the plasma wave). Even though we don’t get any absorption, we *do* get strong reflection of any EM fields in this region. Inside the colored region, the repulsion between electrons is not strong enough to keep them oscillating in phase with the wave, and moreover, not even strong enough to entirely keep them all together in their collective oscillation mode. So two things happen. First, the charges’ oscillations in the plasma wave start developing a non-zero phase difference with the EM field, and so the plasma wave current starts developing a non-zero + 90o phase difference with the EM field. So the current will become a little in phase with the EM field. Remember this is due to the imaginary part of ε being non-zero now. This means it will start absorbing energy as the work the EM field does on the charge displacements is now non-zero over a wave period. And the second thing that happen is, due as well to ε developing an imaginary part, that the plasma wave lifetime becomes finite: since the Coulomb force is not strong enough here to keep the charges collectively oscillating in their plasma wave, they will start to break out of it and settle into single particle excitations. This trend will be exacerbated the further into the imaginary region we go. The plasma wave, such as it is, will become more out of step with the EM field, so more absorption will take place, and this will concomittantly kick more electrons out of the plasma wave entirely. Can imagine that this will also result in transmission going up. One last thing: below we will calculate absorption due to interband transmissions. We will use GF’s, but we can also do it (at least the non-interacting part of the absorption) using a simple TDPT QM argument. Can we do the same for plasmon absorption? I don’t think so, because we don’t have transitions from a single particle spectrum into a single particle spectrum. These are collective excitations.

**Example**

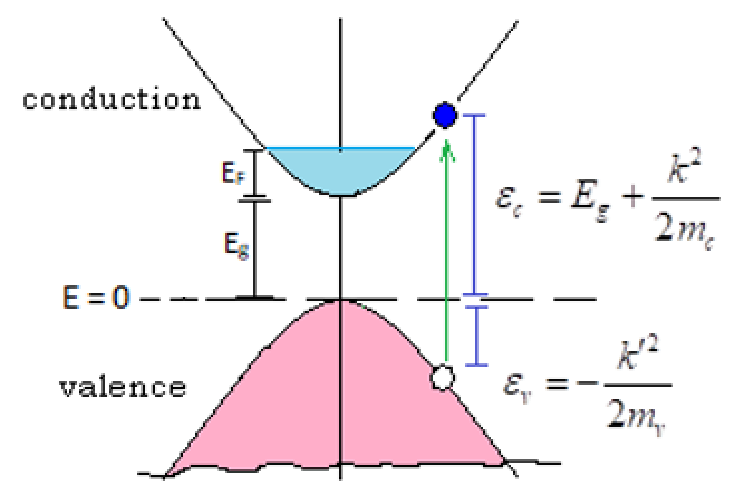
Quick question: Can our EM field can be a light wave at all? Cause a light ray in the absorptive region would have to obey:



So this would put it in region 4. Hmm.

**Absorption by Interband Transmissions**

Now let’s consider a different case of absorption – that coming from interband transitions. Such EM waves are typically in the X-ray range as far as their energy. So here’s the general picture of what’s going on. We have particles being excited from a core valence band to the conduction band.



We can construct a second quantized model to get a more accurate (than the free particle) picture of this process. First we need to write the Hamiltonian between particles/holes. Might look at Quantum Mechanics/Multiple Identical Particles/2nd Quantization Quasiparticles file for more on this. So first let’s define creation/annihilation operators. Let α†k create electrons in either band, and αk destroy electrons in either band. Then we’ll define on top of this creation/annihilation operators for electrons in the conduction band (ck†, ck), and creation/annihilation operators for holes in the valence band (dk†, dk),



So ck† creates a particle with crystal momentum **k**, and dk† creates a hole with crystal momentum **k**, in the sense that when you destroy a valence electron with crystal momentum -**k**, there remains a net **k** crystal momentum in the valence band. And analogously with ck and dk. Now we’ll write down our H (or K = H – μN, really). We seem be focusing on just the particle – hole interaction, ignoring the particle-particle and hole-hole ones, as well as other mixes between the two. We’re going to be calculating the conductivity, and the particle-particle and hole-hole guys would probably just give us the kind of contribution to the conductivity that we’ve calculated before in the Electrons + Impurities folder, just with the disorder interaction replaced by the e-e interaction, like in the previous file. Well, this would in fact be the contribution to the absorption we just examined up above, except that we did it through ε(q,ω), instead of through σ(q,ω). So I imagine if we included the particle-particle and hole-hole stuff, we’d just duplicate the stuff up above. Instead, we want the contribution from the interband transitions. So we have.



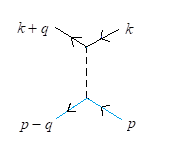
and the energies are given by:



The valence ξ has +μ because when we add a hole, we subtract energy -k2/2mv – μ, and so add energy k2/2mv + μ. Because the c’s and d’s commute, we could write this as:



I think that the FD for the interacting potential V would be,



where only blue (hole) can connect to blue, and black (electron) to black. Qualitatively, we have a hole and an electron scattering from each other by exchanging a virtual photon. Now, to get A(ω) we need Reσ(ω). So we’ll work out the current operator. Recall that the *total* current is just **J** = (e/m)**P**. To get the 2nd quantized representation of the operator we need to do something like,



and α = c when in conduction band and d† when in valence band. So either way, α is destroying an electron, and α† is creating one (might check out Metals/Free Day/Electrons/Excitations for similar analysis),



Note we can cross out that term because a filled band will have net zero momentum.



Now apropos the blue terms, I’m not sure it’s kosher to cancel them out. But…the ground state occupation numbers of the conduction band would have no current. And if we have direct transmission, then the further occupied k-values in the conduction band should match the occupied (by holes) k-values in the valence band. But these will have roughly opposite momenta, since the velocity expectation is v = ∂ε/∂p, and the valence band has negative slope. So the blue guys should cancel-ish. Either way, we’re probably just trying to extract the current associated with the absorption process (a valence electron in the process of being lifted to the conduction band will exist in an oscillatory superposition of valence and conduction band states, and will have an oscillatory current associated with this – see Free Day/Electrons/Absorption file), and so we’re disgarding the current terms associated with the individual bands themselves. So we are left with:



And now since we have direct transmission, these overlap integrals should only be non-zero for k´ = k. And so we can write this as:



In order for the overlap integral to be nonzero, the conduction and valence band states will likely have to differ by something like Δℓ = ± 1. So probably ψv,k would have to be comprised of s-orbital states, and ψc,k of p-orbital states (might see Free Day/Electrons/Nonequilibrium/Absorption file for very rudimentary illustration of how this works out). Now we want the conductivity. The conductivity, as we’ve found in Metals folder, is just equal to:



We don’t have any spatial variation in our problem –> q = 0. So, then,



and,



(and **J** is the current we have formulated above) In a homogeneous system we have:



[Tr means sum over diagonal Cartesian components] Ultimately, we’re interested A(ω) which is Reσ(ω). So,



So we just need the (total) current - (total) current correlation function. We’ll get it via analytic continuation as usual,



Filling in the current,



Our H conserves particle/hole number so we can reduce this to (commutating c’s and d’s again):



The first term describes the time-development of the annihilation of a particle in the lower band and subsequent annihilation of a hole in the upper band, i.e., absorption. The second term describes the time development of the creation of a hole in the upper band and subsequent creation of a partice in the lower band, i.e., emission. I think we just keep the first term apropos our interest in absorption? Would both terms give the same result?

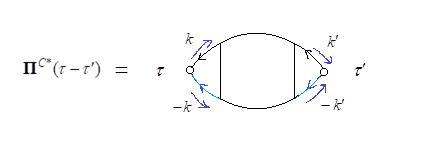


We can guess the Feynman rules. So it seems we can represent this with vertices:

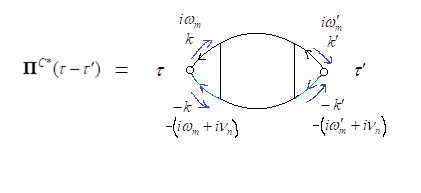
A group of people with different colored squares

Description automatically generated

and then connect into diagram as:



It’ll help to review the way we handled the current-current correlation function in the Metals/Impurities/Conductivity folder. Representing this as FT, implicitly including the ‘external legs’ coming out of the square, we have:



And now:



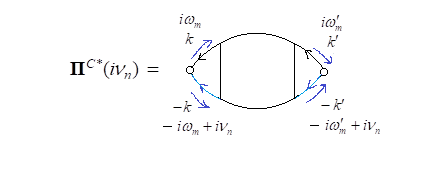
where [….] represents the diagram in terms of its Fourier transform and such. And we note that energy/frequency is not conserved at the left vertex because it isn’t integrated over. Neither right. But whatever energy the top gains, the bottom must lose, because we do integrate over the internal vertices. Also, I guess the energy conservation argument sort of presumes the energies to be positive and going clockwise on bottom, following the top, but then we read the GF’s arguments going against the arrow, so I’ve switched it. That’s why we have what we have. So then,



and thus the Fourier transform of Π would be what we have but with iνn → -iνn. So finally,



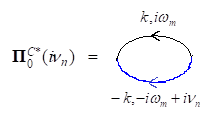
where diagrammatically, […] is given by:



So there. *And I guess we should include a factor of 2 for spin degeneracy too, but he seems to be ignoring that – going to put in.*

**First Order Term**

Let’s consider the first order term.



which is (including factor of 2 for spin degeneracy):



Now,



So,



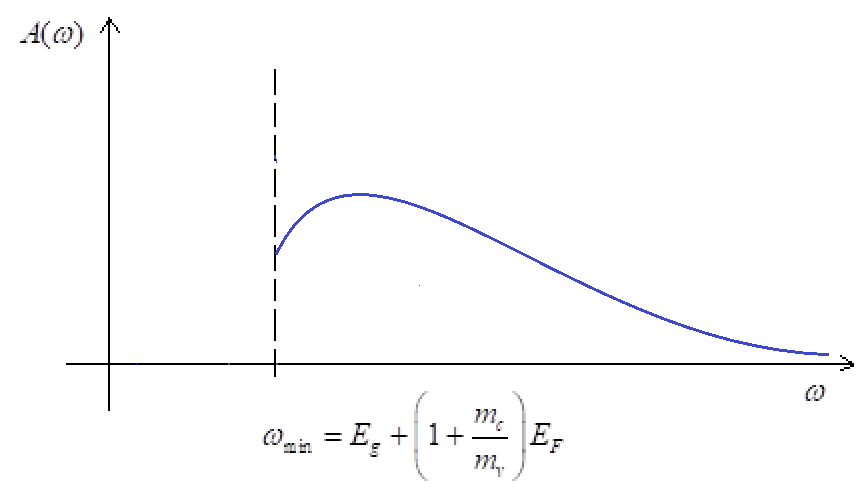
Now taking account of the value of ξv,-k up above, if we plug it into nF(ξv,-k) we should find it to be zero, since it’s +μ, rather than -μ. Then analytically continuing,



So then using A(ω) = (-1/ω)ImΠ0R(ω), and taking 1/3 the Trace, to get the magnitude, thanks to isotropy, we have:



which is what we obtained from the free metal theory (see Metals/Free Day/electrons/absorption). And in that file, we worked this out some more and obtained the following curve.

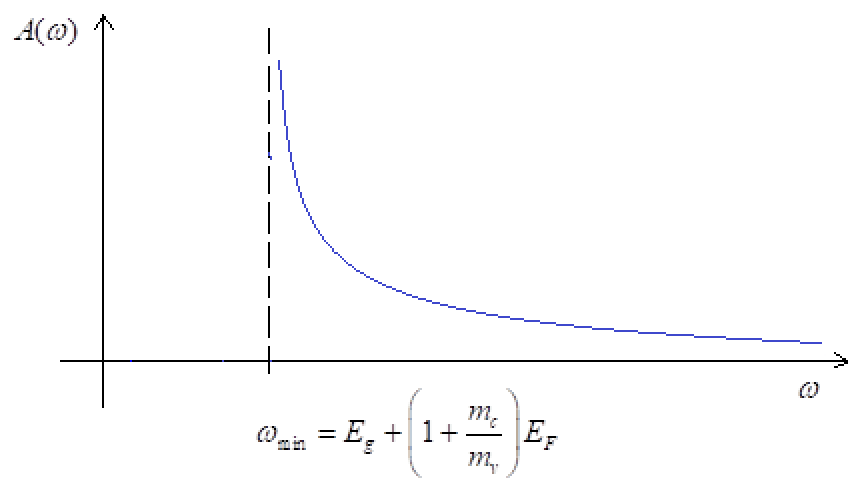


And note that the curve hits the dotted line at ωmin. We see we have non-zero absorption at all frequencies ω > ωmin. Evidently, we would find that the EM field is doing work on the electrons at all frequencies. How are they oscillating? Well, while the electron is making the transition, it exists in a superposition state between the valence and conduction bands. And so it’s oscillating back and forth between them with a frequency ω = εc – εv. When the electron is in the valence band, it contributes a current going to the right (v = ∂εv/∂k is negative), and when it is in the conduction band, it contributes a current going to the left (v = ∂εc/∂k is positive). So its current *is* oscillating back and forth. So I guess the electrons are at least partially oscillating out of phase with the driving EM field at all times. Also note that the rate of the transition is proportional to the strength of the EM field exciting the transition, but not to the frequency of the transition. So the rate of transition *can* be low. So I guess the electrons are at least partially oscillating out of phase with the driving EM field at all times. And probably the largest amplitude of oscillation (strongest current, more specifically) is near the E­­min­.

But now we can go forward. I’m not going to bother, but Mahan now factors in the ee interaction by including ladder and crossed diagrams to get, ultimately:



where ξ0 ~ EF he says. And we’ve made customary approximation that wk = w0 is independent of k. Now we have has a power law *divergence* at ωmin. So we have something like:



Looking ahead to the case of the semiconductor absorption spectrum in the presence of an ee interaction, we’ll observe that the threshold energy/frequency doesn’t change here like it did there. In the semiconductor case, the particle-hole attraction created bound states with negative energy (of course) that thereby lowered the absorption threshold. I guess this doesn’t happen here because the electrons in the Fermi sea screen the potential, thereby weakening it, and preventing it from supporting bound states.

**Orthogonality Catastrophe**

But then it was realized (by Hopfield, Anderson) that from another point of view, we should get A(ω) = 0. The basic idea is that A(ω), like in the independent particle case, is proportional to the transition matrix element (mediated by e/m) between the initial and final state of the system. But we should include the other N particles in the initial and final state. Their inclusion results in an overlap integral between basically the ground state of the Fermi sea w/o the hole potential present (ΦΦi), and the ground state of the Fermi sea w/ the hole potential present (Φf).



The initial state Φi would just be a Slater determinant of N free particle states φi(kr) = sin(kr)/kr.



The final state would be a Slater determinant of free states in presence of the core hole. Whatever that core hole potential is, it would create a phase shift, δs, in the final single particle free states: φf(kr) = sin(kr+δs)/kr, where δ is the s-wave phase shift for one-electron scattering from the core hole potential. The new N-particle wavefunction is just a Slater determinant with these new orbitals,



So what is this overlap, S? Heuristically, we can say that if the overlap between single particle states is say 0.9, then the overlap between N particle states would be ~ (0.9)N, and so ought to vanish in the large N limit. A more rigorous evaluation of S has been shown to come out to:



And so we see indeed that S (and therefore A(ω)) → 0 as N → ∞. So it appears some important terms are missing from the GF expansion of A(ω). One way to find them, apparently, is via an exponential resummation method. To motivate, we start with:



and,



We can write this as:



Can imagine these GF’s are diagonal in k,k´ so:



He says that we can approximate the electron GF as its unperturbed value, perhaps due to screening and such. So:



So we can write,



Then taking FT,



where Av is the spectral function of the valence electron. Then analytically continuing, and constructing the absorptivity,



So under this approximation we see that the absorbtivity is proportional to the valence spectral function. So he starts out evaluating the valence GF via exponential resummation, namely:



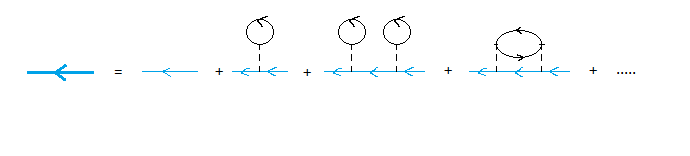
(remember this type of expansion is expected to be effective when dealing with just one particle – which due to nF(ξv) above – is basically what we have?) So first, solving for the F’s:



Then equating, we have:



The G’s are given by the expansion:



So F1(τ) would be (in GFv, seem to be setting nF(ξc,q) = 0 in comparison with θ(τ), which I think can do ‘cause ξc,k comes in with +μ):



(seem to be ignoring spin for real ‘cause no factor of two here) V(k=0) is technically undefined. Could use screened potential I guess. Anyway, this is a self-energy term (‘cause it’s linear in τ and so combines with ξk) coming from the interaction of the hole with the 1023 conduction electrons in the conduction band. Higher order terms in the F expansion will continue to generate V linear τ self-energy terms. But the exact self-energy of the core hole is known from Fumi’s theorem to be (see Quantum Mechanics/Identical Particles/Symmetrization and H’s),



So we’ll replace all linear terms with the Funni Σ above. The role of this Σ is ultimately to shift the threshold energy for the X-ray transition from ωmin = Eg + (1+mc/mv)EF, to ω´min = Eg + (1+mc/mv)EF + ΣF. This ΣF term is analogous to the bound state energy correction to the absorption threshold that we found in the Semiconductor folder. Now he proceeds with the second term, which I’m not going to write down, but which he says begins to account for the Orthogonality Catastrophe. He drops the self energy contribution (the one linear in τ – probably that two balloon diagram above), and keeping just the largest part, eventually gets:



These results eventually give him the following for the spectral function:



The response of the electron gas has a dramatic effect upon the spectral function of the hole. The spectral function has a power law divergence, Ω1-g near the threshold energy. In the absence of interactions (V = 0), the spectral function is a delta function:



So the effect of interaction is to change the delta function divergence of the hole /valence *spectral* *function* into a power law divergence.

A graph of a function

Description automatically generated

And one can now calculate, the effect of interactions on the *absorption* is to change the step function into a power law ‘step’, rather than a diverging step.

A graph and a graph

Description automatically generated

Further terms past F2(τ) in the series also contribute to the orthogonality catastrophe and should be summed in order to obtain an accurate description of the phenomenon. The exact method of summing all these terms has been given by Mahan (1982), and more elegantly by Ohtaka and Tanabe (1983). Several other types of results have been obtained. The most important is by Nozieres and deDominicis (1969), who show that the exact coefficient of the term which diverges like ln(ξ0τ) is:



Turns out α can be positive or negative, and so these terms can preserve the singularity at the absorption threshold, or turn the singularity into zero, rather.

The orthogonality catastrophe is an important feature of many-body physics. The process of switching on a potential occurs in many circumstances, and the physics can be applied to a variety of phenomena. For example, the Kondo effect has this feature, which plays an important role in its theory. Whenever the potential is switched on, the system responds by making electron-hole pairs, which affects the spectral response of all correlation functions which are being evaluated.

**MND Theory**

So apparently there are two competing phenomena. Apropos the absorption spectrum, one cause power law divergence (called excitons) at the threshold, and the other causes power law vanishing (orthgonality catastrophe) at the threshold. An important contribution was made by Nozieres and deDominicis (1969) who solved these two processes together. Their theory is asymptotically exact (i.e. exact for ω near the divergence), and expresses the power law exponents in terms of the angular momenta of the electrons in their final state. Apparently whether we have divergence or convergence (to zero) depends on this angular momentum.

**XPS Spectra**

The X-ray photelectron spectroscopy (XPS) measures the line shapes of photo-electrons excited from the core levels of atoms. A photon, which is usually in the kV energy range, excites a core electron to very high kinetic energy. He discusses how the peak is in the spectra is broadened (meaning of spectroscopic function, and because it’s no longer an exact eigenstate when include these other phenomena) due to interactions with phonons, and plasmons. He notes that Doniach and Sunjic (1970) argued that the orthogonality catastrophe should make the main peak at ω~EF asymmetric, and showed how to characterize its asymmetry. The degree of asymmetry is given by α in fact.