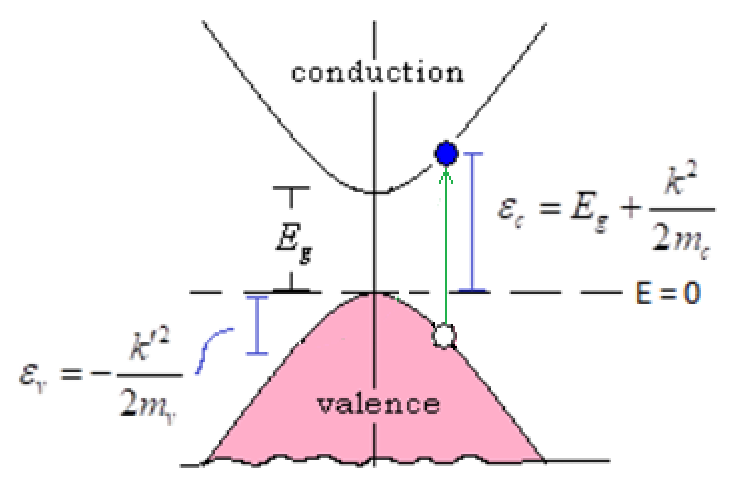
**Interband Transitions**

The color of an object is typically due to the nature of the transitions the substance’s outer electrons make. These outer electrons reside in the valence/conductance bands in semiconductors/metals, and so these energy levels are highly affected by their host. These effects are captured with band theory. But electron-electron interactions as well play a role in optical absorption rates for electron transitions between valence and conduction bands.

Might want to compare the following to the similar analysis we made for metals in the Metals/Interacting Electrons/Nearly Free folder. But now we’re dealing with a semiconductor. So we’ll presuming an entirely filled valence band.

**Naïve theory of optical absorption**

Exciton states play an extremely important role in the understanding of interband transitions in semiconductors. The word exciton is used here to signify the modification of the absorption rate of photons due to the Coulomb interaction between the electron and the valence band hole. The easiest case to understand is when the lowest interband transition is *direct*, which means that the conduction band minimum and valence band maximum are at the same point in k-space. This case is shown schematically, below:



We see we have an electron jumping from the filled valence band into the empty conduction band. Note that the transition would tend to be purely vertical (in the E vs. k plane) because the photon momentum corresponding to a typical optical gap would be pretty small, much less than a reciprocal lattice vector. This is boils down to the fact that the speed of light is so much larger than the speed of an electron, and so has much less momentum for the same energy. This is all consistent with the almost conservation of crystal momentum equation, and conservation of energy equation – see Metals/Free Day, which in our scenario reads (**k**γ is photon momentum, **k**’s are electron crystal momenta, and **G** is RLV):



The equation makes more graphical sense using the extended zone scheme – see Metals/Free Day/Electrons/Absorption. But basically **k**´ is what it is, **k**γ is small, and **G** is in our case the shortest RLV, putting **k** roughly the shortest RLV away from **k**´. This just means it’s in the same spot in the BZ, but in the next band up. As far as actual momentum is concerned, we can see from our picture that we have initially a full valence band with no net momentum. And then we have an electron in the conduction band moving to the right, and hole in the valance band moving to the left (which means in the valence band we have a net one electron moving to the right). So our photon basically took what was a left moving valence electron and flipped it into a right moving conduction electron. So we have net momentum to the right, and current to the left. It is this ‘current’ oscillation that enables the photon/EM field to do work on the electron.

The first attempt at a description of the process is via a simple QM golden rule calculation. Our Hamiltonian is:



We don’t have to worry about commutation relations between and **A**, ‘cause **A** is position-independent as we’ll see in a bit. In the Coulomb gauge + temporal gauge (see EM folder/Waves), we have:



where **k**γ is the momentum of the photon. **k**γ will be negligibly small, as we’ve stated. This is because ω = ckγ is basically the line connecting the initial electron state to the final one, and the slope c is so large compared to the band spectra slopes that kγ must be very small. We’ll presume the initial state is some sort of tight-binding p-valence band |k´σ´,v>, and the final state a tight-binding s-conduction band |kσ,c>.



c´ and ν´ label the site orbital d.o.f. c´ = 1, and v´ = 1,2,3. And I guess c = 1, and v = 3, say. Might check out Metals/Free Day/Electrons/Excitations for calculations of these band states and energies. So the transition rate of electrons in occupied |k´σ´,v> states to empty |kσ,c> states would be to first order (see QM/Time-Dependent/Scattering Perturbation):



Note we’re allowing different effective masses in the two bands. The sum over all kʹ is including all the electrons in the valence band, and the sum over k gives the total rate of transition from any valence state to any conduction state. So this would give the rate of exodus of valence electrons, and hence the rate of absorption of photons I presume. Now the rate of *energy* absorption would then be:



(where in the last line we presume homogeneity) Now we want to extract the absorbtivity. So recall the definition from EM file (Metal-Insulator TD Maxwell’s Equations),



(P(ω) means same thing as <P(t)> in this context) So filling in our constant E,



So the absorptivity is:



Now let’s look at the matrix element. I’ll not yet implement the physical fact that **k**´ ≈ **k**; I’d like to see if this can be justified strictly mathematically. So,



Note e**p**/m is basically a current (or one electron). So we are keeping this combination together for physical reasons. Assuming transmissions are from top of valence band to bottom of conduction band, k´ should be small enough to neglect. Or can reason that -i∇ ~ **G**, the RLV, and so is larger than **k**. So,



I guess the argument is that e-i(**k**-**k**´)·**r** is slowly varying over course of the unit cell and so can be pulled out of a unit cell integral, while ukc\*(r)(-i∇)uk´v(r) is quickly varying over the unit cell, but the same in all unit cells because it is periodic over the unit cell. So could say k must equal k´, roughly, as otherwise the e-i(**k**-**k**´)·**R**\_j phase factor would wash out all the identical unit cell integrals. This is consistent with our argument that the photon has negligible momentum compared to the electron. So we say,



So now we have:



So we come to, performing the trivial sum over spins:



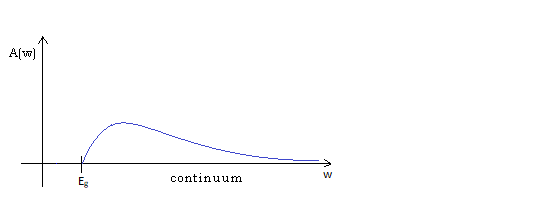
But we can go on,



where the k in wk would be evaluated at √2μ(ω-Eg). And so we have,



Predictably, we don’t get absorption until ω > Eg. But one could not have a priori anticipated the √ behavior near that cutoff. So that’s interesting. We also see that A(ω) → 0 as ω → ∞, as we should expect on general grounds (charges can’t keep up with oscillations as they become increasingly fast, and so barely move at all). Predicted behavior would look something like this:



But the experimental results show behavior that doesn’t resemble at all the predicted sqrt behavior.

**Taking account of two-particle interaction via RSPT**

To clear up this discrepancy, Wannier observed that the interband transition in sc’s was really a two-particle process. The photon of energy, ω, creates two excitations in the semiconductor – the electron in the conduction band of wave vector **k** and energy Eg + k2/2mc, and the hole in the valence band of wave vector -**k** and energy k2/2mv (same thing as electron with wavevector **k** and energy – k2/2mv). The total energy created would be Eg + k2/2mc + k2/2mv = Eg + k2/2μ (note k’s are same because momentum conservation). This is same argument present in the delta function above. So so far, nothing new. But the first point made by Wannier is the particle and hole have a Coulomb attraction between them, and so we’re missing that energy term, and we’re missing the fact that the scattering states in the Golden Rule are actually eigenstates of the Hydrogenic atom, not just independent particle momentum states. So the final state of the system is described by the 2-particle Schrödinger equation:



The wavefunction can be factored into a COM state and a relative state.



where εj is the energy of the relative wavefunction part. The relative energy is less than zero if the two form bound states, and greater than zero if scattering states. So how to update the formula? The point of departure is:



First we’d interpret the matrix element as the relative wavefunction evaluated at zero:



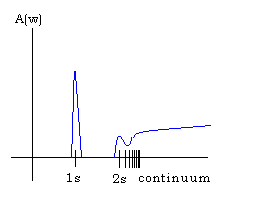
Sure. Then we recognize k2/2μ as the former relative energy between the two free particles. So,



So then making the additional customary approximattion that wj is independent of j, we now have (implicitly doing the spin sum which gives us an extra factor of two):



The summation is over bound and continuum states. Basically, the former formula only summed over continuum states/energies. That the emission rate depends on the point r = 0 can be inferred from the fact that the particle and hole must be in the same physical location in order to recombine or be emitted. Either way, this is called *Elliot’s* formula. The results for the interacting case are quite different. The relative motions of the electron and hole are in s-wave hydrogenic states, either bound or unbound, depending on the orbital motion, and the orbital selection rule – the two states must differ in orbital momentum by ℓ = 1 because of the emission/absorption of a photon. The predicted spectrum is:



The multiple vertical lines are all the n = 3,4,5,…,∞ lines. There are peaks at the bound states; the peaks become less pronounced near the start of the spectrum coming from the continuum, which starts at the last line on the right. In general, it is hard to experimentally determine these peaks since all frequencies tend to be absorbed for anything around the usual crystal thickness.

**Taking account of two-particle interaction by Green’s Functions**

We can derive the same formula via the GF approach. 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. But basic idea is to now consider the conduction and valence bands as our Hilbert Space. And consider excitations above the ground state:



where all the 1’s are for electrons in the valence band with ε < μ, and 0’s for electrons in the conduction band with ε > μ. And now 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 have.



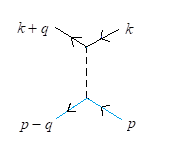
and the energies are given by:



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, the total number of electrons should equal the total number of holes. And further, if we have direct transmission, the 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, and we’ll be 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:



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 in 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 currents,



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



and then to:

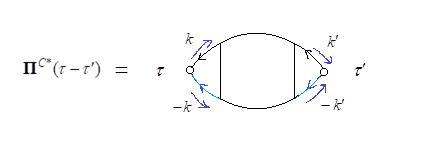


We can guess the Feynman rules. So it seems we can represent this with vertices:

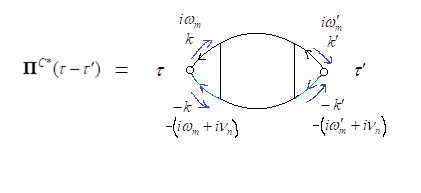
A group of people with different colored squares

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:



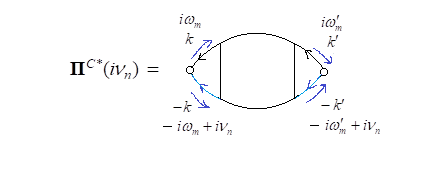
where [….] represents the diagram in terms of its Fourier transform and such. And we note that energy/frequency is not conserved at the left vertex because it isn’t integrated over. Neither right. But whatever energy the top gains, the bottom must lose, because we do integrate over the internal vertices. 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,



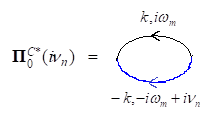
where diagrammatically, […] is given by:



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:



Now,



So,



For a semi-conductor, the occupation numbers are basically zero [note the last, though ξ refers to the valence, if plug that numerical value into nF we’ll get zero]. Now analytically continuing,



where P stands for principle value. So then accounting for the fact that our result is isotropic so that Σ**w**2() = Σ(wxwx**ii** +w­ywy**jj** + wzwz**kk** + cross terms which go to zero by symmetry) = Σ(wxwx**ii** +w­xwx**jj** + wxwx**kk**) = Σ(wxwx)**1** = Σ(wxwx + wywy + wzwz)**1** = (1/3)Σw2**1**, we have, leaving off the **1**. Now using A(ω) = -(1/ω)ImΠ0R(ω), we come to:



And this is what we obtained before, in the single particle theory. The remaining terms are now examined. Fortunately, most are 0. All self-energy terms, for either the electron or the hole, are zero because all contain closed loops and vanish since they are proportional to nF. The only nonzero contributions are vertex diagrams in the form of ladder diagrams. These are shown below,

A diagram of a mathematical equation

Description automatically generated

The first diagram gives us the term we just calculated. The next diagram gives us:



Additional ladder diagrams just tack on another denominator, w, and V term, and these diagrams can be summed exactly. We have,



where,



Now we want to determine the vertex function by solving the integral equation. First we define an auxiliary function, and its inverse Fourier transform:



Turns out it’s easiest to write an equation for **P**(r,ω). Now we operate on both sides of P(r,ω) with ω+i0+ - Eg + ∇2/2μ,



And then fill in the recursion relation,



to get,



For the Wannier exciton system, the matrix element **w**k is taken to be independent of **k** and is a constant, **w**0. In this case, then, we have,



So we have:



And V(r) = -e2/r, in faux-Gaussian units (and it’s attractive ‘cause we’re doing electrons and holes). Now let φj(r) be the eigenfunctions of -∇2/2μ + V(r), with eigenvalues εj. And let’s make an eigenfunction expansion fo P(r,ω),



Then multiply both sides by φj´\*(r) and integrate,



So,



Now recall we want,



well comparing this to:



we see we can write,



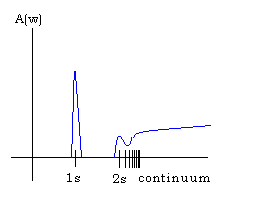
And so,



Consequently the formula for optical absorption becomes, doing the whole isotropy thing/dividing by 3,



This is what we surmised when we tried to modify the free electron result to accommodate the hydrogenic bound states. And we have:



There are other diagrams too, however. There are crossed diagrams, of the sort seen in the study of weak localization (see Metals/Impurities/Conductivity). However, these also are proportional to nF, which, for small T is near 0. Thus there are few many body correlations between the species, and they behave more or less like independent particles. Therefore, this formula constitutes an exact solution to the problem at T = 0 – and a very very good approximation at T > 0.