**Non-equilibrium Properties**

Yep. By the way, since we haven’t discussed phonons, or impurities, etc., there are no mechanisms yet by which photons could be truly *absorbed*. So in our discussion below, we say that the electrons will absorb photons, but once they do, they would immediately reflect them back. So we could call this section Reflection instead.

**Absorption by Free electrons in Crystal Potential**

As we saw in that Conservation of Crystal Momentum file (Metals/Free Day folder), a consequence of the crystal potential is to replace momentum conservation with crystal momentum conservation. So now any photons an electron would absorb would have to be such as to satisfy the conservation of crystal momentum, and conservation of energy equations.



where **G** is some reciprocal lattice vector. So let’s take a look at the band spectrum of GaAs. It has a direct band gap between the valence and conduction bands.

Chart, radar chart

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So the minimum frequency of light that it could absorb (and then promptly reflect, unless there is some mechanism by which it may actually absorb the light) would be across that band gap and represented by that red arrow in the right diagram. Remember the photon arrow has components **photon**\_**arrow** = ℏk· + ℏω, where the two unit vectors point to the right/up respectively, in the graph. And the slope of the arrow represents its velocity, c. c is practically infinite on the scale of this diagram, and so the arrow is basically vertical. And so while the bottom and top of the arrow are a little bit horizontally displaced, by an amount k, it is *very* tiny. And commensurately, while the bottom and top of the arrow are displaced by a little more than Eg = εc – εv, it is only *very* little more. So we can for all intents say ω = Eg, and consequently k = ω/c = Eg/c. Okay well this is the minimum frequency that can be absorbed. But other frequencies can be too. Basically any photon line that connects some point on the valence band with some point in the conduction band will work.

Now let’s take a look at Si.

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It has an indirect band gap, as εv and εc are not vertically aligned. We can get photon absorption at point Γ nonetheless of course, as represented in the right side diagram by the red photon arrow emerging from Γ and connecting directly to the conduction band. But this wouldn’t be the smallest frequency of light that could be absorbed. We can absorb photons with an energy roughly equal to the band gap, but this would require some assistance. Since the slope of the photon arrow is so high, it basically carries no momentum on an energy scale of a few eV’s. On the other hand, because phonon velocities/slopes are so small, they do carry a lot of momentum on the scale of the BZ, but hardly any energy. So for an electron at Γ in the valence band to get to εc, it would have to absorb a phonon (blue arrow) to carry it to the point almost directly below εc (i.e. roughly 80% of the way to X). This phonon would hardly alter its energy though. And then the electron could absorb a photon (red arrow) to carry it to εc in the conduction band. This is called phonon assisted absorption. For all intents then our photon frequency would be ω = Eg, and our phonon wavevector would be k ≈ 0.80(X-Γ), where X-Γ is the distance in k-space between those two points in the BZ. Here’s a that picture of the BZ again,

Chart, radar chart

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Like Si, C has a band gap, but much larger. It’s around 5.5eV. And this corresponds to photon wavelength λ = 220nm. So C would only be able to absorb EM waves with a smaller wavelength than this. This excludes the visible spectrum, which is why diamond is transparent to light. Note EM waves can still affect the electrons (scatter off of them I guess?) as we know that visible light will refract upon entering diamond.

**Naïve theory of optical absorption**

Here’s a more quantitative discussion from Mahan. Might see similar calculation in Metals/Free electrons folder.

Diagram of a diagram of a physics experiment

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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 (green arrow 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.

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/Harmonic 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:

A graph of a function

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But the experimental results show behavior that doesn’t resemble to well the predicted sqrt behavior. This is due to so-called excitions, which we’ll kind of discuss in the electron-interaction file.