**Non-equilibrium Properties**

**Absorption by Free electrons in Crystal Potential**

Things change if we put the electrons in the crystal potential. As we saw in that Conservation of Crystal Momentum file, a consequence of the crystal potential is to replace momentum conservation with crystal momentum conservation. So now the electron would have to satisfy,



for some reciprocal lattice vector **G**. And note **p**, **p**´ are crystal momenta now, and restricted to the first BZ. Can represent such solutions graphically. Kindof don’t have any space in my picture, but **p** is the green point, **k** is either the base of the red triangle (photon going right), or the yellow triangle (photon going left), and **p**´ would be the coordinate of the edge of either triangle. In other words, **p**´ = **p** + **k**. Note that **G** = 0 for our processes here, basically because **k** is so small in comparison to **p** that **p**´ will still be in the 1st BZ, unless, conceivably, **p** were *very* close to the edge of the BZ. ω = kc is the height of either triangle.

A diagram of a mathematical equation

Description automatically generated

The width of k in comparison to p was exaggerated for the sake of illustration. In actuality it is muuuuch smaller than p. And so really, the diagram would look like this below, for both forward and backward photons. Basically the photon line is vertical:

Chart, line chart, histogram

Description automatically generated

So in the graphical solution we’re not drawing the k, just the ω, but we can get the k back as it’s just k = ω/c. In any event, the lattice spacing is such that kmax ~ 2π/a ~ 2π/1nm. So whatever k is, it should be less than this, so kphoton < 2π/1nm → λphoton > 1nm. Visible light is ~ 100nm. So the photons we should expect out of this are up ultraviolet or longer wavelengths.

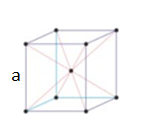
**Absorption in the Alkali metals**

Let’s recall the general band structure of such metals,

Chart, surface chart

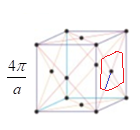
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The green s band accomodates two electrons per unit cell. But there’s only one electron per unit cell for these elements. We saw that the Alkalis typically form a BCC lattice.



And so their reciprocal lattice is FCC (see Electron-Crystal Interaction file) with side length 4π/a.

And further we found that when we draw the Wigner-Seitz cell of the reciprocal lattice,

 A picture containing handcart

Description automatically generated

the smallest radius of the cell (that blue line within the red outline) was:



And the electron filling doesn’t go past this radius, since (see Properties of States),



So kF = 0.88kmin. Since the Fermi surface lies within kmin, it doesn’t overlap any with the 2nd BZ (the first p band). So it will lie entirely with the green (s) band. The smallest frequency at which we get excitation of electrons into an unfilled state would then be the frequency which excites an electron on the Fermi surface to the corresponding k-value in the next band up. This is the 3D analogue of the following 1D construction we made above (eliding possible band gaps),

Chart

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And we can see what this frequency is most easily if we go back to the extended zone scheme.

Chart

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Then we can see that our minimum frequency would be:



(don’t confuse this G for the G that appears in the crystal momentum ‘conservation’ equation – this is not an Umklapp process) Now G, for our FCC recipricoal lattice, would be G = 2kmin (remember the Wigner-Seitz cell boundary consists of all surface that bisect the lines to the nearest neighbor points in the reciprocal lattice, and so G = 2kmin is the reciprocal lattice vector going along the direction of **k**min). So borrowing our results above, we have:



I guess we could’ve also done it this way: just add to kF twice the distance from kF to the BZ boundary plane, find *that* energy, and then subtract off the Fermi energy.



Or since kmin = G/2, could’ve also just done it this way,



Well, in terms of the Fermi energy, this is:



The Fermi energies of some Alkali metals are:

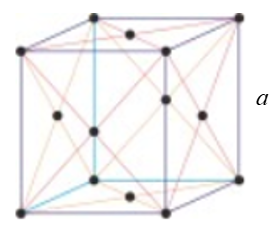
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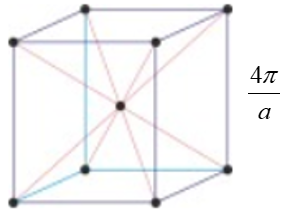
And apparently the measured absorption threshold is around ω = 0.61εF. Note these energies are in the middle of the optical range.

**Example**

Let’s just say that we were able to create an FCC lattice of Li. Assuming a free electron model, just like before, what would be the minimum absorption frequency?



Well, the reciprocal lattice would be BCC, with side length 4π/a.:



The Wigner-Seitz cell would be an octagon looking thing I guess, centered about that middle point. The octagon faces would be half the distance between, say, the atom in the lower left corner, and the atom in the middle. So the closest the BZ boundary would be is:



away from the center. Now we have to compare this to the Fermi momentum. This is:



Therefore, at closest, the Fermi surface is a distance,



away from the edge of the Brillouin zone demarcation plane. The energy directly above this would be:



As a fraction of the Fermi energy, this is:



If we estimate *a* to be 0.4nm, then the Fermi energy would be:



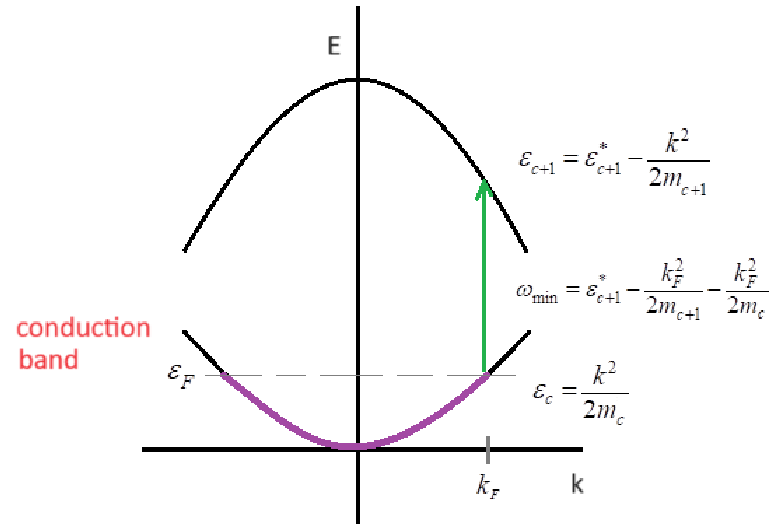
This corresponds to about 217nm light. So in the infrared.

**Absorption in the other metals**

These are more complicated to predict, as their Fermi surfaces are less easily described. The threshold optical absorption frequency in transition metals is frequently given by d electrons jumping into unoccupied parts of the s-band. The frequency is around the orange-ish range, and is what gives gold and copper their color.

**Trying to be more Quantitative**

Okay so let’s try to examine the absorption *spectrum*. We’ll presume a nearly free band spectrum. Something like this::



Great picture I know. And just imagine it’s in 3D. Our Hamiltonian is (see work above apropos not having to anti-commute **A** and **p** because we’re using Coulomb gauge):



Now **A**(**r**,t) = Re**A**e-iωt+i**q**·**r**. In the Coulomb gauge + temporal gauge, we have (see EM notes):



Now let’s consider transitions between different free states, say |**p**> and |**p**´>. According to QM, the rate of this transition for incomming evanescent EM wave is:



where,



And so taking ω > 0, the transition rate would be to first order:



where nF(x) = 1/[eβx + 1] accounts for the thermal occupation of the conduction band [we’ll take the T = 0 special case in a second], and I’m droping the 0 subscript on **E**0. Note we’re allowing different effective masses in the two bands. The sum over all kʹ, k gives the total rate of transition from any conduction state to any conduction+1 state. So this would give the rate of exodus of conducction band 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 I need to put it in a form to compare to one below. So going to do the following,



So now recalling from the EM file, the same,



We can identify the absorptivity as:



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 (of one electron). So we are keeping this combination together for physical reasons. Not sure how to simplify this matrix element. Going to start by writing it as an integral over the unit cell, and a sum over all unit cells,



If k, k´, and q are small, then the exponential factor should be slowly varying, and I think we could approximate it by its value at the lattice point location of the unit cell. I think this is somewhat okay, even if they aren’t small, since crystal momentum conservation must come out of this expression. But whatever the argument is, it’s too subtle for me now. So we’ll just say something like this:



and then we can pull that exponential factor out of the integral. And we’ll also notationally note that the integral over all unit cells is the same, since the u functions are periodic.



And in the last line we note that **k** - **k**´ + **q** must be a reciprocal lattice vector, **G**, in order for the sum to survive. This is our crystal momentum conservation law. Now q will be super small in comparison to k and k´, as we noted previously. So since k is already in the BZ, we expect k´ will be too, and so G = 0. So now we have:



At this point, it’s good to note that if we were dealing with a free particle spectrum, the overlap integral wk would in fact be zero. This is because uk,c+1, ukc would be of form ei**G\_c+1**·**r**, ei**G\_c**·**r** where **G**c+1, **G**c are RLV’s. But **G**c+1 and **G**c would not be the same, and so the uk,c+1 and ukc would be orthogonal. And so the overlap integral would be zero. So just because we reorganized the energy spectrum into bands, and so ostensibly made conservation of energy and momentum possible, we are not saved; we do in fact need a different spectrum, and concomittantly, a different set of unk functions. Anyway, I think for simplicity, we approximate wk as a k-independent constant. So now we have:



When we take the temperature to zero, the nF becomes a step function, requiring,



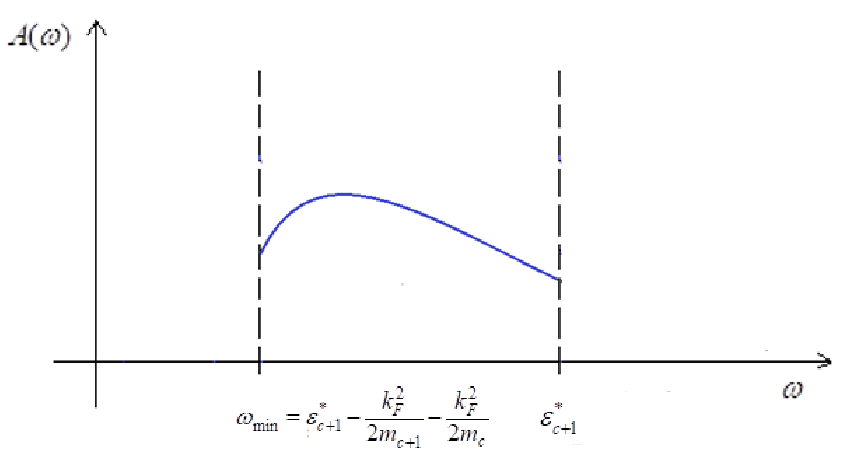
This enforces that ω must be greater than the minimum frequency ωmin,



So altogether, we have:



which looks something like this:



It might seem odd that we have absorption without specifying a mechanism for the energy to be absorbed (like disorder or whatever). But mathematically, we have electrons occupying lower energy levels, and then being bumped up by EM waves into higher energy levels. Technically, this EM wave would then cause the electrons in the higher levels to also transition back down into the lower levels. But in thermal equilibrium, the occupation levels of the lower energy levels are much higher than those of the higher energy levels. And so the rate of transmission to higher levels is much larger than the rate of transmission to lower levels. So we get net absorption of energy. And this is because of the maintainence (somehow) of thermal equilibrium. So complementarily to the prior points, it seems we are kind of assuming that once the electrons get excited, they drop back down to their lower energy level by some mysterious means whereby they dissipate all that energy they acquired into the lattice. There is, notably, no reference to impurity scattering times, or any measure of the strength of any dissipative mechanism. So we are clearly assuming it all just ‘gets absorbed’. Relatedly, recall that in the TDPT Folder/Harmonic Perturbation file, we note that the transition goes as Vni(t-t0) for t – t0 ~ 1/|En – Ei – ω|, which could be quite a long time. So the transition probability could be a *very* slowly oscillating function, certainly much more slowly oscillating than the photon frequency, well, supposing the field strength is not insanely strong.

Another point to make: So evidently, we would find that the EM field is doing work on the electrons at all these frequencies for which we get non-zero A(ω). How are the electrons oscillating? Well while the electron is making the transition, it exists in a superposition state between the valence and conduction bands. So its state looks like c1e-iω\_vt|v> + c2e-iω\_ct|c> = e-iω\_vt[|v> + c2e-i(ω\_c-ω\_v)t|c>]. And so it’s oscillating back and forth between them with a frequency ω = εc – εv, while its making the transition (which can take a relatively long time – the speed of the transition depends on the strength of the field – see QM/Harmonic Perturbation). 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.