**Non-equilibrium Properties**

**Independent Particle Theory of X-ray Absorption**

So above we discussed excited electrons in the conduction band to the next highest available spot. Visible spectra photons are absorbed/given off in this process. Now we’ll look at excited core level electrons being pumped into empty spots in the conduction band. This process usually involves X-ray level photons. We’ll start with the basic description. We have electrons in the core levels (calling it valence bands now) of the atoms (pink), and above, in the valence levels (calling that conduction) band, we have electrons filled up to the Fermi-level. When a photon drops by, it can be absorbed by a valence electron which jumps into the conduction band above the Fermi surface (if photon has high enough energy), creating a hole in the valance. This energy can be absorbed by various processes. An electron can drop back into the hole, delivering the kinetic energy it gains to the lattice in the form of phonons, ultimately converted to heat. Or it can release a giant photon as it drops back. Or it could do a little bit of both, releasing photons to make up some of the energy gained, and releasing the rest as phonons. This is why there is a difference between an absorption spectrum and an emission spectrum.

A diagram of a physics equation

Description automatically generated

EF is obviously the Fermi energy, and Eg is the gap between the conduction band and the valence energy levels. The first attempt at a description of the process was via a simple QM golden rule calculation. 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 (putting in a 1-nF factor to account for Pauli Exclusion principle preventing transitions to occupied levels):



where nF(x) = 1/[eβx + 1], and I’m droping the 0 subscript on **E**0. And there’s a factor of two in front to account for spin degeneracy. 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 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 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 ukc, ukv would be of form ei**G\_c**·**r**, ei**G**\_v·**r** where **G**c,v is a RLV. But **G**c and **G**v would not be the same, and so the ukc and ukv 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:



(the θ function is there because we have no solution to the δ function argument unless the argument of the √ is positive) When we take the temperature to zero, the [1-nF] becomes a step function, requiring,



This inequality makes sense. For instance, if mc = mv, then the threshold energy is Eg + 2EF, which makes sense from the diagram. So we have:



We can get rid of the θ(ω-Eg) guy since the other θ() renders it pointless. And so we have:



Predicted behavior would look something like this:

A graph of a function

Description automatically generated

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 of non-zero A(ω). So the electrons are oscillating. 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. And probably the largest amplitude of oscillation (strongest current, more specifically) is near the E­­min­. 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). Might also check out a similar calculation in the Interacting Electrons/Nearly Free folder. This employs a Green’s Function perspective.

There are several physical mechanisms which can change the shape of the spectrum from the simple one-particle analysis. One is the broadening of the spectrum due to phonons. One interesting fact about this process is that the relaxation time of the phonons is much slower than that of the decaying electrons. It is the phonons that keep the electrons in equilibrium, and so this process wouldn’t quite take place in thermal equilibrium, and one must use non-equilibrium techniques.

Mahan makes a point that the emission spectrum would generally differ from the absorption spectrum. A (phonon-assisted I’m guessing, since it would have to acquire significant momentum to do this, not just energy) electron may be bumped from the top of the valence band to the top of the Fermi sea. And so the threshold for absorption might be in this case ωmin = Eg + EF. But the lowest energy emission process would be an electron at the bottom of the conductance band dropping into a hole at the top of the valence band. And so the threshold for emission would be Eg. In this sense, he says the emission and absorption spectra are kind of complements of each other,

A diagram of a function

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