**Non-equilibrium Properties**

First I’m going to look at absorption (or not) of truly free electrons, just for some context. And then I’ll do it for electrons in a periodic potential. And then last we’ll do it for electrons going from the valence band to the conduction band. This is X-ray absorption, not optical, though the difference doesn’t really matter mathematically.

**Absorption by Free Free electrons (no Crystal Potential)**

So now we’ll look at the absorptive properties of the free electron system, no crystal potential. First we should point out that a free electron cannot absorb radiation. Electrons can be scattered by photons (see Particle Physics/Compton effect file), but they cannot absorb them. To see this we can modify the analysis done in the Compton effect file. What we want to see what, if any, photon with momentum h/λ = ℏk and energy hf incident upon an electron with given initial momentum p can be absorbed. Supposing the photon gets absorbed, our momentum and energy conservation equations will read:



So we are presuming **p** is given, and we’re looking for some **k**, and **p**´ that satisfy the equations. By the way, we can come to same energy/momentum conservation equations via quantum mechanics. I’ll reprise the discussion in Quantum Mechanics/Time-Dependent/RSPT Scattering Perturbation file. So consider an electron being hit by an EM wave. The relevant H would be:



where A(r,t) is the vector potential, and φ(r,t) the scalar potential associated with the EM field. And recall the electric/magnetic field is given by:



There are many options for describing an EM wave. Let’s use the temporal gauge (see EM folder/Free Maxwell Equations TD). This gauge is described by:



So in a source free region, the temporal gauge equations are:



The last equation is the wave equation, and its solution is obviously,



So this is our plane wave. And the associated EM field would be given by:



Note that in order to satisfy the gauge condition (∂/∂t)∇·**A** = 0, we’ll need to make ∇·**A** = 0 itself, which implies **k**·**A**0 = 0. Now let’s expand our Hamiltonian to first order in the perturbation (**A**),



Now note that in the **p**·**A** term, the **p** operator is acting both on **A**, and on any ket that appears to the right of **A**. But since ∇·**A** = 0 means we can slide the **p** past the **A**, combine with the preceding term, and write:



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



Before proceeding, maybe observe that if we considered transitions from p´ → p, we’d get the same result. So this implies we have equal rates of transition from p → p´ and p´ → p. So when p → p´, our electron would be absorbing the wave, and when p´ → p, it would be emitting/reflecting it back (from whence it came!). We’ll say ω is positive and p´ > p, for the sake of discussion. So then,



The matrix element is:



So our scattering rate is:



Important thing is that we have delta functions requiring conservation of energy and momentum. Anyway, back to trying to solve these equations. So we have:



Can dot both sides of momentum equation with itself,



And plug into energy equation, after squaring first,



Using ω = kc, we can make another cancelation,



Now this equation has no solution, as **p**c/√[(pc)2 + (mc2)2] can never have unit magnitude. And so absorption is forbidden. We can also see this graphically. Cause I like to belabor things. Consider a free parabolic spectrum (so we’re doing classical kinetic energy now, not relativistic). And a photon with momentum ℏk, and energy ℏω = ℏkc. This is represented by the triangular thing. Actually three different possible photons are displayed, a yellow, orange, and red. The horizontal side length represents the momentum and the height the energy. Each of the three photons have the same slope, c, though. An electron with momentum p can absorb the photon, and acquire the new momentum p´ = p + ℏk, if when we place the side edge of the thing on the curve at p, the top edge touches the curve as well. This is not happening in the picture below, and in general does not happen ever, except near where the dispersion curve has a slope approaching c. This would happen near where the speed of the electron is c. But we have two problems. First, electrons can’t go that fast. And second, the classical formula for the dispersion curve fails at that speed anyway, and we know from our explicit calculation above, that there never is a point on the relativistic dispersion curve where we get this solution.

Chart, histogram

Description automatically generated

Well, in retrospect, there would technically be a solution at exactly ω = 0. And so our absorption formula would be of form A(ω) ~ δ(ω). And this is consistent with our result looking at absorption in an electron gas with disorder (see Electrons and Impurities). There we find



Using,



we can say,



As we argued. Onward.