**Crystal Excitation Properties**

**Velocity expectation of eigenstates**

So we said that since the energy bands now have curvature, this gives the electrons (or holes) a non-zero average velocity. So we’d next like to calculate the expectation of the velocity of these Bloch electrons. First, the velocity of the electrons is:



and the average velocity would therefore be:



Now suppose we know the energy eigenvalues Eks. Let’s see how we can extract the velocity. Let’s substitute ψ into the Hamiltonian:



And so we can say the Hamiltonian for uks is:



Consider the derivative w/r to k,



So we can say,



And so from the Feynman-Hellman theorem (see Quantum Mechanics/Foundations/General Properties file):



It follows that:



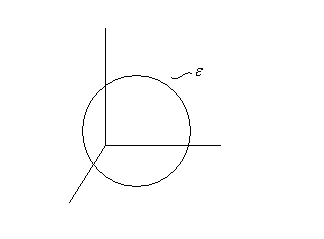
Note how it makes sense that the velocity at the top of the band ought to be zero because the eigenstate there (k = 0) is just the sum over all the individual ψs states. So there is no reason for the particle to favor one spot vs. another and so it ought to just ‘stick around’. And when k = ±π/a, it also sort of makes sense that v = 0, because here the (eikr) phase at neighboring sites is just opposite in sign – basically going from 1 to -1 to 1 to -1. But modulus-wise, the values are the same. And so again, there is basically no difference between sites and so no reason for *transport*. Rather, in the middle of the band, is where we then expect the greatest sight to sight modulus phase difference. So the velocity will be largest in the middle of the bands, and smallest near the band minima/maxima, and edges. Note that when draw the atoms apart again, the bands will flatten, and the velocity expectation will decrease to 0 – meaning localized states.

**Density of States (per unit volume)**

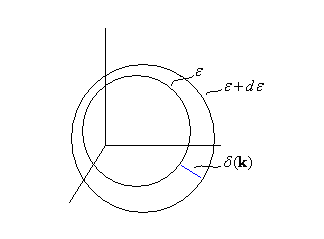
The density of states in a band is:



[2 is for spin degeneracy] εn(k) is a function which assigns an energy to every k-point in the BZ. δ(ε – εn(k)) picks out all the points with an energy ε and so defines a surface in k-space.



And the integral over d3k/4π3 adds up all the points on the surface. We can determine the density of states another way. Add up the number of states between the surfaces (ε, ε + dε), and divide by dε. And so we’ll look at the region in k-space which encompasses this energy range,



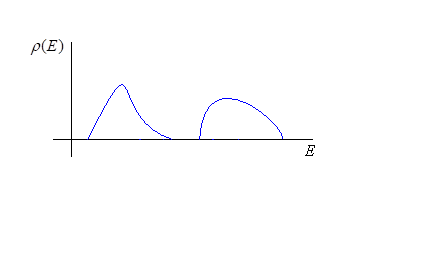
The density of states in there is:



Where we recognize in the second line that we have merely an upside down derivative. And since the velocity of electrons in a band, we have,



The density of states for a typical crystal would look something like below (note that the density of states function above assumed that the energy spectrum was free – forever).



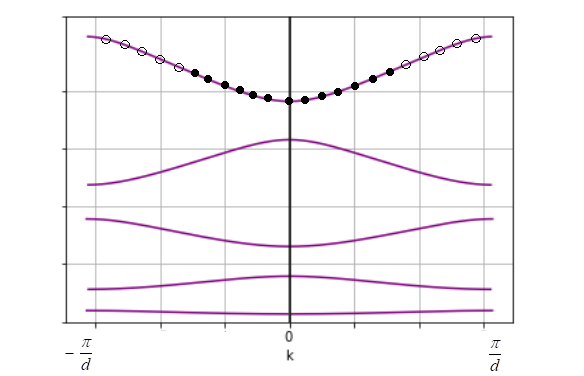
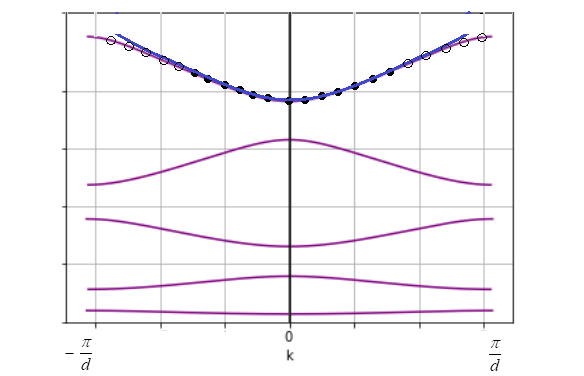
To get the density of states, we would integrate 1/v(k) around a surface (in this case curve) of constant energy, which we’d obtain by looking at the intersection of the z-axis and a constant energy plane z = E. There are gaps in ρ(E) because of the band gaps. Now vn(k) is a periodic function – being just the gradient of a periodic function – and so there are spots where it’s = 0. And so the integrand goes singular sometimes (called Van-Hove singularities), usually in lower dimensions, like we’ll see in 1D, 2D. But in 3D say, support in k-space where the velocity is singular goes to zero faster than v does, and so it doesn’t blow up – rather goes to zero in that case. And since we can pretty much always approximate the band minimums, maximums as quadratic in any dimension, we should expect ρ(E) to behave for real bands like it does for free bands, when near those points.

The density of states (per unit volume) can also be calculated using GF techniques. We’ll recall, it’s just the spectral function. So we can write:



**Approximation of energy levels near band minima/maxima**

So let’s recall our typical band structure. And I’m going to presume we have an unfilled valence band = conduction band. That’s the picture on the left.

Since e- will fill up in order of increasing energy there will be a concentration at band minimums, or a dearth (concentration of holes) at band maximums. We can calculate the properties of the materials by focusing on these particles. And near these minima/maxima we can approximate the energy spectrum with a Taylor series,



where **M** is the mass tensor. This spectrum, out to second order is the fitted parabola in the picture on the right.



Thus we can treat electrons in the band as free electrons, with simply a renormalized mass, (the brand new band mass **M**). The fact that **M** is a tensor (matrix) means that the effective mass is potentially different in each direction. If the Fermi surface is spherically symmetric, then **M** would just be **M** = m\***1**, where **1** is the identity matrix, and m\* the renormalized mass. This accounts for (some of) the renormalization of the coefficients in the heat capacity, etc. The ratio m\*/m is usually O(1), but not equal to. For Cu it’s 1.3, for Iron it’s 8. Well, here’s a table from Aschcroft and Mermin.

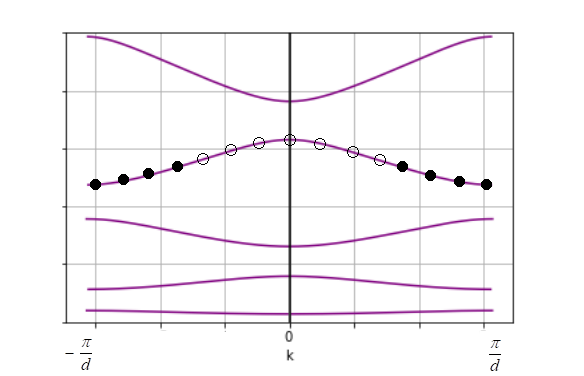
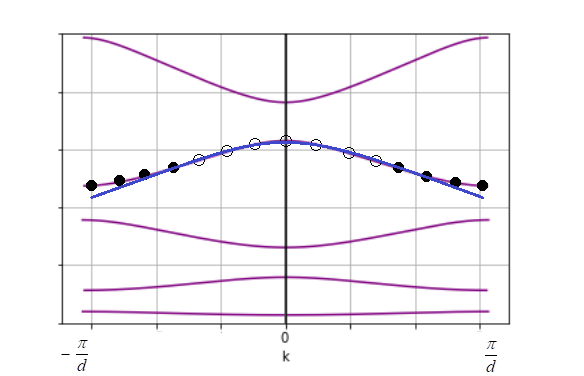
Table

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For future reference, won’t be writing m\* anymore; it will be implicit. And one more thing – we usually neglect the constant ε0. This is okay to do. It’s like changing the reference point where we measure gravitational potential energy from (the floor, the table top, etc.). Still, this could seem to be bad since the energy of a system of N particles will change depending on what we have set ε0 equal to. But this is controlled by the chemical potential, μ. And we always adjust μ to put N particles in our system. So we can change ε0 to whatever we want, as long as we make the corresponding changes to μ to keep N constant. So we can write the energy of the band as:



where nkσ is the occupation number for the k wavevector and spin, and ε(k) is the energy, and the sum goes over all k’s in the band. We could have the following scenario though. The unfilled valence band = conduction band could have a peak at the top. Then the electrons will clustered around the edges, leaving holes at the top.

We could approximate the peak of the band with a parabola. But clearly our parabola wouldn’t constitute a good approximation to the energies of the electrons in the band. But it would be a good approximation to the energies of the holes. And luckily we can reformulate the energy in terms of these holes. So the total energy of the band in any given configuration would be:



where we define nkσ(h) = 1 – nkσ as the hole occupancy. The overall energy constant doesn’t matter, unless we were looking for the overal energy of the crystal or something. So we can write:



We can write the hole occupancy function as:



Now let’s approximate ε(k) near the top. We have,



where in the last term we define the ‘hole’ mass tensor as negative what we did for particles, so as to keep the mass tensor positive (can see our parabola will have negative concavity). Again, we’re going to neglect the constant ε(k0). Now filling this into our formula,



So if we define the hole energy as:



we have:



Notice, nh(ε) now looks like the Fermi distribution function, given εk = -εh. μ has the wrong sign, but really, we could just do μ → -μ, as μ is an arbitrary number equal to whatever we need it to be to have the requisite number of holes in our band. It is a little disconcerting that according to our definitions, it seems our energy will increase as we add more holes. But this is consistent with having set our zero point energy at the top of the band – this makes all of our energy levels negative, and so if we add more particles then we get more *negative* energy. So it makes sense that adding more holes makes the energy more positive (or, closer to zero). Again, it is the chemical potential that will set the number of particles/holes. So moral of the story is we can treat particles and holes the same way. We don’t need separate formalism for the two. But have to treat any given band as being solely comprised of either particles or holes – not both, or we’ll overcount.