**Crystal Excitations**

Now we’ll try the nearly free electron model. This seems to apply pretty well to electrons in the s and small p orbitals. These electrons are generally more loosely bound to the the parent nucleus than those in the d and f subshells.

**Nearly free electron model**

So consider the Hamiltonian of an electron in a typical crystal.



To find the energy levels and eigenstates, we might consider trying perturbation theory, if the potential is weak. So the unperturbed wavefunctions and energies are, for a cubic lattice, say:



And ostensibly we’d plug these into:



So we need <k|Vcrystal|k´>. An important point to observe is that since the potential is periodic over the primitive cell, we can write it as, using the standard finite Fourier transform:



where Vcell = *a*3, and **G**’s are reciprocal lattice vectors. I’m going to rewrite this pair, however, as:



so that it aligns with the discussion below a little better. Anyway, given this, it will not couple all ψk(0) = exp(ikr)’s to each other, since,



where V is entire lattice volume. So this integral is non-zero only if **k**’ – **k** + **G** is 0, which is to say, only if **k**´ - **k** is an element of the recripocal lattice, then ei(**k**´-**k** + **G**)·**r** is periodic over the breadth of the cell, and we can write:



So altogether, the potential only connects the same state or states differing by a reciprocal lattice vector together, and we can say:



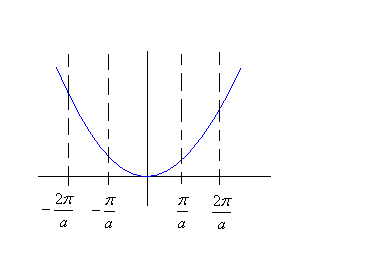
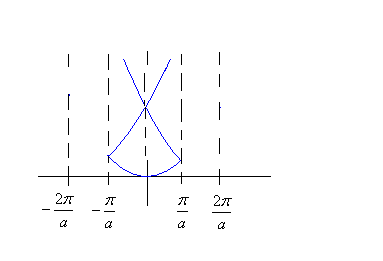
And so now we might forge ahead and apply PT. Problem is, the perturbation (i.e., typical matrix element here) must be smaller than the free particle energy spacings, i.e., we need Vk-k´ < ε(0)k – ε(0)k´, in order for us to reasonably expect the perturbative series is converging. But the periodic k’s of the free particle problem are given by 2πn/L, say. And so the energy spacing is proportional to 1/L2, which becomes super small in the large L limit. And this makes perturbation theory suspect. It would be more appropriate to apply degenerate perturbation theory to all of states whose unperturbed states’ energies are within the typical value of Vcrystal. But I’m not going to do that either. The easiest thing to do is to apply degenerate perturbation theory to the states which are *exactly* degenerate. Note the wavevectors **k** and **k**´ which differ by a reciprocal lattice vector, and also have the same energy k2/2m = k´2/2m are those that satisfy the von Laue scattering condition we discussed in the Crystal Interaction file. So we can say that the **k** states which are connected to others of the same energy via the crystal potential are those that satisfy:



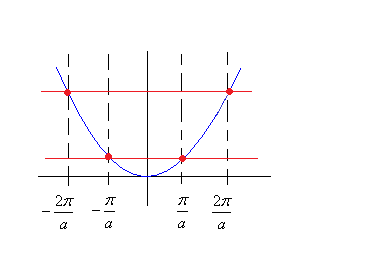
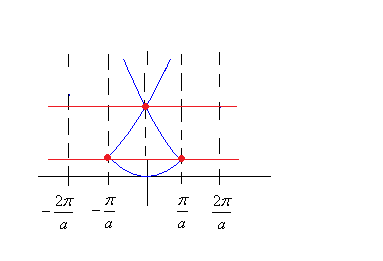
which is to say they lie on a Bragg plane (those planes that bisect the lines drawn to nearest neighbors, next-nearest neighbors, etc.). Thus they will be on the BZ boundaries.

**Specialize to 1D**

Let’s look at this in 1D. The unperturbed spectrum looks like,

The plot to left is called the extended zone scheme. The one to right is the reduced scheme, restricting k to the first BZ, and displacing the part of the spectrum outside that range by a reciprocal lattice vector 2πn/a sufficient to put it within the first BZ (-π/a, π/a). And now we would need to diagonalize Vcr in the degenerate subspaces. The only wavevectors that are degenerate *and* are actually connected to each other via Vcr (see formula above) are the ones at the BZ edges defined by k = nπ/a, because these wavevectors are a RLV, **G**, apart. These are illustrated below (the red dots):

For instance the bottom two degenerate energies are a distance (in k-space) **G** = 2π/a apart, and the top two degenerate energies are a distance **G** = 2(2π/a) apart. So let’s consider two such vectors, **k** and **k**´ = **k** - **G**, and let’s diagonalize Vcr in that subspace. Generically, Vcrystal will look something like this:



And then finding the eigenvalues, we have:



Being a little more careful about affairs would show that the minus sign is what the lower energies approach, and positive sign is what the upper energies approach as k closes in on the BZ value. Well, then, let’s be a little more careful. Another way to get energy levels is to use the Variational Principle. Let’s consider the |k> and |k´=k-G> states again. This time we’ll relax the assumption that k is *exactly* on a Bragg plane, and equivalently that k and k´ = k-G are *exactly* degenerate. Let’s allow k to be in a tiny neighborhood of a Bragg plane. Then |k´=k-G> will be in a tiny neighborhood of its own Bragg plane as well. Now|k> and |k´=k-G> won’t be exactly degenerate, but they will be close to degenerate and they will still be connected by the perturbation Vcr since they are a reciprocal lattice vector apart. And so since <k|Vcrystal|k-G> is non-zero and εk-εk´ is small, <k|Vcrystal|k-G>/(εk – εk-G) will be very large. And so perturbation theory says that these two states will be very strongly connected to each other, and less so to other states (because either their Vcr mediated overlap will be zero, or because the energy denominator will be much larger). So let’s just diagonalize the Hamiltonian in this subspace. Since these states are orthogonal, this is equivalent to using the Variational principle to determine the linear combinations of |k>, |k´=k-G> which best resembles an eigenfunction, i.e., has lowest energy expectation. So let |ψ> = c1|k> + c2|k´=k-G>, and:



Then we need to solve,



where εk = k2/2m. Eigenvalues are:



where k´ = k-G. So we have:



Now we need to figure out if E± is associated with εk or εk´. Well when V→ 0,



If k is within the 1st BZ, and approaching the right BZ boundary from the left, then k´ = k-G is going to be just to the left of the left BZ boundary. So k´ will be negative, and a little larger in magnitude than k. So E+ is associated with εk´, and E- with εk.



And as k approaches the right BZ boundary, and consequently k´ approaches the left BZ boundary, we see:



This verifies that there is a gap in the spectrum at the BZ boundary, and that they don’t instead cross each other, which is what we couldn’t quite demonstrate before.



Now let’s show that the derivative of the spectrum is zero at the zone boundary. So let’s fill in k´ = k-G (and just presuming in 1D)



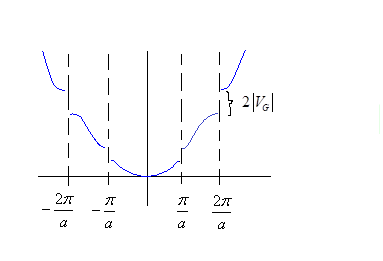
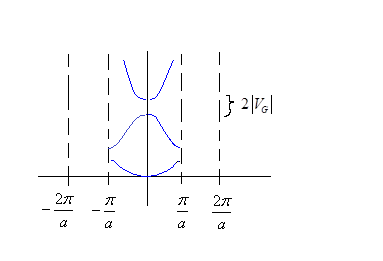
and,



Well as k goes to the BZ boundary, i.e., the Bragg plane, it will approach the value G/2, so,



So there. So now we can say the spectrum will look like, in the two schemes.

Kind of want to mention that the gaps come about because the free spectrum curves away from its given trajectory, and towards the Bragg plane, at the BZ boundaries, not per se´ because the free spectrum gets split at the zone boundaries and shifted up or down. Thus we’d expect, at least in the nearly free regime, the true spectrum to overlay with the free spectrum at all points not close to the zone boundaries (excepting the presence of the uniform V0 term I guess). The picture above doesn’t really do this fact justice. So, recalling how we wrote the free particle spectrum in band format in the Bloch file,



I’ll just emphasize again that this formula would hold still, for k far away from the BZ boundaries (well, except for the V0 term again). It would only fail close to the boundaries, where it would kind of peel away and touch the BZ boundary with zero slope.

Note band gaps are typically ~ eV. Conduction e-‘s can roam over all over the sample as you can see, since the orbitals they occupy overlap with other atoms’ orbitals. Thus, effectively, their wavefunctions extend over the entire sample. It is important to note, however, that the e-‘s are technically in bound states. The potential that these e-‘s feel is periodic (mainly) and therefore, there will be a band structure. The outer most e-‘s will occupy the bottom of a band, or top of one, and thus a free like spectrum (expanding the potential minimum in a Taylor series) is had. Thus we can usually treat these conduction e-‘s as free with a renormalized mass, m\*. That is usually all we have to be concerned about insofar as the band is concerned. The low energy excitations of the system would just be particle-hole excitations of the conduction band electrons. And this will resemble a free system with renormalized mass.

**Example**

Consider a one-dimensional crystal with a periodic potential given by:



where V0 is the potential amplitude, and a is the lattice constant. Use the nearly free electron model to calcualte the energy gap, ΔE, at the Brillouin zone boundary. Given the electron effective mass *m*\* and the lattice constant *a*, which of the following expressions correctly describes the energy gap ΔE at the first Brillouin zone boundary?

So we have, to first order:



And since,



we have,

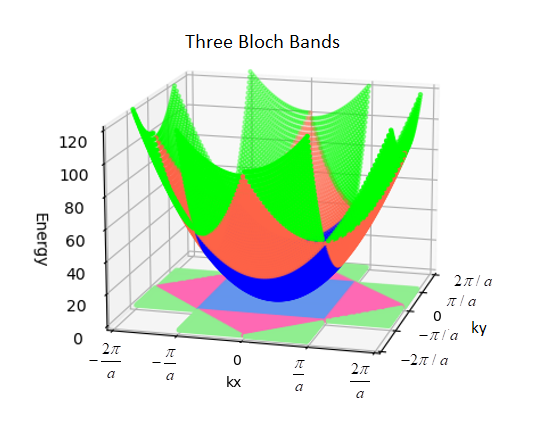


So

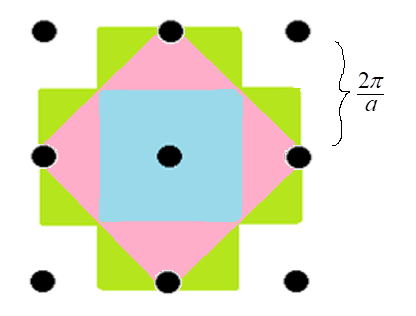


**Specialize to 2D**

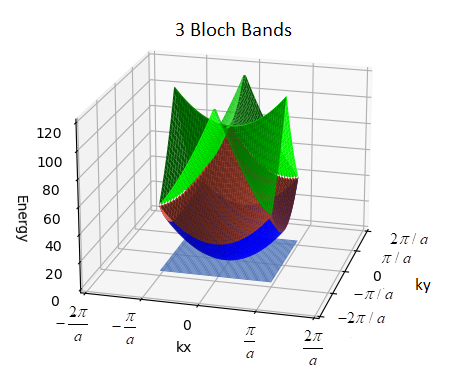
What if we generalize to a 2D system? Then our free spectrum will look like below, as we saw in the Bloch file,



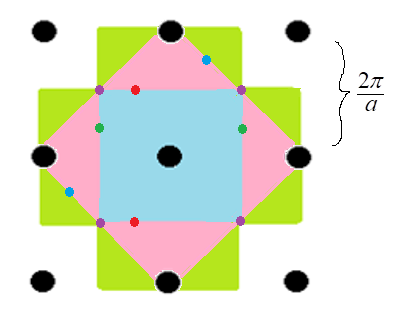
And the first three BZ’s are depicted below.



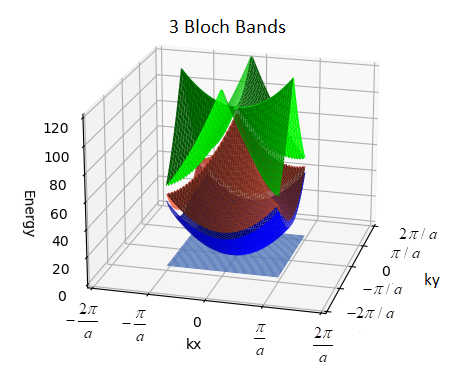
To get the reduced zone scheme for the free spectrum, we’d translate the parts of the free spectrum in the outer BZ’s by the requisite reciprocal lattice vector to get them back into the 1st BZ (blue). So for instance we’d take the part of the spectrum in the 2nd BZ (pink region) and displace the top, left, bottom, right regions by (-2π/a), (2π/a), (2π/a), and (-2π/a). This is something like (I tried to keep the color scheme similar):



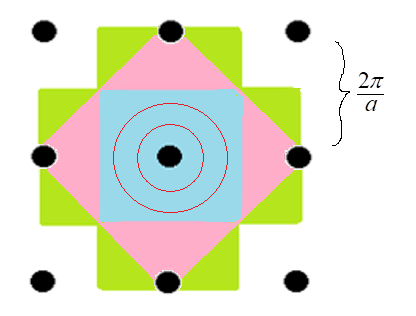
as we also saw in that file. And then as we argued above, the wavevectors on the BZ boundary are degenerate and connected by the crystal potential. For instance, the two red dots are connected, and the two blue ones, and two green ones are too. And the four purple ones (at points where Bragg planes meet we get more degeneracy than elsewhere, as can see, and so we’d have to modify our analysis above and diagonalize a 4×4 matrix)



So by the same degenerate perturbation theory arguments, we’d expect a gap to open up in the spectrum, and get something like this below, actually pretty terrible picture, ‘cause I’m not going to try to get the rounding of the spectrum near the Bragg planes right, and instead, I *did* just shift the free spectrum curves upward, like I said *not* to do above)



There’s a heuristic for drawing the constant energy surface in the nearly free electron approximation. The energy spectrum is very nearly ε = εk except near the Bragg planes. So for small ε, we have something like this:



If our energy is larger, then the free spectrum might cross some Bragg planes. At the Bragg planes is where our perturbative analysis above comes into effect. We know the contour will be deformed to be perpendicular to the plane, but overall area/volume within the contour must be preserved (must it? doesn’t seem like it? well, to preserve the number of electron states encompassed?), with the volume extending into the 2nd zone decreased, and the amount filling the 1st zone increased (this will be in proportion to the strength of the potential, or equivalently, the size of the band gap). So it will look something like this in the extended zone scheme. If we want the reduced zone scheme, then we’d just displace parts of the contour within the 2nd BZ by the requisite RLV to put them in the 1st BZ, just as discussed before. When viewing the illustration, try to keep the above extended and reduced zone energy band picture in mind. If we intersect those plots with our constant energy surface, then we should get the curves we’ve been talking about, traced out below.

A diagram of a square with black dots

Description automatically generated

If we have even larger energy, then we might get something like this below. Again, we just deform the contour to make it perpendicular to any Bragg planes it crosses, keeping area/volume constant (yeah?), but decreasing volume in the higher BZ and increasing it in the lower BZ, in ratio proportional to the band gap between those zones (because the greater the band gap, the fewer electrons will extend into the higher zones, and the more will fit into the lower zone). So something like this perhaps. It’s worth noting that if the band gap between the 3rd and 4th zones is large enough, it could be that all the electrons in the 4th zone would drop back into the 3rd zone. Again, try to keep the energy band pictures in mind when viewing the contours below. These contours are precisely what you’d get by plotting the intersection of the constant energy plane with the energy bands, in either the extended zone, and reduced zone schemes respectively.

A colorful square with black dots and a black circle

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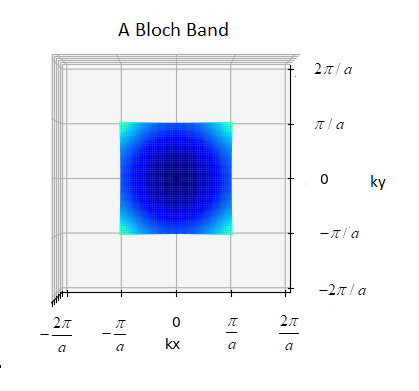
To try to illustrate the energy contours on the energy band graph I made a color map, and then next to it, tried to trace out, in light blue and black, the two reduced zone scheme energy contours above onto the energy band graph. Note that the energy contour above goes into the 4th BZ, and results in those little quarter circles at the corners, but since I only drew three energy bands below, that part of the contour won’t be present in the energy band picture.

A colorful graph on a grid

Description automatically generated with medium confidence A colorful graph of a flower

Description automatically generated with medium confidence

You can sort of see the resemblance. But it is at least clear that a constant energy surface can intersect more than one band, i.e., extend into multiple BZ’s. And you can kind of make out, from a top down view of the first energy band, below, that constant energy surfaces intersect the Bragg planes perpendicularly.



Just going to emphasize again. Recall that we ‘found’ in the Bloch file that the energy spectrum for free particles could be written as:



where **n** is some integer vector **n** = n1+ n2, and the n1,2corresponding to the nth band are the n1,2which give the nth smallest value of εnk for that particular k. Well, except for the constant homogeneous V0 term, this formula will hold still, for the nearly free model. It only breaks down near Bragg planes, where the band gap develops.

**Important Point!**

Last comment. Note that we’ve said nothing about the number of atoms in the unit cell here. So our band structure results are independent of whether we have a basis or not. The only requirement is that the potential is weak, and this potential can represent an atomic Hamiltonian or a molecular Hamiltonian just as well. So if we have a basis of two atoms, say, each with three electrons in the conduction band, then we’d now have six electrons per unit cell in the conduction band.