**Crystal Excitation Properties**

Just gonna make a few general comments on band structure calculations, and Fermi surfaces.

Table

Description automatically generated

and the crystal structure chart,

A table of the elements

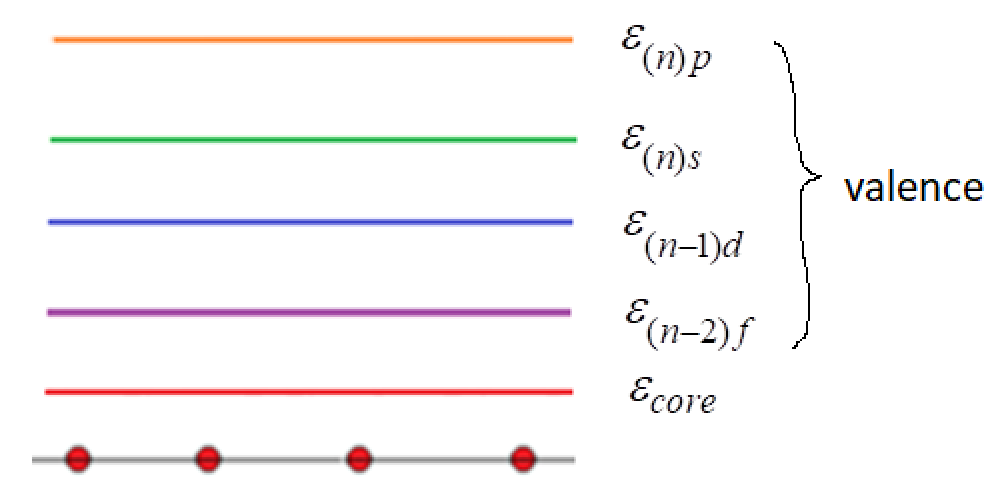
Description automatically generated

A good way to think about band structure is this. Consider the crystal, and all of its unit cells. We’ll pretend for now that there is just one atom per cell. If these cells are far apart, then the atoms don’t interact very strongly with each other, and so the energy levels of the cells are just the energy levels of the individual atoms. The energy levels of the individual atoms would roughly follow Hund’s rules. Remember quantum number n = shell, ℓ = subshell, mℓ = orbital. Recall that according to the Aufbau principle, we can more (or less) fill an atom’s subshells (nℓ) by the periodic table, increasing down and to the right. The energy levels of the shells goes *roughly* like this I think.

A screenshot of a computer

Description automatically generated

We’ll note that this seems to contradict the Aufbau principle, in that according to the above energy diagram, we should get filling in the order 3d, 4s, and 4d, 5s, and 4f, 5d, 6s, etc. Whereas, according to the periodic table and Aufbau principle, we seem to get rather 4s, 3d, and 5s, 4f, 3d, and 6s, 4f, 5d. Well I think the Aufbau principle gives us the correct fillings, but not the correct order in which the electrons are filled/energy level orderings *per* individual aom. I think when you ionize a given atom, the first electron to go is the n\_s, followed by the n-1\_d (if present), followed by the n-2\_f (if present). *If present* is an important caveat, because the referenced electron is often *not* present. And in truth, it seems the n\_s, n-1\_d, n-2\_f levels are all very close in energy, and in fact, overlap somewhat. In general, as applicable, we can *very roughly* represent the valence electron shells like this.



I’m defining the valence electrons as the ones in the last row of the elements electronic structure. So for instance, Carbon’s structure is [C] = 1s22s22p2 = [He]2s22p2. The electrons referred to by [He] would be the core electrons, while the 2s22p2 electrons would be the valence electrons.

It’s important to remember that general ‘s’ subshells have the highest orbital radius, followed pretty closely by the ‘p’s. But then ‘d’s are held fairly close to the parent nucleus, and ‘f’s even closer (see Quantum Mechanics/Time-Independent/Hydrogen atom). So since the ‘s’ and ‘p’ electrons sit relatively far from the nucleus, they are usually described fairly well by the nearly free electron model. ‘s’ more than the ‘p’. Conversely, the ‘d’s and ‘f’s tend to be described by the tight-binding model. Now it seems natural to depict the ‘s’ electrons as having lower energy than the ‘p’ electrons as they are filled in before the ‘p’ ones, according to the electronic structure patterns above. But then might seem odd that the ‘d’ electrons (of previous shell) are depicted as lower than ‘s’ since we typically begin and end filling the ‘s’ electrons before we start on the ‘d’ electrons. Well turns out the energy levels are kind of comparable, as evinced by fact that sometimes an ‘s’ will pop into the ‘d’ level (see Noble metals where s2 electron jumps into d-level to make it d10). But this gets into a problem of trying to shoehorn interacting electrons into single body states. In fact the energy of the ‘d’ states depends on the filling already present in the d subshell I think. So in fact we have to say that once we have written the electronic configuration down, then whatever ‘d’ states are filled in, these same states happen to be lower in energy than the ‘s’ states ex post facto. And whatever ‘d’ states are yet to be filled are actually higher in energy than any of those ‘s’ states. And so ‘naturally’ only *that* many d-states got filled. In effect, we filled the d-states first and the s-states second. The problem gets worse with the ‘f’ electrons. Again we often fill the ‘s’ states before the ‘f’ states. Now the ‘f’ states that do get filled are indeed of unequivocally lower energy than the ‘s’ states preceding. But the ‘f’ electrons are *highly* interacting, and so again it becomes difficult to shoehorn them into independent particle states. But we would say, ex post facto, that whatever ‘f’ states got filled in, these were in fact of lower energy than those ‘s’ states. And the ‘f’ states that didn’t get filled in were higher in energy than those ‘s’ states, and that’s why those ‘s’ states didn’t just drop into the unfilled ‘f’ states. So for instance consider Neodymium. It’s structure is: [Nd] = [Xe]6s24f4 (yeah I thought there’d be a 5d1 but I guess not – that’s why you look this shit up). And we could say that the four 4f electrons are actually at a lower energy than the two 6s electrons, and that the ten empty 4f states remaining are actually at a higher energy than the two 6s electrons. So whichever f’s are filled in, we say they’re lower than the s-d’s, and whichever aren’t filled in, we say they’re higher than the s-d’s. Ordering the energies this way also conforms to the order in which electrons leave the atom when the atom is repeatedly ionized.

Might also seem odd that the, say, ‘4f’ electrons can have energy even at all comparable to ‘6s’ and ‘6p’ electrons, since the ‘4f’ electrons are typically held closer to the nucleus than the more freely roaming ‘s’ and ‘p’ electrons. But have to remember even though the ‘4f’ electrons are held closer to the nucleus, and so would consequently have greater negative energy, being held so tightly, they experience greater e-e repulsion with other ‘4f’ electrons, which makes up for their closer proximity to nucleus. Also, remember that the εs guy comprises one band, the εp comprises 3 bands, εd comprises 5 bands, and εf comprises 7 bands, thanks to the 2ℓ+1 orbitals within each subshell. Of course all of these bands would be degenerate so far.

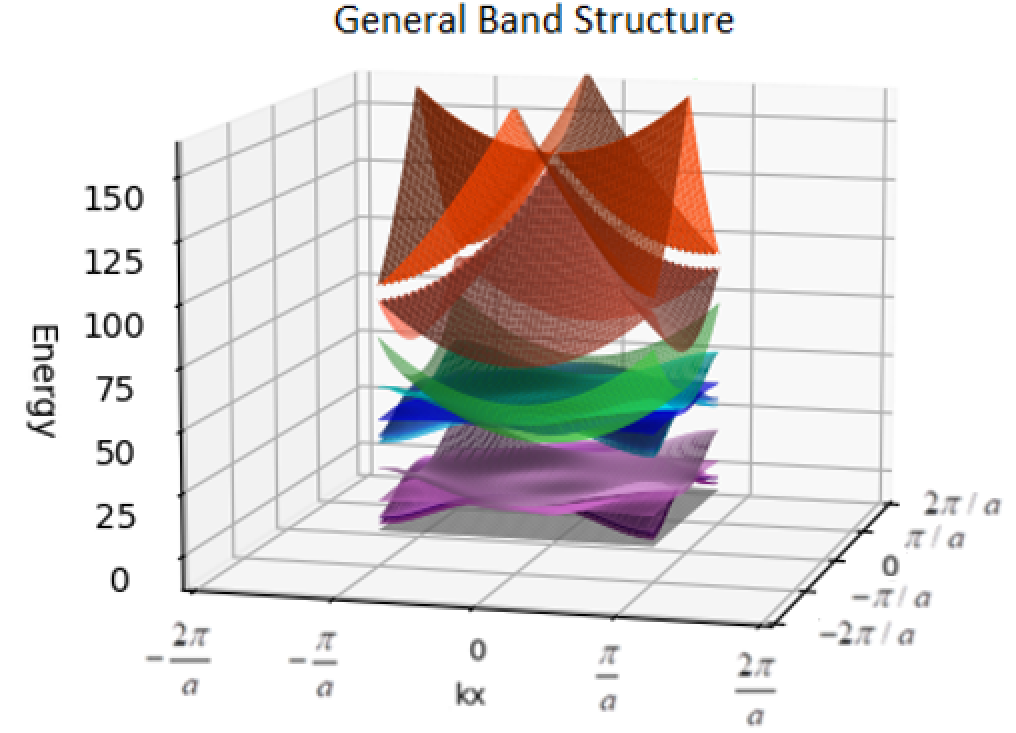
Things change a little bit when we bring these atoms closer together. For metals, the periodic crystal field seems to play a fairly large role, and modifies Hund’s rules somewhat, basically by imparting curvature to the bands. And we often get something like this (maybe I exaggerated how much the ε(n)p guy bends):

Diagram

Description automatically generated with low confidence

This is just a general outline; probably the bands’ prior 2ℓ+1 orbital degeneracy will be lifted somewhat, and so we’d get three mostly distinct ‘p’ bands, five ‘d’ bands and seven ‘f’ bands.

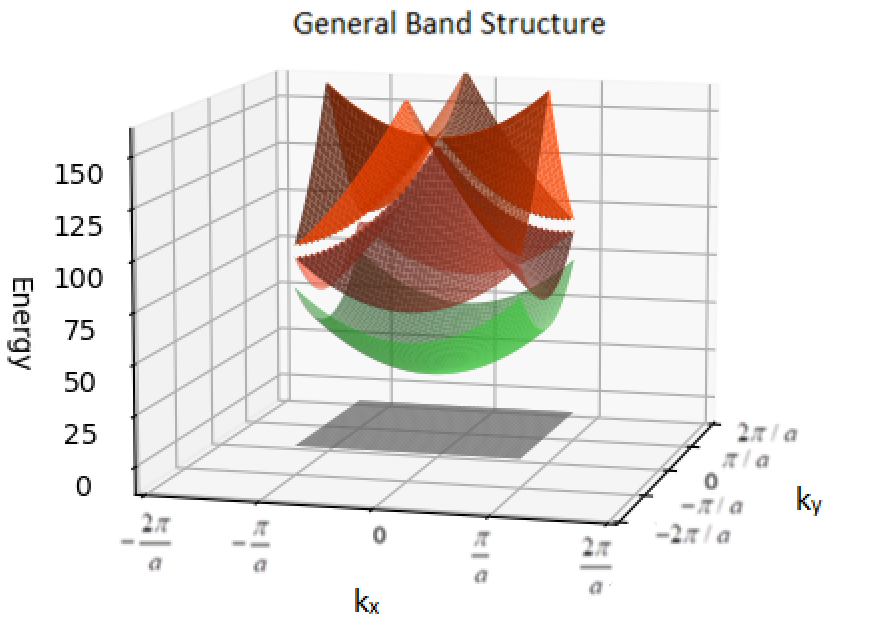
As can see, the ‘s’ and ‘p’ subshells bend quite a bit because they highly overlap spatially (s more than p). And so often the bottom and top of the ‘s’, ‘p’ bands enclose the ‘d’ bands within them. The ‘d’ guys overlap less and so their curvature is less dramatic. The ‘f’ bands curve even less, and seem to be buried below the other bands. The band picture above is an attempt to convey the idea in 1D; below is an attempt in 2D (core levels not shown). There are seven ‘f’ bands shown, five ‘d’ bands, one ‘s’ band, and well, just two ‘p’ bands I guess. There would be another one, but it’s too complicated to show the next one.



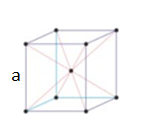
Now keep in mind, my picture for the ‘s’ and ‘p’ bands above were just taken from the nearly free electron model. Since the ‘s’ and ‘p’ electrons are nearly free, typically, I’m just putting the ‘s’ bands and ‘p’ bands in 1-1 correspondance with the first four nearly free electron model bands. But there are of course still higher bands. So it’s not like the bands just stop after the one ‘s’ and three ‘p’s. So if we have a multi-atom basis, giving us a total number of electrons in the unit cell greater than eight, we would just keep filling these extra electrons into higher and higher nearly-free electron bands. Guess I’ll do a quick rundown of the band structure and Fermi surfaces of different classes of metals.

**Alkali metals**

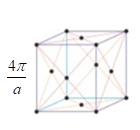
The Alkali metals (Group 1) form a noble gas configuration with an extra electron in the next shell. For instance, Potassium’s electron configuration is [Ar]4s1. This extra electron lies far from the parent nucleus and is heavily shielded from it by the other electrons. This makes the nearly-free electron approximation pretty good for describing this band (one indication of such is that the effective electron mass for such electrons, as can determine from measurements of the specific heat, is very nearly the electron’s actual mass). So the electrons will sit in a band that looks like the green paraboloid. There are no valence d or f bands.



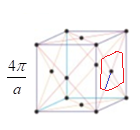
This s band accomodates two electrons per unit cell. But there’s only one electron per unit cell for these elements. Still, whether these electrons will all lie entirely within the green band depends on whether there is any overlap with the p bands (red-orange guys) where these electrons are in the band. So let’s investigate. The Alkalis typically form a BCC lattice.



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



If we draw the Wigner-Seitz cell of the reciprocal lattice (only tried to draw it in that single plane; more 3D picture to right), we get:

 A picture containing handcart

Description automatically generated

And we can see the smallest radius of the cell (that blue line within the red outline) is:



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. Further, since it is fairly far from the edge, it should be pretty spherical. Here’s a picture of the Lithium’s Fermi surface I found on the interwebs.

Shape

Description automatically generated

**Alkaline metals**

The Alkaline metals (Group 2) have a valence configuration [NobleGas]ns2. These typically form all kinds of lattices, including hcp, fcc, bcc. Now we have two electrons per unit cell. And these will sit in the s-band, or spill over into p-bands, if the band gap isn’t too large. And again, these electrons are indeed ‘nearly free’ as indicated by their effective mass from specific heat measurements.

Chart, surface chart

Description automatically generated

Following the calculation above, relevant to the BCC crystal lattice, we can ascertain that kF = 1.11kmin. This means that in the free electron model, some electrons would definitely leak into the 2nd BZ (first p band). We can’t conclude this would necessarily happen here. It depends on the band gap. If the band gap were very large, then in fact the electrons would all lie within, and completely fill up, the 1st BZ (s band). There is of course a band gap, but it isn’t so large that some electrons can’t leak into the 2nd BZ. So we end up with a mostly occupied 1st BZ, a little bit occupied 2nd BZ. This analysis turns out to hold not only for BCC, but also the FCC, and HCP lattices.

**Transition metals**

The Transition metals comprise Group 4-12. But Groups 4-10 have different character than Groups 11, 12. So let’s start with the former. These have a valence configuration [NobleGas]ns2(n-1)dx<9(n-2)f14 (f sub-shell may not be present, but if it is, then it’s completely filled). And they typically form either fcc, bcc, or hcp lattices. Since we have a valence d band, we have a band structure that looks like the green and blue guys below. Well, we’d also have the purple f bands if present, but again, these are always filled.

Chart, surface chart

Description automatically generated

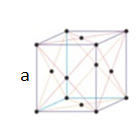
We have 2 + x valence electrons per unit cell. And the s-band + d-bands can accommodate 12 electrons per unit cell. So all the valence electrons lie somewhere within these d-bands and s-band. And the Fermi surface is therefore within this region, and looks pretty complicated. One notable feature of the Fermi surface is much higher density of states than we find in the Alkali or Alkaline metals, which manifests as a much larger heat capacity than other metals.

The Group 11 metals are called the Noble Metals. These include Cu, Ag, Au. These steal an s electron to complete their d-band. So they have the configuration [Noble Gas]ns1(n-1)d10(n-2)f14. Their d-bands lie fairly low within the s-band too. And so the Fermi surface lies above the d-bands, and within the s-band. Consider this illustration from Aschcroft/Mermin:

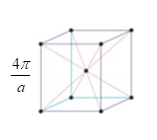
Diagram

Description automatically generated

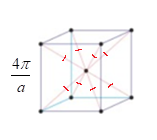
Group 11 metals have an FCC structure.



which makes its reciprocal lattice BCC (see Electron-Crystal Interaction file) with side length 4π/a.



The Wigner-Seitz cell is not something I’m going to try to draw, but the intersections of it with those lines to the nearest neighbors is displayed in red. Well it looks like that structure on the right.

 Chart, radar chart

Description automatically generated

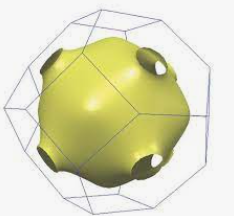
So the shortest distance to the edge of the cell is:



And the electron filling doesn’t go past this radius, since,



So kF = 0.90kmin. So again kF < kmin and we’d expect a fairly spherical surface. But kF is closer to k­min for Copper than for Lithium say. And so I’d expect that the distortions you get near the Bragg planes delineating the 1st and 2nd BZ would start to show. This is a picture of Copper’s Fermi surface.



Parenthetically, I wonder if the Noble metals have such good conductivity because the plethora of d-band electrons is good at screening the lone.

The Group 12 metals include Zn, Cd, Hg. These also have full d bands, with an electronic configuration [Noble Gas]ns2(n-1)d10(n-2)f14 (assuming valence f-bands are present). The band structure is like the Noble metals, with the d-bands lying in the lower part of the s-band. So we can kind of think of Group 12’s as Group 2’s with full d-bands. As with the Group 2’s, I think we get some leakage of the 2 s-band electrons/unit cell into the p-band, because the band gap is not super large.

**Rare Earth metals**

The Lanthanide metals comprise Group 3. These have a valence configuration [NobleGas]ns2(n-1)d1(n-2)fx. And they mostly form hcp lattices. Since we have a valence d and f band, we have a band structure that looks like the green, blue, and purple guys below.

Chart, surface chart

Description automatically generated

The f-band valence electrons lie in the purple band region, which is pretty flat, and so doesn’t contribute to electron mobility, but does contribute to their magnetic properties.

**Other metals**

These are found in groups 13-16. And they have ns2(n-1)d10(n-2)f14npx, electron configuration (if d, f bands present). The d and f bands don’t matter though, being filled, and we can treat s and p electons as nearly free. So basically just the green and orange bands are relevant.

Chart, surface chart

Description automatically generated

Al has a FCC structure, and three valence electrons in the [Ne]3s23p1 configuration. In the free electron model, the Fermi surface would extend into the 4th BZ. As it turns out, band gaps raise the 4th BZ beyond the reach of the three electrons. The 1st BZ will be fully occupied (taking up both ns2 electrons). And so the remaining np1 electron is split between the 2nd and 3rd BZ.

Pb also has an FCC structure, and four valence electrons in the [Xe]6s25d104f146p2 configuration. Its valence electrons also occupy the 2nd and 3rd BZ’s.

Graphite is an hcp crystal of C atoms with 4 atoms per basis (stole picture below). The primitive hcp cell is delineated in black. And we can make out the four atoms/basis feature. The blue atom is the only one entirely within the cell. The two greens are on the surface and contribute one net atom. The four purple atoms also contribute one net atom. And finally, the eight reds also contribute one net atom to the cell. So that’s a total of four. We can see the Electronic structure of carbon is [He]2s22p2. And so I guess 4 valence electrons per atom too. So that’s 16 valence electrons per unit cell. Looks like the band gaps are such there is very little band overlap. So all bands are full, except the penultimate (the 8th I guess), which is nearly full. And the last (the 9th) is correspondingly nearly empty. The associated carrier density of graphite is pretty small ~ 1017e/m3, rather than typical metals ~ 1022e/m3. So conductivity is super small, and it is called a semimetal.

A diagram of a cube with lines and dots

Description automatically generated

Bismuth has electronic structure [Xe]6s25d104f146p3. It forms a rhombohedral crystal structure. The rhombohedral unit cell is delineated below. It has two atoms/unit cell. The blue atom is entirely within the cell, and the eight red atoms contribute a net one atom to the unit cell. So given this and the electron configuration, there are 6 electrons per unit cell. Again there is very little band overlap, but just enough so that the penultimate (3rd) occupied band is nearly full and the last (4th) occupied band nearly empty. It too is considered a semimetal, as its carrier density is on the order of graphite’s.

A diagram of a cube with lines and points

Description automatically generated

So there.

**Non-Metals**

So why are non-metals non-metals? I don’t know. They definitely have filled bands. And that necessitates an even number of electrons per unit cell (though as we have seen, having an even number of electrons per unit cell is not *sufficient* to make an element a metal – see Alkaline metals – because of possible band overlap). But there are clearly non-metals in the periodic table, on the far uppper right, that have an odd number of valence electrons themselves. I’m guessing these tend to form crystal structures with a basis, like Graphite did, with an even number of atoms. This would automatically make them have an even number of electrons per unit cell. Also, I’m guessing the bands these electrons would fill into would be the higher bands in the nearly free model. Apparently there is little overlap (so largish band gap), and so that makes them pretty insulating. Well, actually, as the bands get higher, the overlap should increase, as the band gap should get smaller…can sort of see this from the nearly free electron file drawing of the BZ’s, and also the fact that higher energy levels should get more closely spaced to converge to classical limit. So hmmmm….

**What happens if we have a basis?**

So as alluded to above, everything works same if our lattice has a basis comprising two or more atoms. So there is just a single set of wavefunctions/bands, no matter how many atoms are in the basis, that all the electrons in the basis go into. As applicable, we may put this set of wavefunctions/bands in one-to-one correspondance with the nearly free model wavefunctions and bands. Or we could put it in one-to-one correspondance with tight binding bands. As we discussed in the tight binding file, we could use the Variational Principle to get some kind of approximation to these states. For instance, if we had two atoms in the basis, and their eigenstates, irrespective of all other atoms, were |nℓmℓ>1 and |nℓmℓ>2 respectively, then maybe to first order we could approximate the combined Hamiltonian’s states as |nℓmℓλ> = |nℓmℓ>1 + λ|nℓmℓ>2, where λ = ± denotes the symmetric and antisymmetric combinations. Or we could do a combination – using the tight binding model for ‘d’ and ‘f’ electrons of the atoms, and the nearly free model for the ‘s’ and ‘p’ electrons. Either way, we just get some new set of states |jν>. And the rest would follow as usual, just using the molecular Hamiltonian to define the states, rather than just an atomic Hamiltonian.