**Survey of types of materials**

So here’s the periodic table.

Table

Description automatically generated

And here’s a table of the phases of the elements at standard temperature and pressure, as well as the crystal lattice the solids arrange themselves into. This doesn’t address the basis of the crystal lattice, so it can be that more than a single atom comprises the basis.

A table of the elements

Description automatically generated

The elements will prefer to congretate themselves into configurations: solids, liquids, and gases. And apropos solids, into metals, semiconductors, and insulators. Would like to at least give lip service to this taxonomy. First let’s discuss the periodic table trends. Here’s a table of atomic radius relative sizes. Pretty nifty, though no numbers associated with it, apparently.

A table of the elements

Description automatically generated

**Atomic Radius:** Well CFA says each electron is roughly in a hydrogenic state with Z = 1. So makes sense that as go down the periodic table, radius gets larger, by Pauli Exclusion prinicple. As go across though? One would think it stays the same. As the s subshell has largest radius, followed by p, etc. But I guess here we have to consider more nuance to the CFA. So for ns2p1 atom, say, we have that these three electrons will feel potential due to Z = 3 protons, but ns22p3, say, will feel potential due to Z = 5 protons, by the same token. This is much more attractive, and so will suck these electrons in more. It kind of makes sense, in the same vein, that the Ionization energy goes opposite the atomic radius, increasing to right and up; the atom should hold on to the electron more tightly the more closely it’s held. Here’s a table of ionization energies, the energy an atom must be given to remove an electron:

A chart of periodic table of elements

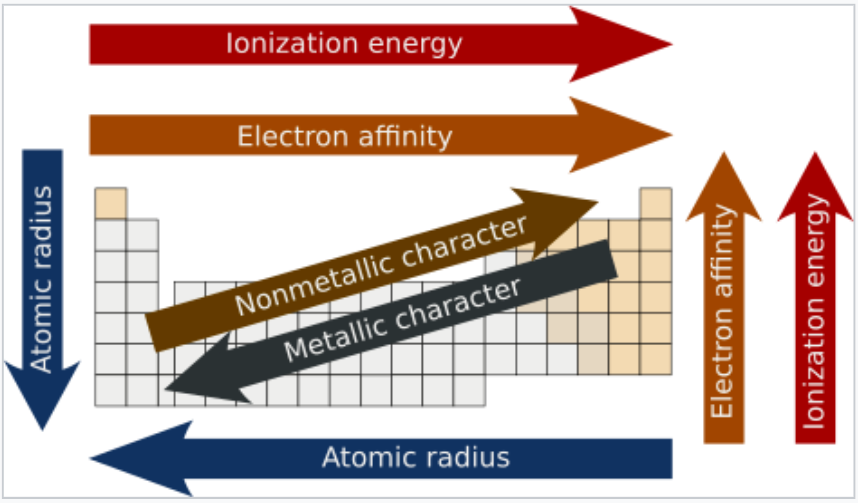
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and one of electron affinities – the energy change of an atom when it gains an electron:

A chart of periodic table

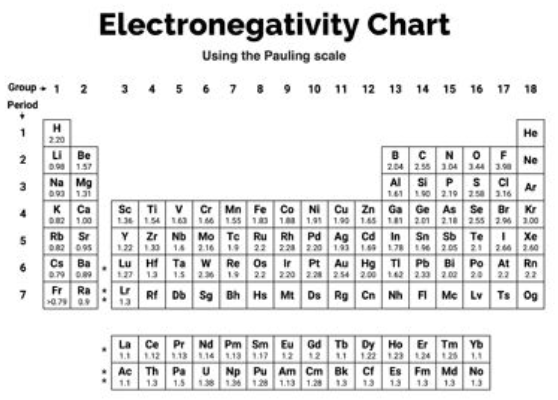
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And the overall trends are here:



**Ionization Energy:** This is the energy required to remove an electron from an atom. Makes sense that the ionization energy should inversely follow the trend of atomic radius. The closer an electron is to the nucleus, the more tightly it’s held, the greater its (negative) potential energy.

**Electron Affinity**: This is the energy drop when an electron is attached to a neutral atom. Why should there be an energy drop? For instance, consider a neutral, but polar, atom. How is an atom polar? I’m thinking that if it doesn’t have a full subshell, then it is ‘polar’ in some sense. As we saw in QM folder/Identical Particles/CFA file, an atom’s electron charge distribution will not be spherically symmetric unless it has an ns2, or ns2p6 configuration. So ns1 atoms will want to acquire and electron to become ns2, a configuration which we’ll note from the affinity table is almost stable. And ns2npx atoms will *really* want to acquire electrons to become ns2np6, also a stable configuration. So if an atom is polar, and if an electron is nearby, it will exert a torque on the atom so that the positive end is closer than the negative end. Then the positive end will attract the electron more strongly than the negative end repels it. And so the electron will effectively bind to the positive end (can’t get tooooo close though, because of Pauli-Exclusion principle). So the electron will presumably occupy one of the empty orbital states on the molecule. Affinity seems to follow ionization energy trends.



**Electronegativity**: This is a measure of how tightly an atom attracts/holds onto electrons it’s sharing with another atom in a bond. If one atom is more electronegative than the other, then their bond, if they have one, will be polar.

**CFA and Hund’s Rules:** It helps to have a basic framework of the energy levels of individual atoms. We’ve discussed this in more detail in QM/Many Identical Particles/Aufbau principle file, and will have discussed this in more detail in the Cond Matt/Metals/Free Electrons/Excitations/Band Structure file. But anyway. A neutral atom has, say, n interacting electrons. And so the excitation structure of the atom can be complicated to determine. In the simple central field approximation (one could say, mean field approximation), you treat each e- as independently feeling the potential of the +n atomic nucleus and the –(n-1) charge of the other electrons, leaving a net +1 charge. So the energy levels are more or less just those of the hydrogenic atom. Remember quantum number n = shell, ℓ = subshell, mℓ = orbital. And we can place the atom’s n electrons one-by-one into its empty (nℓmℓms) states, in accordance with the Pauli exclusion principle. The pure hydrogen atom would have that all states with same n are degenerate, but a little more work taking account of spin-orbit corrections and electron interactions results in an improved energy spectrum that sees energy increasing roughly with n *and* ℓ (kind of like we saw when studied the spin-orbit correction in QM/Time Independent/Spin Orbit file). So according to the Aufbau principle we can fill electrons into their subshells, roughly in order of n,ℓ, but really in order of appearance of the subshells in the periodic table (subshells further down and to the right are filled later; this needs more explanation, but hopefully we recall from Chemistry what we’re talking about). 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 energy diagram seems to contradict the Aufbau principle, in that according to the above energy diagram, we should get filling in the order 3d, 4s, and (skipping 4p) 4d, 5s, and (skipping 5p) 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 atom. 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. For instance, consider the electron configuration of Iridium. It is [Ir] = [Xe]4f145d76s2. We get this filling using the Aufbau principle from Chemistry, where we do the 6s orbital, then 5d orbital, then 4f orbital. But the filling would actually proceed, energetically, in order of 4f’s, 5d’s, 6s’s. But there are three missing 5d states that haven’t been filled. I presume that if Ir acquired an electron, it would fill into the 5d8 state. So we see that the 6s energy levels are actually in the middle of the 5d energy levels. Once we’ve filled electrons into their subshells, we work out the lowest lying energy states of the atom. This concerns Hund’s Rules. These basically tell you that in the unfilled (n,ℓ) subshell, take your k electrons, go to the L-S coupling scheme, and the lowest state will be the max S, max L, min/max J depending on if the subshell is </> half filled. J­z will enumerate the degenerate levels.

**Formation of Metals, Semiconductors, Insulators**

So now I’ll talk about these guys. First we’ll talk about how they stick together I guess.

**Bonding in Real Space**

So how do metals, insulators, etc., stick together? I don’t know. It seems an atom has a basic desire to attain a complete doublet, or octet configuration. I believe this is generally due to the fact that almost all other valence configurations make the atom polar, in that the electric charge distribution surrounding the nucleus is not symmetric. The CFA would predict this to be the case if valence state isn’t ns2 or ns2np6. And if atoms are polar, then they will electrically attract other polar (or non-polar) atoms, as we learn in Physics 2. I think this is the basis for the aggregation of atoms into compounds. But then, how do metals, semiconductors, insulators differ…?

A diagram of metal banding

Description automatically generated

So for **metals**, we’d say that these polar atoms, in sense of an incomplete octet, attract each other. And when they get close enough, the force of attraction is actually large enough to pull off the weakly held valence electrons. So metals tend to bond by giving up valence electrons (ns, np) to reduce to a stable octet. Since metals’ valence electrons have such a large radius, and low ionization energy, the increase in PE of the ionized electrons is fairly small, as the electron charge density distribution doesn’t change that much (see illustration). But the relaxation of their KE is large, as formerly they were bound to a relatively tight space (tight wavefunction curvature = high KE), and now they’re free to roam the entire metal (low wavefunction curvature = low KE, and so many electrons will have very low KE as we build up the Fermi sea). So I imagine there is a net drop in energy in this way, which equates to there being a ‘metallic bond’ between the atoms. And the configuration is stable, as you can see by displacing either the set of ionic cores or electron sea from their present equilibrium position – they will want to go back. Unlike semiconductors and insulaors, we don’t seem to get metal compounds like, say, MnCo, for example. I wonder why not?

A diagram of a covalent bonding

Description automatically generated

**Semiconductors** have a smaller radius, and so higher ionization energy than metals typically do. So they are unlikely to shed all of their valence electrons to attain a complete octet valence state. Instead they will share their electrons with neighbors. Consider, when two atoms share electrons to complete their octets, the bonding electrons will as before lose/relax KE (recall from QM/Time Independent/Variational Principle how an electron in a symmetric state between two atoms has lower KE than the antisymmetric state, because lower curvature, basically). Also as before, they will gain PE, as the charge density expands from encompasing just one atom, to two. But they will also lose a little PE, as the bonding electrons stationed in between the two now somewhat positively charged atoms, draw the atoms inward towards each other. Apparently, the gain in PE from charge density expansion is large enough to compete well with the relaxation in KE so that the electrons do not wholly detach from their parent nucleus, but stay in those bond formations. This amounts to a ‘covalent’ bond I guess. We can also have semiconducting compounds like GaAs. Can see they form a complete octet. And these compounds are usually formed between atoms with similar electronegativies, atoms in Groups 13 and Groups 15.

A diagram of a structure

Description automatically generated with medium confidence

**Insulators** (diamond for instance) also bond by sharing electrons to make an octet. They have *very* small radius, and *very* high ionization energy. So cannot shed electrons too much. But apparently can shed a little - gaining PE, and compensate by KE relaxation and perhaps a little reduction in PE by being drawn together (about shared charge between). What about ionic compounds? This is also kind of sharing, but more like giving. And this would take place between atoms with very different electronegativities, say between Group 1 and Group 17, or Group 2 and Group 16. Note usually ionization energies > electron affinities, but then we get reduction in PE when ions draw closer due to the Coulomb attraction. Unlike with insulator covalent bonding, it would seem we don’t necessarily get relaxation of KE as electrons are transferred rather than shared, and so their spatial confinement doesn’t really relax much.

Then we have bonding between Group 18 elements, i.e., the **Noble Gases**. Each of these atoms has a closed shell and thus doesn’t bond with other atoms hardly at all. Each of the atoms’ e-‘s are glued to the atom more or less. Not sure how purely non-polar atoms bind, but I guess when they get close enough, they may induce some sort of polarization in the atoms’ charge distributions, and as we saw in the Electrodynamics/Dipole-Dipole interaction file, polar atoms will want to adhere to each other as a way to lower their energy. Well, they say that this is due to the VanderWaals force. Apparently a given Noble Gas atom does have an instantaneous electric dipole moment, p1, which *averages* to zero over some microscopic time constant. Nonetheless, while it exists, it creates an electric field, E1 which induces a dipole in any nearby atom, p2. That atom’s dipole moment will be proportional to the electric field so p2 ~ E1. And therefore the interaction energy between them will be ΦVdW ~ -p1p2/d3, where d is their separation. But E1 ~ p1/d3. So the interaction energy will be ΦVdW ~ -p12/d6. Since p12 does not average to zero, there is always an attraction between the two atoms. But it is very weak, which is why aggregations of such atoms don’t exist in the gas state (they typically/only bond in pairs), only at very low temperatures. And even when they do, the electron wavefunctions of the electrons in the outermost shell will remain highly localized about their parent atom, so the band structure, such as it is, will be pretty flat.

**Bonding in k-space**

We discussed how things play out in position space. Now let’s go to k-space and look at band structure. 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. That is, they go in order of (n,ℓ) according to the Aufbau principle, and the mℓ degeneracy is split by the spin-orbit interaction, e-e interaction, etc., giving lowing lying energy levels according to Hund’s rules. As it turns out, bringing the atoms closer together introduces them to the potential from neighboring atoms, the so-called crystal field. The crystal field ends up playing a larger role than the spin-orbit interaction and e-e interaction, and so we’ll retreat from Hund’s rules. So at this level, we expect each orbital (nℓmℓ) in one of those atoms to have its own energy level, i.e., Enℓm\_ℓ (with mℓ basically being a degenerate quantum number – but whatever).

If the atoms are far apart, they don’t feel the potential of any of the others, and so, to zeroth order, Enℓm\_ℓ would be N-fold degenerate. And so if the atoms were far apart, the energy levels would look something like on the left below. Apropos the diagram, the energy levels ε1,2,3,4,5 = Enℓm\_ℓ would correspond to higher and higher values of (n,ℓ). And each line would actually represent, implicitly, a 2ℓ+1 fold degeneracy of mini-lines all at that energy, corresponding to the degenerate quantum number mℓ. Also, we’ll note that I kind of presumed the each of the orbitals was completely filled, which they ought to be for even Group # atoms, in the periodic table above. Okay, well when we now bring the atoms closer together to create their compound, the crystal field will split the degeneracy of the N Enℓm\_ℓ’s, to a degree proportional to how much the corresponding subshells (or really orbitals?) overlap, and the flat energy level will be turned into a band, Enℓm\_ℓ(k), which will look probably nothing like what I drew to the right below. But yeah. *Now* the electrons individually have mean velocities, thanks to the curvature of the bands. But the velocity averaged over the entire band should be zero.

A screenshot of a math test

Description automatically generated with medium confidence

One more word of clarification. My diagram seems to imply that all the bands with the same (n,ℓ) quantum numbers are still degenerate, i.e., Enℓm\_ℓ(k) = Enℓm\_ℓ´(k), but they need not/probably won’t be. And we’d see, say, ε4­­­­, split into 2ℓ+1 mini-bands: ε4,m\_ℓ=-ℓ,ε4,m\_ℓ=-ℓ+1,…, ε4,m\_ℓ=ℓ. These mini-bands might overlap completely with themselves for some range of k, and separate for other ranges of k. And we’d not expect the difference between mini-bands to be as great as the difference between bands with different ℓ’s. In what follows, I’ll continue to elide the distinction between mini-bands, for simplicity. Anyway, now let’s use all this band stuff as a basis to make a distinction between metals/semiconductors/insulators.

**Metals**

If we supposed that valence oribitals (nℓmℓ again) of the individual atoms weren’t completely filled to begin with (say we’re in an odd numbered Group in the periodic table above), then when the atoms are brought together to form the solid, the valence band (now conduction band) of the solid will be partially empty…well it’ll be exactly half-empty. And so when we set up an electric field, it will drive the half-filled band’s electrons along the band inducing a current. So such an atomic compound would be considered a metal.

A diagram of electrical circuits

Description automatically generated with medium confidence

This seems to suggest a classification: odd #’ed Group = metals, even #’ed Group = insulators. But in fact it’s not quite so, because often the bands overlap, so that even what we might think to be an insulator, can become a metal, with partially filled bands. As depicted below:

A diagram of mathematical equations

Description automatically generated

Bands are more likely to overlap when their band width – literally the energy width of the band, i.e., highest energy of band minus lowest energy of band – is large. And as we’ll see the band width is proportional to how much the orbitals spatially overlap. We’d expect outer subshells like s, and maybe p, to have large bandwidth because they overlap a lot. And as a consequence, the bands might intersect, as two are depicted to do above. But d and f subshells wouldn’t overlap so much and so their corresponding energy bands will have low curvature. Its important to remember that each of these states is technically a bound state still. But due to overlap of the states (in real space), the electron can travel the length of the solid. One can also think of it as tunneling. If you put the e- in between two wells (like illustrated in Kronig-Penny model) it can tunnel through the potential barrier into the other well, and so on.

**Semiconductors**

Semi-conductors’ band picture generally looks something like this:

A screenshot of a math test

Description automatically generated with medium confidence

They have completely filled bands, but the next band up (the conduction band), which would be empty, is not to far from valence band (highest filled band). Therefore, at room temperature, it is reasonable to expect some valence band electrons will have jumped up into the conduction band. And so while semiconductors won’t conduct at T = 0, they will at room temperature at least, both due to the populated (but not filled) conduction band and the depopulated (but not empty) valence band. The reason for the lack of overlap between bands would ostensibly be due to the lack of spatial overlap between subshells/orbitals of nearby bonded atoms. This is due to the fact that semiconductors are usually mid p/mid p bonded guys, like Ge (which have 4 e- in their valence shell and so often bound covalently with 3 other neighbors). And p orbitals have smaller radius than s orbitals. We can generalize this discussion to compounds too, like GaAs. Well 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 |n´ℓ´m´ℓ>2 respectively, with energy levels Enℓm\_ℓ (we’ll presume same atom/same spectrum for simplicity) 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. And our energy spectrum would be something like E(λ)nℓm\_ℓ(k) = Enℓm\_ℓ(k) ± ΔE(12)nℓm\_ℓ(k), where ΔE(12) is some overlap integral 1<nℓmℓ|H|nℓmℓ>2 (see QM/Time-Independent/Variational Principle)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, and using the total number of conduction band electrons of the molecule, rather than the number of either of the individual atoms. For instance, consider GaAs, which I think forms a structure with two atoms per basis. Ga has 3 valence electrons and As has 5 valence electrons. On the left is their valence band structures if they were alone in the unit cell, and to the right is their structure, within our approximation, when together.

A diagram of mathematical equations

Description automatically generated

Moving on,

**Insulators**

Diamond is quasi-insulator. Insulating bands look kind of like semiconductor bands (really, the lower lying bands should have less curvature than the top ones, but too lazy to change picture),

A diagram of lines and lines

Description automatically generated with medium confidence

They have completely filled bands, and the next band up (the conduction band), which would be empty, is fairly far from valence band (highest filled band). Therefore, even at room temperature, there will be an exponentially small number of electrons to populate the conduction band, and so we will have no appreciable room temperature conductivity. So the difference between semiconductors and insulators is rather a difference in degree than in kind. Insulating elements are found in the upper right hand side of the periodic table. Their ionization energies are rather high, and their atomic radii low. So their valence electrons stick close to their host nucleus, and there is very little orbital overlap between neighboring atoms. And since there is little spatial overlap, there is only little band width/curvature. So the bands remain far apart. We can generalize the discussion above to include ionic compounds, like NaCl. If we treat it like we did semiconductors, then we’d say the individual bands of Na and Cl would join in roughly symmetric/antisymmetric manner to give us E(λ=∓)nℓm\_ℓ(k) = Enℓm\_ℓ(k) ± ΔE(12)nℓm\_ℓ(k), where Enℓm\_ℓ(k) are the bands for either atom’s valence electrons and ΔE(12)nℓm\_ℓ(k) is an overlap integral or something [see QM/Time-Independent / Variational Principle]. But this would indicate the valence electrons would tend to spend *equal* time on either atom, or in between the atoms. This isn’t what happens though; instead one atom (Na in this case) transfers electrons to the other (Cl). I think the resolution is that the we are neglecting the attraction between the ionized Na+ and Cl-. When we take account of the Coulomb attraction, which comes about when an electron spends more time on the Cl atom than on the Na atom (which would correspond to the antisymmetric combination λ = -1 above?), then we’d see that the λ = -1 bands get dropped way below the λ = +1 bands. And it kind of looks like this:

A diagram of mathematical equations

Description automatically generated with medium confidence

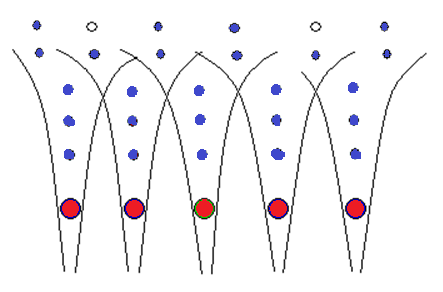
So much for the band picture. But as stated, the overlap between orbitals of neighboring atoms is super small, which means that the crystal field ends up having less influence on the energy levels than good old Hund’s rules. The upshot is that for insulators, I think we can treat Hund’s rules as more important than the crystal field, and its concomittant band picture.

**Doping**

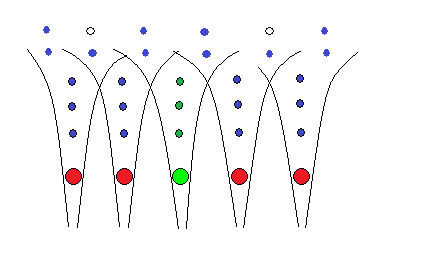
So metals and semiconductors are often doped with impurities, either on purpose or just because there are limits to refinery. So I want to discuss this a little bit.

**Metals**

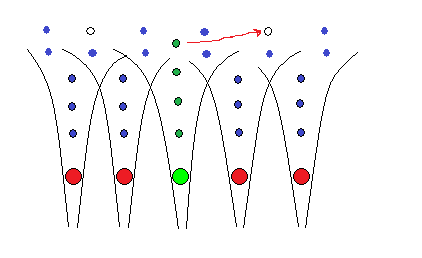
Undoped metals look like this, basically:



But metals often come with impurities. And so we might expect a real space ‘band’ structure like this for these:



The impurity might not lose any of its electrons to the Fermi sea, but due to its disruption of the periodicity of the lattice, will effectively exert an electric potential on those electrons. Or if the impurity’s valence electron is high enough, then it’s possible the conduction band electrons can screen the impurity nucleus’s influence on the valence impurity electron and it could jump into the conduction band.

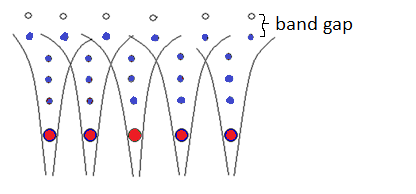


If it does, then in addition to the potential it will exert on the Fermi sea of electrons, now it will contain an extra state that the electrons can drop into, and pop out of. If the impurity atom has otherwise magnetic properties (i.e. Hund’s rules give it a net magnetic moment), then the interaction between electrons in the quasi-localized site and the conduction band often takes the form of an ‘exchange interaction’, like happens in other situations. An example of such a scenario is Au or Mn impurities in Cu.

Note that the filled conduction band contributes no screening or anything. This is because there is no σ(ω) if the band is full, and therefore there should be no ε(ω) either, by consequence. Unrelatedly, it would seem that a nearly-free electron model would be best for metals, but I’ve seen the tight-binding used too.

**Semiconductors**

Undoped semiconductors would look like this.



They have a band gap, and so they do not naturally conduct at T = 0. But we can change this by adding impurities. There are two possibilities. One is to add impurities with more valence electrons (these are called n-type SC’s because the additionally electron(s) will contribute negative charge carriers to the current). The additional valence electron will typically occupy an energy level (called the donor level) just below the main conduction band. And thus at relatively low T’s they will readily populate the conduction band. An example would be Ge:As.

Chart, diagram

Description automatically generated

Another possibility is to dope with impurities with fewer valence electrons, like Ge:Ga.

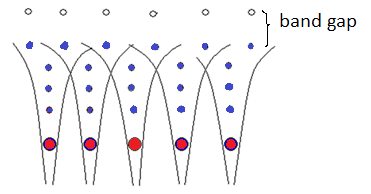
Chart, diagram

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Then the extra-valence level of the impurity will often take an energy level just above the valence of the main set of atoms (Ge in our example). This energy level is called the acceptor level. Then a Ge electron will jump (with probability depending on the temperature) into extra valence level of the impurity, creating a hole in the main valence band. Because this will create an effective (+) charge in the valence, these types of SC’s are called p-type. It would seem that modeling this valence/conduction band would be best with say a tight binding model. One can map a range of behavior with the tight-binding model, from insulator to full conductor, by the # of nearest neighbors, δ to be large. Remember the bandwidth is basically proportional to δ.

**Insulators**

Now for what it’s worth I’ll throw insulators in here:



The main distinction between insulators and semi-conductors is the band gap, as aforementioned, which is much larger, so that even at room T, there are negligible electrons in the conduction band. I don’t suspect doping changes this enough?

A diagram of a diagram of a diagram

Description automatically generated with medium confidence

One thing is that insulators can often be doped with magnetic impurities to give them magnetic properties.

**Formation of Quantum Fluids**

Hg is only element in the periodic table which is a fluid at standard temperature and pressure. But many other form fluids at higher or lower temperatures. N2 gas condenses to a fluid at around 77K. But we’ll be more interested in quantum fluids. Specifically 4He and 3He. These attract each other via the usual Van der Waals forces and are examples of an interacting Bose and Fermi gas, respectively. Near T = 2K, they condense from a gas to a liquid and have many novel properties owing to the fact that they are *quantum* liquids – the thermal wavelength is larger than the atoms’ mean spacing. I *think* all other liquids can be treated classically.

**Interactions, Excitations, Thermal and Nonequilibrium Properties**

We cannot study the whole complete system at once, and so we’ll isolate different interactions to see what effects each has and what is important, etc. I guess this will basically be a breakdown of what we’ll be talking about in each folder and such.

**Metals**

In the Free Day folder, we’ll start with free electrons in a static periodic crystal field, and look at their excitations. We’ll see how the crystal potential reorganizes the electron energy spectrum into bands, each corresponding to a Brillouin zone in k-space. The energy gaps between the bands provide the basis for being able to make a distinction between metals, semiconductors, and insulators. We’ll also look at what happens when we place a metal in a magnetic field. In that case, at least for a free spectrum, the part of the electron energy spectrum perpendicular to the field (say kx, ky) gets chunked into quantized orbitals circulating the field lines, with a degeneracy proportional to the field strength. We’ll calculate the heat capacity and find it linear for all applicable temperatures, in contrast to the 3nkBT/2 value we’d expect from Maxwellian statistics. When we calculate the electric susceptibility, we get a constant value -> the Thomas-Fermi result. The dielectric function, on the other hand, is just 1 at this point, because we are presuming the electrons do not interact. The magnetic susceptibility is calculated next. At T = 0, it looks like we can find an oscillatory magnetic susceptibility, called the de Haas van-Alphen effect, which is a consequence of the ground state energy rising and lowering in an increasing magnetic field as electron energy levels rise with the field, but also become more degenerate, enticing electrons to drop down to lower levels. At non-zero temperatures, this effect washes out, and we find a generic diamagnetic response from the orbital motion of the electrons, but a paramagnetic response from their spins. These are of the same order, but the paramagnetic response is about three times as large. When we calculate the time-dependent electric susceptibility, we find a purely real result, indicating that at this level, the current will oscillate in phase with the external field, and metals will not absorb any EM radiation (well, since we’re saying ε = ε0 at this stage, they will not even reflect, which is okay, because we’re presuming the electrons do not create E fields since they’re non-interacting). We calculate the time-dependent magnetic susceptibility as well, and find it also to be purely real. The next non-equilibrium property to consider is the conductivity. In ultraclean samples, we’ll find that the current is not steady in a constant E field. Nor does it just accelerate forever, as it would in a strictly free particle spectrum. Rather it will *oscillate*, at least if E is aligned along some RLV (any linear combination of the RLV basis), and we can calculate the frequency of these *Bloch* oscillations. If we cosider motion of particle in **B** field, then we get customary orbits in k-space about the B field, but we still have Umklapp scattering (i.e., the electron gets knocked back into 1st BZ by RLV every time it leaves the 1st BZ). This can result in closed orbits, or non-closed orbits, depending on the shape of the Fermi surface. If we consider the motion of electrons in an **E**, **B** field, then at least for free spectrum, we would get the expected orbits about, and acceleration along, the **B** field lines, superimposed on top of a gradual drift in the direction of **E**×**B**. Last up is Absorption.

Then we’ll consider the effects of impurities, on conduction electrons mainly, i.e., in metals. We’ll also consider the interaction between conduction electrons and magnetic impurity valence electrons. These will take the form of an e-e interaction, but I’ll put it in this part since it seems to fit better.

Next we’ll look at the e-ph interaction. We’ll do this for metals, where there are a lot of electrons in the conduction band, then for semi-conductors, where there are few electrons in the conduction band, and then finally for insulators, for which the electrons are mainly immobile.

Then we’ll look at e-e interactions in earnest. First we’ll do e-e interactions between conduction electrons in the context of the nearly free electron model, and the tight-binding model (Hubbard). And we’ll look at such interactions between conduction electrons and valence band electrons, both for metals and semi-conductors and insulators, sort of, mainly in context of optical absorption. Finally we’ll look e-e interactions in the context of direct exchange, among insulators.

After that we’ll consider the combined effect of the e-e interaction and e-mobile lattice interaction in metals. This will give rise to superconductivity.

2. Two-particle bound states. Sometimes particles will bind together, like in the SC state, into a bound pair. And this pair will be just like a H-atom – with all the accompaning states. Often the two spins will join in a spin singlet (state with zero net spin). This usually happens to the k and –k states since they are degenerate. I suppose that in general we could have multi-particle bound states or something too. These ‘molecules’ can have KE (from center of mass) and angular momentum about that (in the classical limit). Not sure how that connects with |nlm> relative states quantum mechanically.

3. In addition to these, we can collective modes, basically coupled HO states. We can have charges coupled to each other, in which case we have charge density waves. That’s the excitation structure of the lattice, and *an* excitation structure of interacting electrons in a gas. We can also have spin density waves for both magnetic atoms in a lattice – Heisenberg model, and also for interacting electrons in a gas. Just the Coulomb interaction itself can give rise to this, as the Fermi statistics will tend to anti-align the spins.

*Magnetic susceptibility*

This is generally paramagnetic for s’s and d, f’s. And it is usually diamagnetic for p’s.

This is consistent with atomic calculations, since there will be no paramagnetic response (only diamagnetic) for filled and ½ filled – 1 shells according to quantum theory. The transition elements are usually quite magnetically susceptive since all of the ℓ shell electrons add to give a relatively large net magnetic moment. The rare earth elements have more exaggerated properties than the transition elements since there are more f-electrons than d-electrons (or can be) and so have greater angular momenta, resulting in greater magnetic susceptibility. In fact holmium metal is about 30 times as ferromagnetic as Fe.

Says metals and insulators both can have paramagnetic/diamagnetic response ala Hund’s rules, and also ferromagnetic response according to exchange interaction. But insulators and metals are still slightly different in this same regard. So need to figure out how they differ.

*Electrical resistivity*

The upper s and d, f’s orbital atoms have low resistivities because of their orbital overlap with other atoms. Unfilled ns1, ns2 configurations are also relatively highly conductive. Consider the transition metals again. Elements in the configuration nd4, nd9 would prefer to have a filled or ½ filled d shell to a filled s shell, and so they borrow an electron from the s-shell to accomplish this. This leaves a lone s-electron. s electrons are always furthest from the nucleus. Thus such elements (like Cu, Au, Ag) have low resistivities. On the otherhand, since nd5, nd10 configurations are quite stable, such elements have a higher than typical resistivity. The rare earth elements have even more exaggerated properties than the transition elements since their f-electrons overlap with neighbors even more.

**Semiconductors**

Another sort-of example would be Ga1-x­MnxAs (x is doping level). This is technically a semiconductor, GaAs, doped with Mn. The As would normally ‘borrow’ the three electrons from Ga so they form a complete octet. I think it will do so with Mn too, but will have to borrow from d-subshell. In any event, the d-subshell will be unfilled, and so have a net moment. The excitations of these ions are also described by Hund’s rules, but with the caveat that we set L = 0 (the angular momentum is said to be quenched). This modification comes about due to the influence of the crysal field on the relatively extended d-states. This is called crystal field splitting.

**Insulators**

We can go a long way treating insulators as a whole by simply looking solely at their constituents’ individual properties – the noble gasses properties are not very collective, except at very low temperatures where they can liquefy. The individual atoms’ excitations are given by Hund’s rules.

Insulators that take the form of ionic compounds, like NaCl, CaBr2, etc., are a little more interesting. A good starting point is again to just look at the properties of the individual ions and then ‘add the two together’. Hund’s rules will suffice for the low lying excitations of the ions. And when constructing these states, we would treat them as having/missing those extra electrons that make them ions. Since these ions will typically have filled subshells then, they would have no magnetic properties, as they’d have no net dipole moment. Well actually, I guess they’d display weak diamagnetism as a consequence. Since they are charged, there will be a long range Coulomb interaction between ions as well. This should make harmonic lattice oscillations possible. I’d also think that since the potential within each atom’s neighborhood should be altered somewhat by the aforementioned Coulomb potential (the crystal field in this context), that this would change Hund’s rules a little. I think this is called crystal field splitting.

Some ionic compounds are formed with lanthanoid and actinoid metal ions (I guess the lone 5d, 6d electron detaches?). Such ions would have empty f, subshells, and that should give these ions a net magnetic moment. So in addition to all of the foregoing interactions, these should have magnetic properites which will generate further interactions. These unfilled f subshells of neighboring lanthanoid/actinoid ions will interact via Coulomb repulsion (all electrons will, but I guess the interaction between these guys is notable kind of). This gets modeled as an exchange interaction ~-κ**J**·**J** (where **J** is net magnetic moment from Hund’s rules) which will induce magnetic ordering (ferromagnetic, anti-ferromagnetic). And there will consquently also be a magnetic dipole-dipole interaction between such ions. It is the dipole-dipole interaction that ends up responsible for ordering the moments into domains.

Some ionic compounds form with transition metal ions, like Fe. These also have net magnetic moments, and so the foregoing applies to them. But because the d-subshell electrons are so far from nucleus, they are strongly affected by the crystal field, which modifies Hund’s rules. So the ground state multiplet’s are exactly what we’d think they are.

Ionic insulators especially (I-VII, II-VI) have full shells, and so are diamagneic. Also, low temperature semiconductors (III-V, IV-IV) would be diamagnetic I think. Some insulators have ionized lanthanide/actinoid elements in them [Sm2O3, Gd2O3]. Gd and Sm are triply ionized, and have respective valence electron cofigurations Gd = [Xe]4f85d06s2 → Gd3+ = [Xe]4f75d06s0, and Sm = [Xe]4f65d06s2 → [Xe]4f55d06s0. With unfilled f-subshells, they’d exhibit strong paramagnetism. Some insulators have ionized transition metal elements in them. One is Y3Fe5O12. Fe is ionized and has an unfilled d-subshell.

4. Magnetic fields will excite a paramagnetic and diamagnetic response – it will tend to make the **J**’s align, while making the charge orbit the field too – a diamagnetic response. These will compete with each other as they are of opposite signs.

Y3Fe5O12, and other garnets exhibit Ferromagnetism at low T. This is best-ish described by Heisenberg model. Ga1-x­MnxAs can exhibit Ferromagnetism too, due to interaction between magnetic moment of Mn and of the spins of the holes.

**Quantum Fluids**

Near the end we’ll consider superfluids, namely 3He, and 4He. These interact through the Van der Waals force, which is the attraction between instantaneous dipole moments. Since this is a weak attraction, they can be treated as ideal gasses down to pretty low T’s, whence they liquefy below a certain critical temperature. We’ll study their liquid properties.

We also get two-particle bound states in super-fluids. In He3, the bound state will form a triplet, rather than a singlet spin state, and so you can get magnetic spin waves too.

There would also be a weak Van der Waals attraction between the atoms. But again, this isn’t important until low T’s. Due to closed subshells, they should display weak diamagnetism.

**Photons**

Finally, we’ll look particularly at the interaction of light with matter, first with phonons, and then with electrons in both metals and insulators.