A little quantum chemistry.

These notes are <u>not</u> a substitute for reading the book and working problems.

The exclusion principle.

First let's go back to the one dimensional box and put *two* electrons in. Don't worry, I'm not going to do all the details, just give you the idea of what is going on. Schrödinger's time independent equation now looks like

$$\frac{-\hbar^2}{2m}\left[\frac{\partial^2\psi(x_1,x_2)}{\partial x_1^2}+\frac{\partial^2\psi(x_1,x_2)}{\partial x_2^2}\right]+V(x_1,x_2)\psi(x_1,x_2)=E\psi(x_1,x_2)$$

where $\psi(x_1,x_2)$ is the wave function for finding electron one at location x_1 and electron two a location x_1. The energies for each electron get quantized just like for one electron, you can normalized the function to get the constant A as before and the probability for finding the two electrons is $\psi^*(x_1,x_2)\psi(x_1,x_2)dx_1dx_2$ just like you might expect (if you are bored one day you can probably work all this out for yourself). For the infinite strong one dimensional box of width L this wave function looks like $\psi(x_1,x_2)=\psi_n(x_1)\psi_m(x_2)=Asin(\frac{n\pi x_1}{L})sin(\frac{m\pi x_2}{L})$, where n and m are the energy quantum number for each electron (they can have different energies).

Now the interesting part. Notice that the probability for finding the electron has the property $\psi^*(x_1,x_2)\psi(x_1,x_2)=\psi_n^*(x_1)\psi_m^*(x_2)\psi_n(x_1)\psi_m(x_2)=\psi^*(x_2,x_1)\psi(x_2,x_1)$. In other words since electrons are indistinguishable (all electrons look alike) you could close your eyes, switch positions for each (electron one goes to location x_2, electron two goes to x_1) open your eyes and not know the switch was made. So the order of the wave functions doesn't matter and which electron is where doesn't matter either.

The second thing to notice is that if we put minus signs in front of $\psi(x_1,x_2)$ we would have the same probability because we always multiply two wave functions to get a probability, the minus sign doesn't matter. This means that there are actually *two* possible wave functions, $\psi(x_1,x_2)$ and $-\psi(x_1,x_2)$ which end up giving the same probability. To completely describe the case of two electrons in a box we have to include both. There are two possible ways to do this (C is a constant determined by normalization):

$$\psi_S=C[\psi_n(x_1)\psi_m(x_2)+\psi_n(x_2)\psi_m(x_1)]$$

or

$$\psi_A=C[\psi_n(x_1)\psi_m(x_2)-\psi_n(x_2)\psi_m(x_1)].$$

In the first case, the symmetric case if $n=m$ (the electrons have the same energy; i.e. same quantum state) the probability is doubled (remember switch locations doesn't change anything). In the second case, the anti-symmetric case, the probability is zero for two electrons with the same energy. This is the exclusion principle; electron wave functions are anti-symmetric so they always give a probability of zero for two electrons being in the same state. The class of all subatomic objects which have this property are called *fermions*; an electron is an example of a fermion.

The symmetric wave function does not apply to electrons but applies to another class of particles called *bosons*. A photon is an example of a boson. Bosons have a double probability of being in the same state; they like being in the same state, just the opposite of electrons. This is how lasers can work; photons are bosons so it is possible to create a situation where they will all have exactly the same energy. If you can get them all headed in the same direction you have a laser (more on that later).

Super conductivity occurs because two electrons can interact with each other through the crystal structure of the solid around them in such a way that the pair forms a boson called a Cooper pair. Once electrons combine to form a Cooper pair they act like bosons and all want to have the same energy; so they travel together in lock step without resistance (thermal motion of the crystal atoms can block individual electrons but a large number of Cooper pairs all in the same state can't be blocked so easily).

Three dimensions.

Your book does a pretty good job of explaining the three dimensional case for a hydrogen atom: ***Read the chapter!***

Basically the same thing happens as did for the 1-D case but now, since there are three dimensions there are three boundary conditions (three limitations on the range of the wave function) and so three quantum numbers, n, l, m. The energy is quantized, the angular momentum is quantized and the z-component of angular momentum is quantized. In the case of the energy of a hydrogen electron, restricting the electron to be trapped in r direction by the potential well ($V = -kq/r$) created by the proton in the nucleus gives $E_n = \frac{-13.6eV}{n^2}$ where n can be 1, 2, 3 etc. For $n = 2$ we have $E_2 = -3.40eV$ and for $n = 3$ we have $E_3 = -1.51eV$, the lowest three energy levels available to an electron in a hydrogen atom.

Wait, wait, how do we know all this is true? If an electron changes from the $n = 3$ to the $n = 2$ energy level it has to give off $-1.5eV - (-3.4eV) = 1.9eV$ of energy. This energy is in the form of a photon with an energy $E = 1.9eV = hf$. Notice that because the energy levels are quantized the photon cannot have $1.92eV$ or $1.89eV$, it has to have exactly $1.9eV$. So it has to have a fixed frequency or color. If we heat hydrogen up or run current through it so the electrons get bumped up a few energy levels and then fall down, giving off photons, this is the color of light given off. In fact, this color is unique to hydrogen; other atoms have different energy levels and so electron transitions will give off different colors of photons. This is how we know, for example, the composition of the sun; the specific colors of photons given off tell us what energy levels are there and these energy levels are specific to a certain element. There are more than just two energy levels per atom so we get a collection of specific colors of photons for each element. This is called *discrete spectrum*.

The Stern-Gerlach experiment showed that something was missing from Schrödinger's equation. These experiments showed there was an unpredicted fourth quantum number associated with the magnetic field of the electron. This came to be called electron spin

(but electron magnetic moment would be more accurate- because the electron magnetic moment is quantized it interacts with external magnetic fields in a certain way).

Dirac realized that Schrödinger's equation didn't include relativity. When he modified the equation to include relativity with time as a fourth dimension, he found the missing quantum number, the electron spin. So a complete description of an electron trapped around a hydrogen nucleus is described by a wave function in three dimensions plus time and has three quantum number $\psi_{n,l,m,s}(r, \theta, \varphi, t)$.

The three ways an object gives off light.

The way we see most objects is by *reflected light*. If an object appears green it is because it absorbs other colors and reflects green. This has to do with the kinds of molecules on the surface of the object; some molecules preferentially absorb certain colors and reflect others.

A second type of light given off by an object is called a *discrete spectrum* which was discussed above: From Schrödinger's equation and empirical results, we find that the energy levels available to electrons in an individual molecule are discrete; an electron trapped in the electrical potential of a nucleus inhabits fixed energy levels. These levels are determined by the number of protons in the nucleus (and other nearby protons and electrons in the case of complex molecules) and so will be different for each different molecule or atom. If the electron changes from one energy level to another it must give off (or absorb) a discrete amount of energy, exactly equal to the difference between the two energy levels. This energy may turn up as thermal (i.e. random kinetic) energy but often it is given off as an electromagnetic wave with a fixed frequency. The relation between the energy given off (or absorbed) and the frequency of the wave emitted is $E = hf = hc/\lambda$.

The picture of discrete energy levels for individual molecules can change somewhat when there is a large number of molecules close together in a gas, liquid or solid. In a gas collisions with other molecules can cause an atom to emit a photon with a little more or a little less energy, shifting its frequency a bit (think of the extra energy a baseball would have if thrown from a moving car versus a stationary car). The result is that, depending on the temperature and density of the gas, the discrete spectrum may be smeared out and a *continuous spectrum* of waves is emitted. This is called *blackbody radiation*.

In a solid each atom contributes energy levels which overlap with those of its neighbor resulting in a nearly continuous set of energies available to the electron. Since the molecules (and electrons) of any object above absolute zero have a range of possible kinetic energies due to their temperature we would expect these oscillating electrons to give off a broad spectrum of electromagnetic waves. This does occur but the calculation is again a quantum mechanical one which takes into account the fact that an electron trapped in a solid still has some energies levels which are forbidden to it. Once again we get a blackbody spectrum.

Broadly speaking, for solids, liquids and gases the thermal motion of their atoms results in the emission of a broad, continuous spectrum of electromagnetic waves called a *blackbody spectrum*. The loss of this energy in the form of emitted photons will cause the radiating object to cool, even if it is not in direct contact with any other material. The earth receives energy from the sun solely from this mechanism.

A tiny bit of solid state physics.

As mentioned, the discrete energy levels in single atoms overlap with their neighbors if you put a large collection of atoms together. So discrete energy levels become broad *bands* of energy levels. There may still be energies which are forbidden called energy *gaps*. Whether a band is full of electrons or not depends on the particular atoms making up the solid.

Electrons may fill and be limited to a lower band, called the valence band, with no chance to change their energy in which case the solid is an *insulator*. If the lower band overlaps with an empty band, called the conduction band, so that there are plenty of free energy levels available to the electrons they can move around in the solid and the material is a *conductor*. In the case where the valence band is filled with electrons but is close enough to the empty conduction band that electrons can jump across (for example due to thermal kinetic energy) the material is an *intrinsic semiconductor*.

When an electron moves into the conduction band it leaves behind a hole in the valence band. Holes act as if they are positive charge carriers. An electron which moves into a hole is equivalent to the hole moving in the opposite direction.

The forbidden energy levels in the gap can also be modified for a particular substance by adding trace elements to the material (a process called doping) which will provide energy levels in the gap which act as stepping stones for the electrons to reach the conduction band. If the doping leads to extra electrons in the conduction band the material is called an n-type semiconductor (n for negative charge carriers). If the doping material ends up creating more holes in the valence band the material is a p-type semiconductor (positive charge carriers).
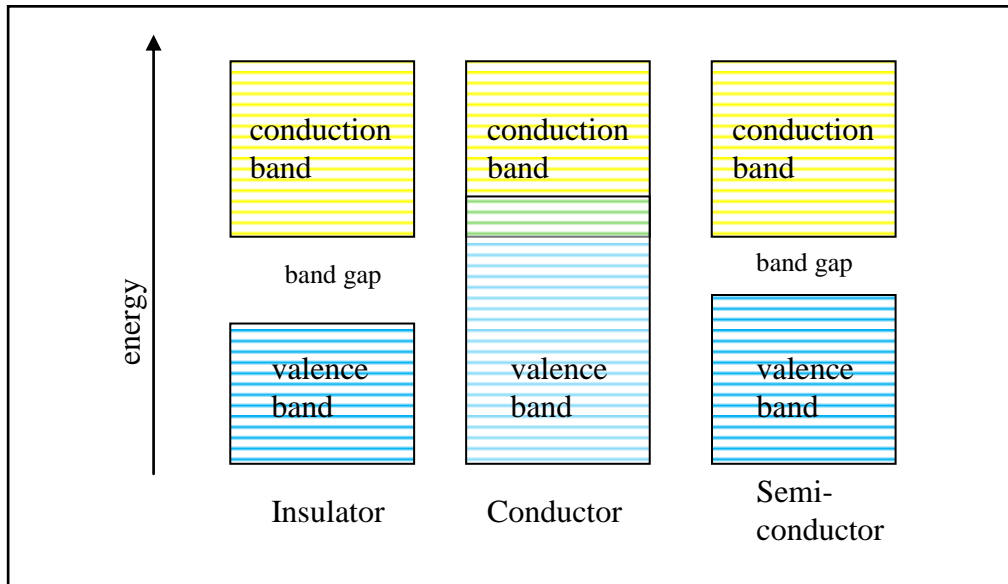
Figure 1. Blue represents energy levels full of electrons (the valence band), yellow represents energy levels which are empty and available for electrons to move to (the conduction band). In the first picture the band gap is so large the electrons cannot move from the valence band to the conduction band so the material is an insulator. The second figure show overlapping bands so the electrons do have energy levels to move to and the material is a conductor. The last drawing shows a semi-conductor; the electrons may be able to jump across the band gap if they have enough thermal energy.

The basis of the behavior of LEDs and also solar cells and several other electronic devices such as transistors and diodes is the combination of two (or more) semiconductors which have their band gaps at different energies. Solar cells and LEDs are based on joining a piece of n-type semiconductor with a p-type semiconductor. This is called a *p-n junction.* A schematic diagram for a p-n junction acting as a LED is shown in Figure 2. When the holes and electrons recombine at the junction the energy of recombination is emitted as electromagnetic radiation. Solar cells, basically work this way but in reverse; incoming solar photons cause new electrons and holes to form which can be used to power an electric circuit (with current flowing *into* the battery).
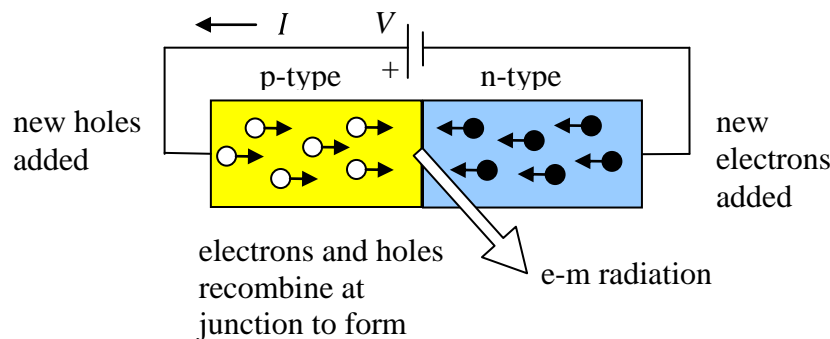

Figure 2. At the junction between p-type and n-type semiconductors under an applied voltage, V holes will recombine resulting in energy given off as light. Recall that conventional current, I actually indicates electrons traveling in the opposite direction.

The band gap determines the energy of the photons given off. This means that normally an LED will only produce a narrow range of colors with photon energies equal to the band gap energy. Designing a material with a band gap which gives off visible light is difficult due to limitation of the material making up the LED. The first commercial LEDs produced light in the infrared range. Ultraviolet and monochromatic LEDs followed this development. LEDs can also be made into solid state lasers which are used to read and write CDs. The ability to create DVDs which hold more information compared to a CD, had to await the development of blue LED lasers which have a higher resolution due to smaller wavelengths. Producing a broad spectrum of photons so that white light is emitted has been a challenge and white LEDs are just now reaching the market.