

# Thoughts for the Day

## CH301 Fall 2010

### 10/07/10

#### Multi Electron Atom

#### Electron Spin

First we need to introduce the idea of electron spin.

Electrons have an intrinsic angular momentum. That is they have an angular momentum that is not associated with them orbiting around anything. This is “thought of” as spin as we would like to take a complicated QM idea and put it in a nice classical picture. The electron has one of two spins that for lack of a better terminology we call spin up and spin down. These each have the same angular momentum but with opposite sign. We can give these a quantum number,  $m_s$ , that has values of either  $+1/2$  or  $-1/2$ .

#### Multi-electron atoms

The complications come from that fact that there are now more than 1 electron. To illustrate this we will look at He. But the rest of the atoms are the same but the problems just get worse. What do we need to do? Solve the Schrödinger equation. What do we need to do for this? We need to write down the Hamiltonian. In this case it will look like the following

$$\hat{H} = \frac{-\hbar^2}{2m} [\nabla_1^2 + \nabla_2^2] + \frac{e^2}{4\pi\epsilon_0} \left[ \frac{-Z}{r_1} + \frac{-Z}{r_2} + \frac{1}{r_{12}} \right]$$

The first two terms are the “take the 2<sup>nd</sup> derivative” terms. There are now 2 of them as we need to take the 2<sup>nd</sup> derivative with respect to the coordinates of electron 1 (the kinetic energy of electron 1) and with respect to the coordinates of electron 2 (the kinetic energy of electron 2). This is more math, but it is nothing more than twice the effort involved with one electron. The second part is the potential energy part. It has two terms with are the attraction of the electrons to the nucleus. These are both negative as they are attractions. They depend on the distance of electron 1 to the nucleus and electron 2 to the nucleus. Again this is simply the sum to two one electron problems. All of the difficulty comes from the last term. This is the repulsion of the electrons for one another. It depends on the distance between them with is a function of the coordinates of *both electrons*. As such, the coordinates cannot be separated. This makes the math essentially impossible.

How do we get around this? We make an approximation that even though we know the coordinates cannot be separated, we will separate them any way. Thus the true wavefunction depends on the coordinates of the all of the electrons in a complicated interconnected way. However, we will assume that the coordinates of one electron are independent of any of the

others. For helium this will have the following implications. The true wavefunction depends on the positions of both electrons simultaneously. But we will approximate the true electronic wavefunction as the product of two one-electron wavefunctions.

$$\psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) \approx \varphi_1(r_1, \theta_1, \phi_1) \varphi_2(r_2, \theta_2, \phi_2)$$

Now it is not that we are ignoring the effects of having two electrons. The wavefunction for electron1 can depend (and does depend) on the wavefunction for electron2. However, the explicit dependence of the coordinates on each other is lost. That is electron1 will now depend only on the “average” of electron2. The correlation of the electrons has been removed.

This is the “orbital” approximation. It is a good one in two ways. You’d like an approximate to both do a reasonable job of getting the answer correct and provide some physical insight. When we calculate the energies for multielectron atoms in this way we get reasonable numbers. Best of all we can actually think about the answers. It is hard enough to try to interpret one electron wavefunctions. I don’t want to try to wrap my head around wavefunctions that simultaneously deal with the coordinates of 82 electrons. As such, we like to imagine “each electrons in its own orbital”. However, it is important to know that while this might help us to gain some insight into a problem (say the fact the ionization energy of sodium is low due to “shielding” of the outermost 3s electron by the Ne core), the whole idea is actually a fantasy. The real wavefunction depends on the coordinates of all of the electrons at the same time.

So we have decided that we will solve our problem by making it easier by approximating the true wavefunction with a product of one electron wavefunctions or “orbitals”. How will we find these orbitals. This is a challenge as they are no longer solutions to the Schrödinger equation. However we benefit from the fact that if we make approximation in a particular way we are guaranteed that when we calculate an energy it will be higher than the true energy. Therefore we can adjust our guesses of the wavefunctions until we get a lower energy. What are we going to do about the Hamiltonian since it has a term in it that depends explicitly on the coordinates of multiple electrons (the  $1/r_{12}$  term that gave us all the problems in the first place). We are going to deal with the electron-electron repulsion in a new and approximate way. For any given electron we will look at its interaction with an “average field” from the other electrons. To solve the problem will now require iteration since the field comes from the wavefunctions that we are getting from the field.

How is this done (in a quick and dirty hand wavy explanation). First we guess at the one electron wavefunctions for all the electrons in the atom. Then we pick an orbital (say the one for the electron we have numbered 1) and we find the average field generated by all the other electrons in the system. Then we optimize a new function for the first orbital that minimizes the energy. Then we move on to electron 2 and do the same. At the end of this we will have new orbitals for the all the electrons in the system. However, this means we now have a very different average field than we started with. So we start over again. We look at electron 1, average the field of the others and find a new and better orbital for electron 1. Repeat for all other electrons. Now repeat again for electron 1....After a while we will find the things stop changing. That is the orbitals that we find from the average field yield the same average field.

This is the idea that we have a “self-consistent field” SCF. This is the self-consistent field orbital approximation.

What are we changing in the orbital functions to “find” better ones? There are many ways to do this. For us we will wrap up all of these ideas into one. We will use the H-atom wavefunctions as our initial guess and we will tweak them by changing their nuclear charge. Therefore each orbital will have its own  $Z_{\text{eff}}$ . All of the effects of e-e repulsion or “shielding” will be captured by this one parameter. The wavefunctions will all look the same as the H-atom wavefunctions since they are the same. The only difference will be  $Z_{\text{eff}}$  instead of  $Z$ . Therefore the distances in the radial distribution function will change.

We can use this  $Z_{\text{eff}}$  to approximate energies of electron orbitals

$$\epsilon_n = \frac{-Z_{\text{eff}}^2(n)}{n^2} \text{ where } Z_{\text{eff}} \text{ is a function of } n \text{ as it can be different for each orbital}$$

We can also just substitute in  $Z_{\text{eff}}$  for other Hydrogen wavefunction ideas such as the average radius which. Just plug in  $Z_{\text{eff}}$  where you would use  $Z$ .

What will the solutions look like?

Here we need to dig in deeper again. We have two problems that we will deal with now. One is that the electrons in the atom are indistinguishable. That is, we’d like to label them 1, 2, 3, ... but we can’t actually tell the difference between any of them. The other problem is that they are fermions. Let’s deal with the first problem first. Let’s imagine writing down a wavefunction for He (as it has only 2 electrons and things get messy more quickly with more electrons). I might think that the ground state had two electrons in 1s wavefunction with each electron having opposite spin. As such I might write down the wavefunction as

$$1s(1)\alpha(1)1s(2)\beta(2)$$

Where the 1 and 2 denote the coordinates for electron 1 and electron 2 respectively. The alpha and beta are the spin wave functions. They are not mathematical functions but simply mean this one is spin up (alpha) and this electron is spin down (beta). What is the problem with such a wavefunction? There cannot be any differences between electrons 1 and 2. That is they are identical. As such one cannot be spin up and the other spin down. They both have to be spin up and spin down at the same time. So we need to write a new function that tries to capture this idea. We’ll write the function this way

$$1s(1)1s(2)[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

Now electron 1 is up and down at the same time and yet always opposite of electron 2! Note: as I have left off some constants that will keep the function normalized.

However, there are still problems with my wavefunction that have to do with electrons being fermions. The wavefunctions for fermions must be anti-symmetric with respect to electron exchange. That is if I swap the coordinates of electron 1 and electron 2 I should get the same function with opposite sign

$$\psi(1,2) = -\psi(2,1)$$

What happens with my function?

$$1s(1)1s(2)[\alpha(1)\beta(2) + \alpha(2)\beta(1)] = 1s(2)1s(1)[\alpha(2)\beta(1) + \alpha(1)\beta(2)]$$

when I swap 1 and 2 I get the same thing. Same sign. This is symmetric. In order to make it antisymmetric I need to have a different combination of the spin functions. Let's subtract them.

$$1s(1)1s(2)[\alpha(1)\beta(2) - \alpha(2)\beta(1)] = -1s(2)1s(1)[\alpha(2)\beta(1) - \alpha(1)\beta(2)]$$

Now when I swap 1 and 2 there is a change in sign.

This has enormous consequences for us. This is why there are periodic trends in the elements. Without this all the elements would look essentially the same. Why? Because this is what limits us to having more than two electrons in the same orbital. Let's look at what would happen if I picked the same orbital and spin for both electrons in He. My wavefunction would be

$$1s(1)1s(2)\alpha(1)\alpha(2)$$

This is always symmetric with respect to electron exchange. All the electrons have the same quantum numbers. As such, if this was valid I could look at Li and make a wavefunction that was

$$1s(1)1s(2)1s(3)\alpha(1)\alpha(2)\alpha(3)$$

I could in fact do this for all the electrons in every element. But it is not valid. The wavefunctions must be anti-symmetric. Therefore I discover that every electron must have a unique set of quantum numbers. This consequence of the electrons being fermions and needing wavefunctions that are anti-symmetric with respect to exchange is called the "Pauli exclusion principle".

So as I put electrons into Li I have two in the lowest energy 1s orbitals (spin up and spin down) and then I am forced to use a higher energy n=2 orbital.

We can use this principle to build up the structure of all of the atoms by placing electrons into orbitals. 2 electrons in each. Starting with the lowest energy orbitals 1s and building up. This is the "aufbau" principle (building up in German).

To accomplish this we need to know the energies. Now that we are not in Hydrogen our orbitals energies are not exactly our hydrogen energies. Now all the orbitals with the same  $n$  are not degenerate. The energies increase as  $l$  increases. Therefore the order is

$$\epsilon_{ns} < \epsilon_{np} < \epsilon_{nd} \dots$$

So in filling up the orbitals we want to use the order

$$1s < 2s < 2p < 3s < 3p$$

We then encounter situations in which we have several electrons to put into degenerate orbitals. Say in carbon. We have 2  $p$  electrons and three orbitals. Where to put them? It turns out that the energy is lower if they do not have paired spins. Thus we want to put them in different orbitals first before we put them in the same orbital where we have to pair the spins. This leads to different properties for different elements. Materials with unpaired electrons are “paramagnetic” and they interact strongly with a magnetic field. Materials with no unpaired electrons are “diamagnetic” and have a weak repulsive interaction with magnetic fields.

We can then build things up until we get to the 3d orbitals. These end up very close in energy to the 4s orbitals. We find that energy of 4s is slightly lower than 3d. So we fill the 4s first. However, at some point we have experimental evidence that is better predicted from a different orbital configuration so we make exceptions to these rules. There are many, but they tend to occur in the same places. The elements have structures in which they have either  $\frac{1}{2}$  filled or completely filled shells. Thus the structure for Cr is  $[\text{Ar}]4s^1 3d^5$  and Cu is  $[\text{Ar}]4s^1 3d^{10}$ .

The same trend is followed in the next row with the 4d levels. The energy levels of the 4f orbitals are significantly different from the other  $n=4$  electrons and they slip in between 6s and 5d. Thus the full order is

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p$$

Some exceptions are less obvious

$$\text{U is } [\text{Rn}]5f^4 6d^1 7s^2$$