Lecture 21

It is fairly easy to write down an antisymmetric wavefunction for helium since there are only two orbitals, and therefore only two combinations to worry about, but things get complicated quickly when you consider atoms with three or more electrons. John Slater of MIT introduced **the use of determinants to construct antisymmetric wavefunctions.**

BUT ... WHAT is a DETERMINANT? Consider a 2 x 2 matrix, $\begin{matrix} a & b \\ c & d \end{matrix}$. Its determinant,

symbolized by $\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc$ Note two properties of these determinants that are useful in evaluating determinants. First, if you interchange the rows or columns of the matrix, the sign of the determinant changes. Thus we see that

$$\begin{vmatrix} c & d \\ a & b \end{vmatrix} = cb - ad = -\begin{vmatrix} a & b \\ c & d \end{vmatrix}$$

Second, if any two rows or columns are identical the determinant is 0. Thus

$$\begin{vmatrix} a & b \\ a & b \end{vmatrix} = ab - ab = 0$$

How do we construct a wavefunction using determinants? First we construct a matrix of spin orbitals. In the first row of the matrix, we put the orbitals that the first electron can occupy, and assign the first electron to them. This is the same as saying that the first electron could be in any one of these orbitals. Thus for helium we have two orbitals, $1s\alpha$ and $1s\beta$. The first row of the matrix now becomes

$$1s\alpha(1) \quad 1s\beta(1).$$

In the second row of the matrix we put the same orbitals, but assign them to the second electron, since the second electron also could be in these orbitals. Thus the second row of our matrix becomes

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

The wavefunction is the determinant of the matrix,

$$\psi_{He} = \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} = 1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1),$$

which is the antisymmetric wavefunction we obtained earlier. **All wavefunctions generated by determinants will be antisymmetric**. We can see this because interchange of electrons in the wavefunction is equivalent to interchanging rows in the matrix, which changes the sign of the wavefunction.

The wavefunction as we have written it is not normalized. To normalize it we need to multiply it by $2^{-1/2}$, so the overall wavefunction is

$$\psi_{He} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix}$$

A wavefunction generated this way is called a **determinantal wavefunction.**

What about the case of lithium? Let's use the determinantal method to find an appropriate wavefunction. Let's start with our earliest guess that the ground state of lithium is composed of three 1s orbitals,

$$\psi_{Li} = 1s(1)\ 1s(2)\ 1s(3).$$

In this case the first two terms in our first row will be $1s\alpha(1)$, $1s\beta(1)$, but the third term will have to be $1s\alpha$ or $1s\beta$ as well, since we have no other choices for spin states. We'll choose $1s\alpha(1)$.

Our first row now becomes

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

Now in the second and third rows we put electrons 2 and 3, respectively, in the same orbitals. Our wavefunction now becomes

$$\psi = \frac{1}{\sqrt{3}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 1s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 1s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 1s\alpha(3) \end{vmatrix}$$

But notice now that our first and third columns are identical. We have already noted that if two rows or columns of a matrix were identical, that the determinant is 0. Therefore this wavefunction built from three 1s orbitals is also zero. In other words the probability is zero that such a wavefunction can exist for lithium.

This is equivalent to the prediction of the Pauli exclusion principle as we know it. Remember that according to this principle, no two electrons can have the same four quantum numbers. But what are the three sets of quantum numbers we just used to try to describe the lithium ground state?

$$1s\alpha = \psi_{100\frac{1}{2}}$$

$$1s\beta = \psi_{100-\frac{1}{2}}$$

and

$$1s\alpha = \psi_{100\frac{1}{2}}.$$

So this set of orbitals which yields a determinantal wavefunction of 0, also has two electrons with the same set of quantum numbers.

In fact we will see that this is a general rule. **Unless all the spin orbitals we put in a row of our matrix are different, two of the columns will be the same, the determinant will**

be zero and therefore the wavefunction will vanish. If the orbitals are not all different, then

two must be the same, and if their spin orbitals are the same, their quantum numbers will be the

same. Thus we see that the sixth postulate yields the following conclusion: If two electrons in

an atom have the same quantum numbers, the wavefunction of the atom will be identically zero.

This is the Pauli Exclusion Principle as we learned it in General Chemistry.

To actually construct our Li wavefunction, we construct a matrix with the three lowest

available spin orbitals, $1s\alpha$, $1s\beta$ and $2s\alpha$. Our first row will be

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

and our second and third rows will put our second and third electrons, respectively, in the same

orbitals. Our determinantal wavefunction is

$$\psi_{Li} = \frac{1}{\sqrt{3}}\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$

How do we calculate the determinant of a 3 x 3 matrix? If our matrix takes on the general form

$$\begin{matrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \\ c_1 & c_2 & c_3 \end{matrix}$$

then our determinant is given by the linear sum of three two by two determinants and is equal to

$$\begin{vmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \\ c_1 & c_2 & c_3 \end{vmatrix} = a_1\begin{vmatrix} b_2 & b_3 \\ c_2 & c_3 \end{vmatrix} - a_2\begin{vmatrix} b_1 & b_3 \\ c_1 & c_3 \end{vmatrix} + a_3\begin{vmatrix} b_1 & b_2 \\ c_1 & c_2 \end{vmatrix}$$

A two by two determinant has two terms, so a three by three determinantal wavefunction will

have six terms. Why the heck do we need six terms? Let's start out by writing one version of

our ground state wavefunction,

$$\psi = 1s\alpha(1)\ 1s\beta(2)\ 2s\alpha(3).$$

This wavefunction has the flaw that it distinguishes between the three electrons, because it

identifies specific electrons with specific orbitals. To write a wavefunction in which all

electrons are equivalent, we need to include all the ways that the three electrons can be in the three orbitals. This results in a total of six different configurations. The only antisymmetric combination of these six configurations is given by the Slater determinant, and when written out in full is

$$\psi_{Li} = 1s\alpha(1)1s\beta(2)2s\alpha(1) - 1s\alpha(1)1s\beta(3)2s\alpha(2) + 1s\alpha(3)\,1s\beta(1)\,2s\alpha(2)$$

$$- 1s\alpha(2)\,1s\beta(1)2s\alpha(3) + 1s\alpha(2)1s\beta(3)2s\alpha(1) - 1s\alpha(3)1s\beta(2)2s\alpha(1).$$

Note that when we had two electrons and two orbitals our antisymmetric wavefunction took only two terms. Going to three electrons meant that we had to juggle six terms. In general we will find that an atom with n electrons will require n! terms. Obviously with such a huge number of terms it would be very time consuming to identify all the required configurations even without the complication of having to find the one that is antisymmetric. The task would be nearly impossible without the simplification offered by the Slater determinant. The Slater determinant can also be used to construct excited state wavefunctions, by using a set of orbitals in which one or more is not in the lowest available orbital.

How do we write a determinantal wavefunction for a n electron atom? First we list our n orbitals, $\phi, \phi_2, ..., \phi_n$. FOR EXAMPLE IN THE CASE OF BE WITH FOUR ELECTRONS, WHAT SPIN ORBITALS WOULD WE USE? [$1s\alpha, 1s\beta, 2s\alpha, 2s\beta$]. Now we construct our matrix. The first row is all n orbitals with electron 1 in them. The second row is all n orbitals with electron 2 in them. This is continued until we have one row for each electron, i.e.,

$$
\begin{array}{ccccc}
\varphi_1(1) & \varphi_2(1) & \varphi_3(1) & ... & \varphi_n(1) \\
\varphi_1(2) & \varphi_2(2) & \varphi_3(2) & ... & \varphi_n(2) \\
& \cdot & & & \\
& \cdot & & & \\
\varphi_1(n) & \varphi_2(n) & \varphi_3(n) & ... & \varphi_n(n)
\end{array}
$$

Let's construct the matrix for beryllium. WHAT WOULD THE FIRST ROW BE? THE SECOND ROW?

Thus our Slater matrix for beryllium is

$$1s\alpha(1) \quad 1s\beta(1) \quad 2s\alpha(1) \quad 2s\beta(1)$$
$$1s\alpha(2) \quad 1s\beta(2) \quad 2s\alpha(2) \quad 2s\beta(2)$$
$$1s\alpha(3) \quad 1s\beta(3) \quad 2s\alpha(3) \quad 2s\beta(3)$$
$$1s\alpha(4) \quad 1s\beta(4) \quad 2s\alpha(4) \quad 2s\beta(4)$$

To get the antisymmetrized wavefunction we just take the determinant of our matrix. The only step we have left is to normalize the wavefunction. This is simple. For an n electron atom we simply multiply our Slater determinant by $\dfrac{1}{\sqrt{n}}$. WHAT WILL OUR NORMALIZATION CONSTANT FOR BE BE?

<u>Lecture 22</u>

When we use our Slater determinants to determine the proper form for the ground state wavefunctions the atomic orbitals we use are not hydrogen-like orbitals, but the correct orbitals for that particular atom. For helium we used the variational method to approximate the correct orbitals. This yielded a 2% error, which is not acceptable in atomic and molecular calculations. To obtain better results, we use a form of variational method called the Hartree-Fock approximation.

The physical basis of the **Hartree-Fock** method can be summarized as follows. We know that the effect of the interelectron term, $\dfrac{e^2}{4\pi\varepsilon_0 r_{12}}$, is important in determining the energy of the helium atom. **Maybe our one electron wavefunctions will be more accurate if, instead of ignoring the interelectron repulsion, they include the potential of our electron interacting with the other electron at its average interelectron distance.** In other words, we replace the variable r_{12}, which is equal to r_1-r_2, by the term r_1 - $<r_2>$, which we know how to calculate. Then the term for r_2 in the interelectron repulsion term in the Hamiltonian is a constant and the interelectron repulsion term is equal to $\dfrac{e^2}{4\pi\varepsilon_0(r_1 - <r_2>)}$. Notice that since $<r_2>$ is a constant, a one electron Hamiltonian containing this term is now a function of one variable. As a result we are now capable of treating one electron wavefunctions which include the interelectron repulsion.

Let's **show how the Hartree-Fock approach works by returning to helium**. We start by writing our two-electron wavefunction as the product of two one-electron orbitals,

$$\psi(r_1, r_2) = \phi_1(r_1)\phi_2(r_2)$$

The probability distribution of the electron in orbital 2 is given by

$$\phi^*(r_2)\phi(r_2)\ r^2 dr_2.$$

Since this is a distribution in space of a charged particle, the electron, we can view this as the charge distribution. Because of this, **the average, or effective, potential that electron 1 experiences due to the position of electron 2 can be written as**

$$V_1^{eff}(r_1) = \int \phi_2^*(r_2) \frac{e^2}{4\pi\varepsilon_0 r_{12}} \phi_2(r_2) r_2^2 dr_2$$

We now define the Hamiltonian for a single electron as

$$\hat{H}_1^{eff} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} + V^{eff}(r_1)$$

The Schrödinger equation for this effective one electron Hamiltonian is

$$\hat{H}_1^{eff}(r_1)\phi_1(r_1) = \varepsilon_1\phi_1(r_1)$$

and is called the **Hartree-Fock equation**, in this case for the helium atom. In this equation, ε_1 is called the **orbital energy**, the energy of the single electron orbital. It is important to realize that **once the orbital wavefunctions are determined by solving this Schrödinger equation, the total energy is then given by**

$$E = \int\int dr_1 dr_2 \phi_1^*(r_1)\phi_2^*(r_2)\hat{H}\phi_2(r_2)\phi_1(r_1)$$

where $\hat{H}$ is the complete helium Hamiltonian,

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r_{12}}\right)$$

If we plug this into our equation for E, we can break it up into three integrals,

$$E = \int dr_1 \phi_1^*(r_1)(-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1})\phi_1 + \int dr_2 \phi_2^*(r_2)(-\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2})\phi_2 + \int\int dr_1 dr_2 \phi_1^* \phi_2^* \frac{e^2}{4\pi\varepsilon_0 r_{12}}\phi_2\phi_1$$

We represent this sum as

$$E = I_1 + I_2 + J_{12}.$$

What are the meanings of these three terms? Let's consider I_1 and I_2 first.

$$I_1 = \int dr_1 \phi_1^*(r_1)(-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1})\phi_1$$

Note that the Hamiltonian for this term is just the hydrogen-like Hamiltonian for He. Helium has

hydrogen-like orbitals only when it is singly ionized. This means that I_1 and I_2 are the energies

the electrons would have if they were in orbitals of the helium ion, i.e., the energies they would

each have if there was no other electron. This means that the third integral

$$J_{12} = \int\int dr_1 dr_2 \phi_1^* \phi_2^* \frac{e^2}{4\pi\varepsilon_0 r_{12}}\phi_1\phi_2$$

contains the whole effect of the two electrons interacting with each other. It is called the

coulomb integral.

How do we solve the Hartree-Fock equation? First of all **the angular part of the**

Hartree-Fock equation is exactly the same as that for the hydrogen like atom, since our

effective interelectron potential depends only on r and not θ or ϕ. This means that we can write

our Hartree-Fock orbitals as

$$\phi(r_1) = R(r)Y_l^m(\theta,\phi).$$

If we substitute this wavefunction in our Hartree-Fock equation, we obtain a radial equation,

$$[-\frac{\hbar^2}{2m_2 r_1^2}\frac{d}{dr_1}(r_1^2\frac{d}{dr_1}) - \frac{Ze^2}{4\pi\varepsilon_0 r_1} + \frac{l(l+1)}{2m_e r_1^2} + V^{eff}(r_1)]R(r_1) = \varepsilon_1 R(r_1)$$

It appears that we've reduced the Hartree-Fock equation to an ordinary differential equation that the theoretician can then solve using the same methods that yield the solution to the hydrogen atom. But there's a problem here. Remember that

$$V^{eff}(r_1) = \int dr_2 \phi_2^*(r_2) \frac{e^2}{4\pi\varepsilon_0 r_{12}} \phi_2(r_2).$$

What this means is that the solution to our equation is part of our Hamiltonian. **We need to know our answer even before we can start!**

It is this last statement of the problem that suggests how we proceed. The **procedure for solving the Hartree-Fock equation** is as follows.

1) Choose a trial function ϕ. This will usually be a product or linear combination of hydrogen-like orbitals.

2) Calculate V_1^{eff} with the trial function.

3) Calculate a new ϕ by solving the radial equation.

4) Compare the old and new ϕ's.

5) If the new orbital wavefunction is different from the old, we take the new orbital ϕ, calculate a new V_1^{eff} and repeat the process until at step four there is no discernible difference between the old and new orbitals.

At this point the calculation is finished, the initial and final orbitals are consistent with each other, and for this reason, this method of solving the Hartree-Fock equation is called the **self-consistent field method**. The Hartree-Fock Method gives an energy of E = -

$2.8617 \dfrac{me^4}{(4\pi\varepsilon_0)^2 \hbar^2}$ as the energy of the helium atom, compared with the best experimental value

of $E = -2.9033 \dfrac{me^4}{(4\pi\varepsilon_0)^2 \hbar^2}$.

It is interesting to ask at this point what **the source of the difference between the exact energy and the self consistent field energy** is. Remember that we assumed at the beginning that

$$\psi(r_1, r_2) = \phi(r_1)\phi(r_2).$$

This product implies that the positions of the electrons are completely independent. But **this is not a valid assumption**. Remember that because the electrons have the same charge they repel each other, so one electron is less likely to be in the region occupied by the other electron. This means that the motions of the electrons are not entirely independent. We say that **the electron positions are correlated**. We call the difference between the exact energy and the self-consistent field energy the **correlation energy**, i.e.,

$$\text{Correlation energy} = E_{exact} - E_{SCF}.$$

The calculation of these correlation energies that would allow calculation of atomic and molecular energies without further correction, is an extremely active field in computational chemistry.

<u>Lecture 23</u>

At this point we've shown the power of the sixth postulate, the Pauli exclusion principle, in predicting **ground state atomic wavefunctions**. For example, in carbon with its six electrons, two electrons go into the 1s orbital, and two go into 2s orbitals, which means that the remaining two go into 2p orbitals for a ground state configuration of $1s^2 2s^2 2p^2$.

Unfortunately this is not an unambiguous description of the ground state. While the 1s and 2s orbitals are filled and can have only one configuration, the 2p orbitals can hold up to six electrons, and the two 2p electrons could be in one of two distinguishable configurations, $2p_x \, 2p_y$ or $2p_x^2$. These configurations will not be equivalent in energy, since two electrons in the same orbital will be closer to each other than electrons in two different orbitals. We need to find a way to distinguish between these two configurations without having to write them out fully, and a way to determine which configuration is the ground state configuration.

We can make **a simple physical argument that allows us to determine the ground state configuration.** Remember that for the helium atom, the interelectron repulsion term is given by

$$V = \frac{e^2}{4\pi\varepsilon_0 r_{12}} = \frac{e^2}{4\pi\varepsilon_0 |r_2 - r_1|}$$

where $|r_2 - r_1|$ is the separation between the two electrons. This tells us that **for the helium atom the interelectron repulsion is lowest when the electrons are as far apart as possible**. For multielectron atoms, the interelectron term is given by a sum of pairwise interelectron potentials, i.e.,

$$V = \sum_{i=2}^{n} \sum_{j=1}^{n-1} \frac{e^2}{4\pi\varepsilon_0 |r_i - r_j|}, i \neq j.$$

In other words the interelectron repulsion term for a multielectron atom is obtained by taking the repulsion term for every combination of two electrons and summing them. **This term is minimized when all of the electrons are as far from each other as possible**.

Now consider the carbon atom in the configuration $2p_x^2$. Because both electrons are in the same orbital, they are located in the same region of space. However for the configuration $2p_x$ $2p_y$, the electrons are separated and the interelectron term will be lower in energy. This suggests that **in general, the ground state will be the one in which the pairing of electrons within a degenerate set of orbitals is minimized**. So for nitrogen, for example, we would expect the configuration

$$N \ 1s^2 \ 2s^2 \ 2p_x \ 2p_y \ 2p_z$$
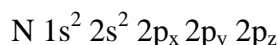
which results in the widest possible spatial distribution of electrons.

Writing out these electron configurations as we have done above gets a bit bulky and it is convenient to have a shorthand notation that represents these states unambiguously. In addition we can state a simple rule to determine atomic ground states in terms of this shorthand notation.

These shorthand notations are called **term symbols**. **A term symbol takes the general form $^{2S+1}L_J$, where S is the total spin angular momentum of the atom, L is the total orbital angular momentum, and J is the total angular momentum of the atom**. A typical term symbol might be $^2P_{3/2}$, which is read as doublet P three halves. The doublet indicates that S = 1/2 since our setting the superscript 2 equal to 2S + 1 and solving for S yields S = 1/2. Note that **the total orbital angular momentum is represented by a letter**. In analogy to the orbital angular momentum of single electrons where we have $l = 0$ is s; $l = 1$ is p; $l = 2$ is d; $l = 3$ is f and

so on, **for total orbital angular momentum we have L = 0 is S, L = 1 is P, L = 2 is D, L = 3 is F, etc.**

Note that all of the quantities that are involved in term symbols, S, L, and J, are vector quantities. In addition, note that **this form of the term symbol implies that L and S are well defined quantities, i.e., that there are quantum numbers from which these values can be directly determined**. What we mean here by well-defined quantities is that if a quantity is well defined then its value when measured will be one of several values which is stable for a substantial time. If the value is continually fluctuating it is not well defined. In general, for multielectron atoms this is not a valid assumption for L and S. **In general, among the three quantities L, S, and J, only J will truly be an eigenvalue**. In other words, we will be able to make observations that reflect the value of the total angular momentum J or which depend on there being a definite value of J, but not ones that yield L or S exactly. **However, for the specific case of light atoms, where the atomic number Z < 40, L and S are so close to being well defined, that we can treat them as if they are.**

How do we determine the total spin angular momentum, total orbital angular momentum, and total angular momentum for an atom? For light atoms, the quantities L and S are defined by

$$L = \sum_i l_i$$

and

$$S = \sum_i s_i$$

In other words, when the total orbital angular momentum is a well defined quantity, it is given by the sum of the orbital angular momenta for each of the electrons in the atom, and when the

total spin angular momentum is a well defined quantity, it is given by the sum of the spin angular momenta for each of the electrons in the atom. Finally J, the total angular momentum for the atom, is given by

$$J = L + S.$$

This scheme, where the total orbital angular momentum, L, and the total spin angular momentum, S, are summed to give the total angular momentum, J, is called either **Russell-Saunders coupling** or **spin-orbit coupling**. Again, this scheme is valid only for $Z < 40$.

The alternative means of determining total angular momentum is good for $Z > 40$, and is called **j-j coupling**. According to this scheme, **the total angular momentum is first determined for each electron** by the relation

$$j_i = l_i + s_i,$$

and then **the total angular momentum for the atom is determined by summing the total angular momenta for the electrons**, i.e.,

$$J = \sum_i j_i$$

It is a useless, but interesting piece of trivia that a 1950's physicist turned science fiction novelist chose J. J. Coupling as his pen name.

Now back to our term symbols. To write a term symbol for a given electronic configuration we need to know, L, S, and J. Unfortunately, these are difficult to determine directly. To see this consider our definition for L,

$$L = \sum_i l_i$$

Note that **we are adding vector quantities**.

Addition of vector quantities does not yield

unique results when, as in our case, only the

magnitude of the vector is specified.

Consider the case where $l_1 = 3$, and $l_2 = 1$.

There are many ways to add these two

vectors. Two possible ways are when the

vectors are aligned in the same direction and when the vectors are aligned in opposite directions.

Notice that even though the same two vectors are added the sums are very different.

As a result **we resort to an indirect method of determining L, S, and J**. What we will

do is **determine M, M$_S$ and M$_J$, and deduce L, S, and J from them**. The reason that this

procedure is superior is that **since m, and m$_s$ are the z components of their respective angular

momenta, they are scalars**. Therefore the sums

$$M = \sum_i m_i = \sum_i l_{zi}$$

and
$$M_s = \sum_i m_{si}$$

are easy to determine. **Since the rules that relate the values of z components of the angular

momentum to the angular momentum itself are simply defined, i.e.,**

$$M = 0, \pm 1, \pm 2, \dots, \pm L$$

and
$$M_S = 0, \pm 1, \pm 2, \dots, \pm S,$$

we should be able to deduce the values of L and S. We are able to deduce L and S because if an atom exists with a certain L state, all of the M states that go with that value of L must be present.

Let's consider as a first example an atom with an ns^2 configuration. **We will only need to consider the valence electrons of an atom since L and S are both 0 for a filled shell**. The procedure for determining the term symbol is first to **set up the following table**:

m_1	m_{s1}	m_2	m_{s2}	M	M_S
0	1/2	0	-1/2	0	0

The left side of the table consists of the value of m and m_s for each electron. For an ns^2 atom in the ground electronic state, there is only one possible set of these quantum numbers, with both electrons in the ns orbital, one having spin up and the other spin down. This means that m = 0 for both electrons, while m_s = 1/2 for one and -1/2 for the other. **The right side consists of the z component of the total orbital angular momentum for the atom, M, and the z component of the total spin angular momentum for the atom, M_S.** In this case $M = m_1 + m_2 = 0$, and $M_S = m_{s1} + m_{s2} = 0$. To deduce L we note that the lowest value of L which could give rise to M = 0 is L = 0, so we deduce that L = 0. Similarly $M_S = 0$ implies that S = 0. All that remains is to determine J. Since $M_J = M_S + M = 0$, we can deduce that J = 0. Thus for this filled subshell, L = 0, S = 0, and J = 0, and our term symbol is $^1S_0$.

This result is not just a special case. In general, **whenever your electron configuration consists only of completely filled subshells, L = 0, S = 0 and J = 0**. This is wonderful news since it means that for an atom like C, which has the configuration $1s^2\ 2s^2\ 2p^2$, we need only

consider the 2p electrons in determining our term symbols. Let's make up our table for carbon.

There are 15 possible sets of quantum numbers m and m_s. They are

m_1	m_{1s}	m_2	m_{2s}	M	M_S	M_J
1	1/2	1	-1/2	2	0	2
1	1/2	0	1/2	1	1	2
1	1/2	0	-1/2	1	0	1
1	1/2	-1	1/2	0	1	1
1	1/2	-1	-1/2	0	0	0
1	-1/2	0	1/2	1	0	1
1	-1/2	0	-1/2	1	-1	0
1	-1/2	-1	1/2	0	0	0
1	-1/2	-1	-1/2	0	-1	-1
0	1/2	0	-1/2	0	0	0
0	1/2	-1	1/2	-1	1	0
0	1/2	-1	-1/2	-1	0	-1
0	-1/2	-1	1/2	-1	0	-1
0	-1/2	-1	-1/2	-1	-1	-2

| -1 | 1/2 | -1 | -1/2 | -2 | 0 | -2 |

Note that since electrons are indistinguishable that the sets of quantum numbers

$$0 \quad 1/2 \quad -1 \quad 1/2 \quad \text{and} \quad -1 \quad 1/2 \quad 0 \quad 1/2$$

are identical, and only one of these configurations needs to be written down.

Now we need to use our table to determine the different term symbols that arise when we put two electrons into 2p orbitals. It is usually easiest to begin with the highest value of M. In this case the highest is M = 2. Note that there is only one value of M_S when M = 2, M_S = 0. We immediately conclude that S = 0 for this state. Now for L. If M = 2, then the lowest value of L which can give rise to this M is L = 2. So this state has L = 2, and S = 0 and is a ^1D state. FOR L = 2 WHAT ARE THE ALLOWED VALUES OF M? [2, 1, 0, -1, 2] This means that there are four other configurations of our ^1D state which have these values of M, and M_S = 0. If we label these five configurations as ^1D configurations, we have 10 remaining.

The largest value of M remaining is M = 1, which suggests that L = 1. WHAT ARE THE VALUES OF M WHICH ARISE FROM L = 1? [1,0,-1] Now notice that if we look at the values of M_S which go with M = 1, that we have three different configurations, M_S = 0, 1, and -1. If we look at M = 0, we find the same three values of M_S, and looking at M = -1 gives us the same three values of M_S. WHAT DOES S HAVE TO BE IN ORDER FOR M_S TO RANGE FROM -1 TO 1? [1] Thus for these 9 configurations, we have L = 1 and S = 1, and our term symbol is ^3P. Why do we have 9 configurations which are labeled ^3P? The answer is that we have three different orientations for the orbital angular momentum when L = 1, which are each split into three different configurations by the presence of three different orientations of the spin angular momentum. If

we label these 9 configurations as ^3P, then we have one remaining, with M = 0 and M_S = 0. The lowest values of L and S which yield these values are L = 0 and S = 0, a ^1S state.

Notice that we have said nothing about the **total angular momentum J** yet. We will use our values of M_J to assign values of J, just as we used values of M and M_S to assign the values of L and S. First **we need to determine the range of J values associated with given values of L and S**. Remember that we obtain J by adding the two vectors, L and S, which represent the total orbital and spin angular momenta. Remember also that the magnitude of the sum of the two vectors depends on the orientation of the two vectors. As we said earlier, the largest sum will arise when the two vectors are aligned as much as possible in the same direction. Thus the **maximum value of J will be L + S**, with the spin and orbital angular momenta aligned. The minimum sum of the two vectors will arise when the two vectors are aligned in opposite directions. It follows that **the minimum value of J will be |L - S|**, where we take the absolute value because it is the magnitude of J we are interested in.

Lets consider our ^1D state first. For this state L = 2 and S = 0, so we expect only one value of J, J = 2 + 0 = 2. WHAT VALUES OF M_J DO WE EXPECT FOR A J = 2 STATE? [2, 1, 0, -1, -2] Note these are the values of M_J associated with our five ^1D configurations, so all five configurations have J = 2, and the complete term symbol for these configurations will be $^1D_2$. Now lets turn to our ^3P configurations. For these configurations L = 1 and S = 1. WHAT ARE THE POSSIBLE VALUES OF J FOR A ^3P STATE? [J = 2 , 1, 0] WHAT ARE THE POSSIBLE VALUES OF M_J, WHEN J = 2? Notice that five of our ^3P configurations have these values of M_J, and therefore we label these five configurations as $^3P_2$ configurations. WHAT ARE THE POSSIBLE VALUES OF M_J

WHEN J = 1? Notice that three of our remaining ^3P configurations have these values of M_J, and we label these configurations as $^3P_1$ configurations. Our remaining ^3P configuration has $M_J = 0$. What will J be for this state? Therefore the term symbol for this state will be $^3P_0$. Finally our ^1S state has L = 0 and S = 0. WHAT IS J? Thus our final term symbol will be $^1S_0$. Our fifteen configurations have resulted in five electronic states for our np^2 configuration, $^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$, and $^1S_0$. Note that what we have done here is identified the different electronic states which go with each configuration.

What we have not yet done is to **determine the relative energies of these states**. We can order these states by calculating their energies using quantum mechanical methods we have already covered, and a great deal of computer time, but it is also possible to quickly order them **according to three rules established by the German spectroscopist Friedrich Hund**.

The rules are as follows:

1. The state with the largest value of S is the most stable, and stability decreases with decreasing S.

2. For states with the same value of S, the state with the largest value of L is the most stable.

3. If states have the same value of L and S, then, for a subshell which is less than half filled, the state with the smallest value of J is the most stable; for a subshell which is more than half filled, the state with the largest value of J is the most stable.

Let's apply these rules to carbon. Our five states are $^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$, and $^1S_0$. There are three states, $^3P_2$, $^3P_1$, $^3P_0$, which are triplets, with S = 1, so according to our first rule one of

these will be the stablest state. All three of these are P states with $L = 1$, so we can't use our second rule to distinguish them. To use our third rule, we must first determine whether the subshell is more or less than half filled. Since an p subshell can hold up to six electrons, our np^2 state is less than half filled and our rule states that the lowest energy state will be that with the smallest value of J. Thus $^3P_0$ is the ground state for C, $^3P_1$ is the first excited state, and $^3P_2$ is the second excited state. This leaves two states, $^1D_2$ and $^1S_0$, both of which are singlets, so we can't use our first rule. Our second rule tells us that the state with higher L will be lower in energy, so our third excited state will be $^1D_2$, and our fourth excited state will be $^1S_0$.

To see that this ordering of states matches our original common sense approach lets just look at the configurations which go with $^1S_0$, our highest state, and $^3P_0$, our lowest state. The $^3P_0$ state has the configuration

$$0 \qquad 1/2 \qquad -1 \qquad 1/2$$

which has electrons in two different orbitals and the same spin. This is exactly what we figured our lowest state should look like. The $^1S_0$ state has the configuration

$$0 \qquad 1/2 \qquad 0 \qquad -1/2$$

which has both electrons in the same orbital with opposing spins. Again, this is exactly what we predicted based just on the idea that the electrons should be as far removed from each other as possible.

Lecture 26

We've now completed our treatment of the quantum mechanics of the atom. I'd like to spend just a little time to review some of the consequences of our results. The most chemically significant consequences of our results are the aufbau principle, which results in the structure of the periodic table, and the periodic trends in size and ionization energy.

The **aufbau principle** is simple. It says simply that **we obtain the ground state electronic configurations of atoms by filling our orbitals starting with the orbital of lowest energy, and when this is filled moving on to the next orbital, and so on. The Pauli principle tells us that we are restricted to 2 electrons in each spatial orbital**. As a result, each s subshell can hold two electrons, each p subshell 6 electrons, each d subshell 10 electrons and so on. Our Hartree-Fock calculations tell us that the energies of the orbitals of multielectron atoms in the absence of an external field depend on both n and *l*, i.e., the energy depends not just on the shell but on the subshell as well. This yields the structure of the first two rows of the periodic table in an extremely straightforward way. When we get to the third row, we need to explain the absence of electron configurations involving d orbitals. The answer here is simply that **when we calculate the energies according to the Hartree-Fock method, that the energies of orbitals follow the order 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p**. In other words there is some factor that allows the energy of a 4s orbital to be lower in energy than a 3d. We can see what this is if we look at the radial functions for 3d and 4s. Even though the bulk of the electron density is closer to the nucleus for 3d than for 4s, remember that all s orbitals have some electron density very close to the nucleus. It is the presence of this density close to the nucleus, called core penetration, that

brings the energy of ns orbitals slightly below n-1 d orbitals. Note however, that the energy difference is small.

Our results can also explain periodic trends. First of all, we note that all species with the same valence electron configuration will have similar chemical properties. This is the basis of the chemical group numbers. One property that is important is the size of atoms. There are two opposing factors that control **atomic sizes**. The first is the value of the principal quantum number n. Remember that **as n increases the average radius, <r>, increases**. The second is that **as the effective nuclear charge increases, coulomb attraction causes the atomic radius to shrink**. The experimental observations about atomic size are that as one goes down a chemical group, the size of the atom increases, while if one goes across a period, the size of the atom decreases. In short, as one goes diagonally from the bottom left of the periodic table to the upper right, the atomic radius decreases.

This is easy to explain. As one goes down a group, because of shielding, the effective nuclear charge stays essentially constant, but the principle quantum number increases, so the radius of the atom increases. In contrast, as one moves across the periodic table, the principle quantum number stays constant, but the effective nuclear charge increases, so the atomic radius decreases.

Another important periodic property is the **ionization energy**. The **ionization energy is the energy necessary to remove an electron from an atom or ion in its ground electronic state**. The **first ionization energy is the energy necessary for the reaction**

$$A \rightarrow A^+ + e^-,$$

while the second ionization energy is the energy necessary for the reaction

$$\mathbf{A^+ \rightarrow A^{+2} + e^-}.$$

It is observed that **the first ionization energy decreases as we go down a group, and increases as we go across a period**. Once again we can explain these observations from our previous results. The decrease in ionization energy as one goes down a period is because the effective nuclear charge exerted on the valence electrons remains approximately constant as we go down a period, but the distance between the nucleus and the valence electrons increases. Remember that Coulomb's law is

$$V(r) = -\frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

If the charges are staying the same and the radius is increasing as we go down the group the energy necessary to remove the electron must be decreasing as well. The general trend that the ionization energy increases across the periodic table can be explained when we realize that the effective charge is increasing across the periodic table, at the same time that the atomic radius is decreasing. Both of these factors serve to increase the energy necessary to remove the electron from the atom. There are some deviations from this general trend. For example when we go from Be which has a $2s^2$ configuration to B which has a $2s^2$ 2p configuration the ionization energy goes down slightly. This is a result of the special stability associated with filled subshells. There are also anomalies which indicate that **half filled shells have a special stability as well**. Thus when we go from N with the configuration $2s^2$ $2p^3$ to O with configuration $2s^2$ $2p^4$, the ionization energy decreases slightly.

Finally, we note that if we look at the sequence of first, second, third ionization energies, that **there is a gradual increase in ionization energies until an ion is obtained with a noble**

gas configuration, at which point the ionization energy jumps drastically. For example C

has a first ionization energy of 11.26 eV, a second ionization energy of 24.38 eV, a third of 47.88

and a fourth of 64.49 eV. The fourth ionization gives C^{+4} the noble gas structure of He. The

fifth ionization energy is 392 eV. The reason for the gradual increase in ionization energy is the

increase in effective nuclear charge as electrons are removed. The reason for the drastic increase

when the fifth electron is removed is that we are moving down one principle quantum number

and in addition to the increase in effective nuclear charge, the radius is much smaller as well, so

the ionization energy jumps drastically.