9 Electron Spin and the Pauli Principle

I will digress and talk about electron spin in general--how it was discovered and what some of its properties are. Then I will go back and treat the lithium atom and see what role electron spin plays.

9.1 Electron Spin

Recall that at the end of our treatment of the hydrogen atom we discussed the Zeeman Effect. If you remember, the hydrogen atom can have a magnetic moment due to the orbital motion of the electron

$$\boldsymbol{\mu} = -\frac{|e|}{2m_e}\mathbf{L}$$

In our discussion of the Zeeman effect, I explained that this magnetic moment would interact with an external magnetic field **B** and add a term to the energy

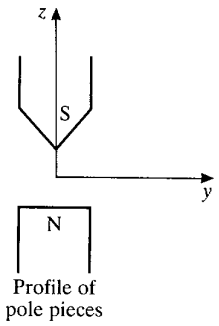
$$U = -\boldsymbol{\mu}\cdot\mathbf{B} = \frac{|e|}{2m_e}\mathbf{L}\cdot\mathbf{B}$$

If we take the magnetic field to be along the *z* axis **B** = B_z then the interaction is

$$U = \frac{|e|B_z}{2m_e}L_z$$

We know that the eigenvalues of the $\hat{L}_z$ operator are $m\hbar$, so the energy levels are split according to their value of the *m* quantum number. (Remember the *m* quantum number represents the projection of **L** on a the space fixed *z*-axis. We know that there are 2*l*+1 values of *m* for every *l*, so a given level is split into 2*l*+1 levels. *l* can take on the values *l* = 0, 1, 2, .)

The magnetic field in this case was assumed to be homogeneous (the same everywhere so each atom in a sample experiences the same field). However, let us consider the case in which we have two magnetic plates shaped something like this.



Let us say that we pass a beam of neutral atoms through such an inhomogeneous magnetic field. Since the magnetic dipole moment is proportional to $\hat{L}_z$ and its eigenvalues are quantized we can write:

$$U = \frac{|e|B_z}{2m_e}m\hbar$$

Using the definition of the force

$$\mathbf{F} = -\nabla U$$

We find that the exerted force in the *z*-direction is given by:

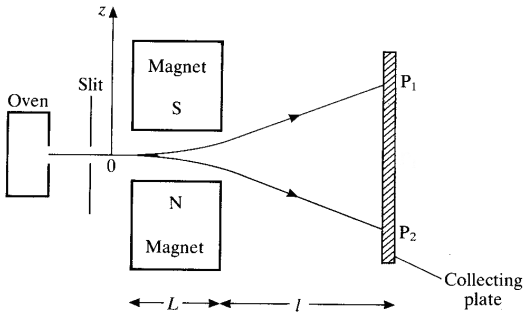
$$F_z = -\frac{\partial U}{\partial z} = -\frac{|e| m\hbar}{2m_e}\frac{\partial B_z}{\partial z}$$

One thus expect that the force on the atoms will split the one beam up into several discrete beams of atoms depending on their *m* quantum number. The one beam should split into 2*l*+1 beams, since that is how many *m* states there are.

In 1922, Otto Stern and Walter Gerlach performed an experiment which was designed to do just that. In the so-called ***Stern-Gerlach experiment*** they used a beam of silver atoms from an oven beam source and sent it through an inhomogeneous magnetic field like the one I have shown schematically, with the field oriented in the *z*-direction.

They expected it to split states with different projections of the angular momentum in the *z*-direction, that is different *m* states.

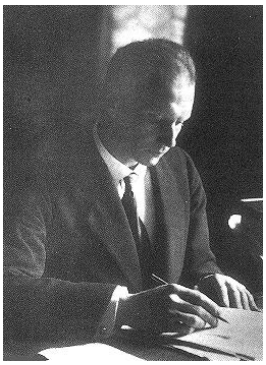
What they observed was the following:



They observed that the original beam of silver atoms only split into <u>*two*</u> beams.

To be able to split into an even number of *m* states, *l* must be half integral, and for there to be exactly two states, *m* must be ± 1/2, since *m* ranges from + *l* to -*l*. The Stern-Gerlach experiment therefore suggests the *existence of half-integral values of the angular momentum.* Recall that our treatment of orbital angular momentum indicated that the only allowable values of *l* were integral values.

[Otto Stern]



[Walther Gerlach]

From these experiments Stern and Gerlach postulated the existence of another type of angular momentum, called ***spin angular momentum***, that could take on half-integral values.

Note that a silver atom has many electrons, so this experiment did not prove that the spin angular momentum of an electron is 1/2. However, it did prove that it must involve half-integral values. A collection of particles each with angular momentum will have some overall angular momentum that is the vector sum of the individual values. There is no way to get a net spin of 1/2 if at least one of the particles had a spin of half-integral value.

Within the quantum mechanical framework we have developed in this course, the existence of spin angular momentum cannot be explained without the introduction of additional hypotheses.

Note: A more sophisticated treatment of quantum mechanics that takes into consideration relativistic effects was developed by Dirac in the early nineteen thirties. From this treatment the concept of spin angular momentum arises naturally. However such a treatment is beyond the scope of this course.

Wolfgang Pauli introduced a way in which spin angular momentum could be incorporated into a non-relativistic treatment of quantum mechanics by taking a few additional postulates. We will follow his approach.

The additional postulates we must include are:

1. ***The spin operator is an angular momentum operator.***

   This may sound trivial, but we are making assumptions based on the results of experiments which deflect atoms in magnetic fields. Such observations are consistent with this postulate but don't prove it. Hence it must be taken as a postulate.

   The definition of what is and isn't an angular momentum is based on the commutator relations. The definition of angular momentum is an operator $\hat{S}$ whose components satisfy the relations

   $$\left[\hat{S}_x, \hat{S}_y\right] = i\hbar\hat{S}_z$$

   $$\left[\hat{S}_x, \hat{S}^2\right] = 0$$

   and the cyclic permutations of this commutator.
   This implies that $\hat{S}^2$ and $\hat{S}_z$ commute and have a common set of eigenfunctions. However, the spin angular momentum in contrast to the orbital angular momentum cannot be represented by the position and momentum operators. It is therefore not possible to write down the spin eigenfunctions in the usual way. In order to represent these functions one has to use the concepts developed by Heisenberg (in the beginning of this course I already mentioned that quantum mechanics can be represented in two different but equivalent ways)

   In the bra-ket notation as introduced by Dirac the orbital angular eigenfunctions are represented by:

   $$|l, m\rangle$$

   which is equivalent to the Schrödinger eigenfunction:

   $$Y_l^m(\theta, \varphi) = N_{nl} P_l^{|m|}(\cos\theta) e^{im\varphi}$$

   The eigenvalue problem as we have seen before

$$\hat{L}^2 Y_l^m(\theta,\varphi) = l(l+1)\hbar^2 Y_l^m(\theta,\varphi)$$

$$\hat{L}_z Y_l^m(\theta,\varphi) = m\hbar Y_l^m(\theta,\varphi)$$

is in Dirac's notation written as

$$\hat{L}^2 |l,m\rangle = l(l+1)\hbar^2 |l,m\rangle$$

$$\hat{L}_z |l,m\rangle = m\hbar |l,m\rangle$$

One could show that the eigenvalues simply depend on the commutation relations and hence will hold true for any angular momentum operator.

In the case for spin angular momentum one can therefore write:

$$\hat{S}^2 |s,m_s\rangle = s(s+1)\hbar^2 |s,m_s\rangle$$

$$\hat{S}_z |s,m_s\rangle = m_s\hbar |s,m_s\rangle$$

As was the case of orbital angular momentum, the value of m_s can range from -*s* to +*s*. However, the allowable values of the quantum number *s* are different than those of orbital angular momentum.

2. A given particle has a unique value of the quantum number s, and is said to have a spin S. The electron is a spin 1/2 particle (s = 1/2).

We therefore have a fixed spin quantum number. This is different from orbital angular momentum where we can have many *l* values. The projection of the spin angular momentum can still vary, but each particle has a unique value of *s*.

Also, its intrinsic magnetic moment is given by

$$\boldsymbol{\mu}_S = -\frac{|e|}{m_e}\mathbf{S}$$

as compared to

$$\boldsymbol{\mu}_L = -\frac{|e|}{2m_e}\mathbf{L}$$

for the orbital moment.

At the present time the existence of particles with spin ranging from 0, 1/2, 1, 3/2, 2, . . . up to higher values such as 11/2 are known. Protons and neutrons also have half-integral spin.

3. All spin operators commute with all orbital operators.

Thus they depend on different variables. One might think of explaining spin classically as the motion of the electron spinning on its axis which would give rise to an intrinsic angular momentum. To do this, we would have to describe the electron as a solid body with spatial extent and would need 3 more coordinates to describe its orientation (in addition to 3 for it's position)

The theory we are considering postulates that the electron behaves as a point that requires only 3 coordinates to fix its position. Thus spin angular momentum is not derived from any position or momentum variable. We cannot write a classical mechanical expression for this operator.

That is, Spin has no classical analog.

Another way to view this is that for other quantum mechanical quantities that we have dealt with, we know from the Bohr Correspondence principle that as the quantum number gets large, the behavior of a quantum mechanical system approaches that of its corresponding classical system. Because the spin angular momentum of electron is limited to 1/2, this can never happen and the Bohr Correspondence Principle does not apply. Spin is therefore entirely a quantum mechanical quantity.

Spin Eigenfunctions

Because spin operator cannot be written as a function of classical mechanical variables, its eigenfunctions do not depend upon classical mechanical variables. It can therefore be difficult to get a feel for the eigenfunctions of the spin operators.

Since there are only two eigenvalues of $\hat{S}_z$ for an electron, there must be only two eigenfunctions, one for each eigenvalue.

$$\hat{S}^2\left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle \qquad \hat{S}^2\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle$$

$$\hat{S}_z\left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle = \frac{1}{2}\hbar\left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle \qquad \hat{S}_z\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle = -\frac{1}{2}\hbar\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle$$

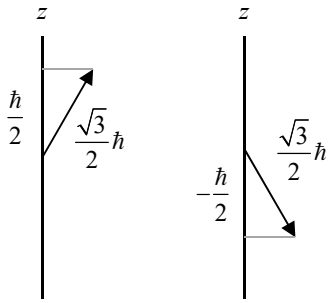
The magnitude of the spin vector is:

$$|S| = \sqrt{s(s+1)}\hbar$$

For $s = \frac{1}{2}$ we find

$$|S| = \frac{\sqrt{3}}{2}\hbar$$

and since the projection of this vector on the *z*-axis can have magnitudes from -*s* to *s*, the only possible values of m_s is ± 1/2 ħ



It can be a little difficult to get a good physical feel for the nature of the eigenfunctions. These functions are discrete functions. They simply represent a spin up or spin down (*i.e*. projection +1/2 or -1/2). In stead of using braket notation the two eigenfunctions of the electron spin are therefore often simplified as spin up, $\alpha = \left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle$, and spin down, $\beta = \left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle$.

Since the spin operators are Hermitian (one could show this from the commutation rules), then the spin eigenfunctions form a complete orthonormal set. In a formal sense we can write the orthonormality as

$$\int \alpha^* \alpha \, d\sigma = \int \beta^* \beta \, d\sigma = 1$$

$$\int \alpha^* \beta \, d\sigma = \int \beta^* \alpha \, d\sigma = 0$$

where σ is called the spin variable and has no classical mechanical analog.

Now that we know about spin eigenfunctions, we should have been using them all along in our discussion of hydrogen and helium.

We postulated that the spin and spatial parts of the wave function are independent. This seems reasonable since the spin eigenfunctions are independent of spatial coordinates. In the Hamiltonian, the spatial operators don't do anything to spin coordinates. In the absence of a field, there are no spin terms in the Hamiltonian (to a high degree of approximation). We can therefore write

$$\psi(x,y,z,\sigma) = \begin{cases} \psi(x,y,z)\,\alpha(\sigma) \\ \psi(x,y,z)\,\beta(\sigma) \end{cases}$$

The complete wave function ψ is called a ***spin-orbital***.

For a hydrogen-like atom, for example, a spin-orbital would be

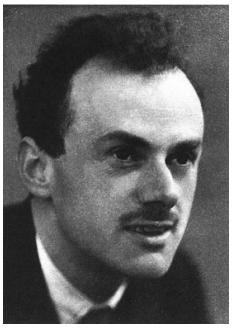
$$\psi_{1,0,0,\frac{1}{2}} = \sqrt{\frac{Z^3}{\pi}} e^{-Zr} \alpha$$

(or the equivalent function with β) in which the forth quantum number in the subscript represents m_s.

Having introduced the concept of electron spin, we are now ready to introduce the ***Pauli Exclusion Principle*.**

You probably remember the Pauli Exclusion Principle in the form of *no two electrons can have all the same quantum numbers*, however it is actually more general than that. I will introduce it in a general form from which the usual statement of the principle results.

Wolfgang Pauli



Paul Dirac

9.2 The Pauli Principle

The Pauli Principle arises from considering how to treat identical particles in quantum systems. You will see in a moment that there is an important relationship to spin angular momentum.

In classical mechanics, two indistinguishable particles cause no special problems. If we know the initial conditions of the particles and the forces acting on them, we can follow the trajectories of each one of them and thus tell them apart.

In Quantum Mechanics, the Heisenberg Uncertainty Principle tells us we cannot follow the trajectories of individual particles. Thus if two particles have all the same intrinsic properties (mass, charge, spin), we cannot tell them apart. Thus, the wavefunction cannot distinguish between identical particles. This leads to certain very important restrictions.

The implications of this simple principle are enormous - it is responsible for the periodic behavior of the elements, and hence is at the core of chemistry!!!

Consider a wave function for *N* identical particles. Let the symbol q_1 represent the space *and* spin coordinates of particle 1, q_2 those for particle 2, etc.

We can write our wave function

$$\psi = \psi(q_1, q_2, \ldots, q_i, \ldots, q_j, \ldots q_N)$$

I will define the permutation operator $\hat{P}_{ij}$ as the operator which exchanges all the coordinates of particles *i* and *j*.

$$\hat{P}_{ij}\psi(q_1, q_2, \ldots, q_i, \ldots, q_j, \ldots q_N) = \psi(q_1, q_2, \ldots, q_j, \ldots, q_i, \ldots q_N)$$

We need to find the eigenvalues of $\hat{P}_{ij}$, i.e.:

$$\hat{P}_{ij}\psi(q_1, q_2, \ldots, q_i, \ldots, q_j, \ldots q_N) = c\,\psi(q_1, q_2, \ldots, q_i, \ldots, q_j, \ldots q_N)$$

If we operate twice on our wavefunction,

$$\hat{P}_{ij}\hat{P}_{ij}\psi(q_1, q_2, \ldots, q_i, \ldots, q_j, \ldots q_N) = \hat{P}_{ij}\psi(q_1, q_2, \ldots, q_j, \ldots, q_i, \ldots q_N) = \psi(q_1, q_2, \ldots, q_i, \ldots, q_j, \ldots q_N)$$

it leaves the function unchanged.

We find:

$$\hat{P}_{ij}\hat{P}_{ij}\psi(q_1, q_2, \ldots, q_i, \ldots, q_j, \ldots q_N) = \hat{P}_{ij}\, c\,\psi(q_1, q_2, \ldots, q_i, \ldots, q_j, \ldots q_N) = c^2\,\psi(q_1, q_2, \ldots, q_i, \ldots, q_j, \ldots q_N)$$

Thus $c^2 = 1$

You can see that the eigenvalues of $\hat{P}_{ij}$ will be ±1.

If ψ is an eigenfunction of $\hat{P}_{ij}$ with eigenvalue +1, ψ is unchanged upon interchange of the coordinates of particles *i* and *j*. We call an eigenfunction with eigenvalue of 1 *symmetric* with respect to interchange of particles *i* and *j*.

If ψ is an eigenfunction of $\hat{P}_{12}$ with eigenvalue -1, we call it *antisymmetric* with respect to interchange of particles *i* and *j*.

Thus, a wave function for a system of identical particles must be *symmetric* or *antisymmetric* with respect to interchange of *any two* particles. Since the particles are identical, it can't matter which pair you interchange.

The wavefunction must be symmetric or antisymmetric with respect to any possible interchange of two identical particles.

That is:

$$\psi(q_1,q_2,\ldots,q_j,\ldots,q_i,\ldots q_N) = \pm\psi(q_1,q_2,\ldots,q_i,\ldots,q_j,\ldots q_N)$$

All particles in nature are divided into these two categories:

- Particles whose wave functions are ***symmetric*** with respect to interchange (+ sign) are called ***Bosons***.
- Particles whose wavefunctions are ***antisymmetri*** (- sign) are called ***Fermions***.

Furthermore:

- half integral spin particles (electrons, positrons, neutrons, protons) are Fermions
- integral spin particles (photons, mesons) are Bosons

These are relations form the so called spin-statistics theorem, which can be proven by invoking relativity.

Composite particles behave as their net spin. The ^{3}He isotope is a Fermion, whereas ^{4}He is a boson. Due to this difference the two isotopes behave very different at temperatures close to absolute zero, ^{4}He follows Bose statistics whereas ^{3}He follows Fermi statistics.

Since electrons are Fermions, we have another Fundamental Postulate of Quantum Mechanics. *The wavefunctions of a system of electrons must be antisymmetric with respect to interchange of any two of them.*

This is the PAULI EXCLUSION PRINCIPLE.

One cannot write an antisymmetric wave function for an atom that has more than two electrons in one orbital. This has interesting implications, and gives rise to the periodic behavior of the elements. It turns out that Bosons do not have this restriction. If electrons were Bosons, all electrons could go into the same orbital. *Think how this might change chemistry!!*

In hydrogen, since there is only one electron, we don't need to worry about symmetric or antisymmetric behavior with respect to particle interchange. Since the Hamiltonian is independent of spin, the wave function is just a product of spin and spatial parts.

Now let's go back to Helium and consider the effect of the Pauli Exclusion Principle. (We will then go to lithium). Specifically, let us see why it was ok to neglect spin in our previous treatment.

We can write the ground state helium wave functions as

$$\psi = 1s(1)1s(2)$$

where the 1*s* functions could be Hartree-Fock orbitals for example. The parenthesis denotes which particle (one or two).

To take spin into account, we must multiply the spatial function by a spin eigenfunction. The total wave function must satisfy the Pauli Exclusion Principle and be antisymmetric.

We will use notation such as $\alpha(1)\beta(2)$ which means particle 1 has spin up, and particle 2 has spin down. That is the number in parenthesis refers to the particle, not a spin quantum number.

For our helium atom with spatial wavefunction 1*s*(1)1*s*(2) we can have four possible spin functions:

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

The first two functions are perfectly valid spin functions, since they don't distinguish between identical particles.

However, the last two violate the principle of indistinguishability. They distinguish between the two electrons. If we apply the permutation operator to these last two, we find they are neither symmetric or antisymmetric.

However, if you take normalized linear combinations of these two you can generate a symmetric and an antisymmetric function.

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) \pm \beta(1)\alpha(2)\right]$$

So we have 4 normalized two-electron spin functions.

$$\left.\begin{array}{c} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right] \end{array}\right\} \quad \text{symmetric}$$

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \quad \text{antisymmetric}$$

We now want to combine the spatial and spin parts.

Since 1*s*(1)1*s*(2) is symmetric with respect to exchange, we must multiply it by an antisymmetric spin function since the overall wave function must be antisymmetric.

We only have one choice. Thus the zeroth-order wavefunction is

$$\psi = 1s(1)1s(2)\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

So you can see that like hydrogen, the wave function for helium can be factored into a function of the spatial coordinates times a function of spin coordinates.

To a very high degree of approximation the Hamiltonian for a helium atom (or for hydrogen for that matter) is independent of spin coordinates. In this case, the energy will not be affected if we neglect the spin part of the wave function (because it can be factored in this way).

Leaving off the spin part didn't really change the problem. This is not so when you have 3 electrons as in the case of Lithium. To treat the Lithium atom, our normal procedure would be to construct a Hartree-Fock wave function as a product of one-electron functions. Following in the manner in which we dealt with the ground state of Helium, we would write the spatial part of the wave function as a product of 1*s* single electron functions:

$$\psi = 1s(1)1s(2)1s(3)$$

Let us follow this line of reasoning and see where it goes wrong. Consider spin and the requirements imposed by the Pauli Principle. Since the zeroth-order wavefunction $\psi = 1s(1)1s(2)1s(3)$ is symmetric with respect to electron exchange, we need to find an antisymmetric spin function involving 3 electrons. It turns out that it is easy to construct totally *symmetric* spin functions for 3 particles but impossible to construct *antisymmetric* spin functions.

Consider for a moment how to construct an antisymmetric combination of 3 functions *f*, *g*, and *h*.

With 3 electrons, you get 6 permutations of these functions:

f(1)*g*(2)*h*(3) *g*(1)*f*(2)*h*(3) *h*(1)*g*(2)*f*(3) *f*(1)*h*(2)*g*(3) *g*(1)*h*(2)*f*(3) *h*(1)*f*(2)*g*(3)

We need to combine these to make an antisymmetric function that does not distinguish between electrons. One could show that a general method for constructing such an antisymmetric function for 3 electrons is to use a determinant that includes all the possible functions

$$\psi = \frac{1}{\sqrt{6}}\begin{vmatrix} f(1) & g(1) & h(1) \\ f(2) & g(2) & h(2) \\ f(3) & g(3) & h(3) \end{vmatrix}$$

Note that the rows contain contributions from the same particle and the columns contain contributions from the same function. (We could have done this for helium).

The fact that this determinant will give us the proper antisymmetric combination of these functions can be easily seen from the properties of determinants. Interchanging two electrons amounts to the interchange of any two rows, and we know the interchange of any two rows of a determinant causes the determinant to be multiplied by -1. That is exactly the property we are looking for.

Recognizing this as the most general way to construct an antisymmetric combination of 3 functions (or *n* functions for that matter), we are ready to see the restrictions due to the Pauli Principle. (We actually did this for helium when we formed the linear combination $\alpha\beta-\beta\alpha$)

The functions *f*, *g*, and *h* may each be either α or β. If we let *f*= α , *g*= β, *h*= α

we get the determinant:

$$\psi = \frac{1}{\sqrt{6}}\begin{vmatrix} \alpha(1) & \beta(1) & \alpha(1) \\ \alpha(2) & \beta(2) & \alpha(2) \\ \alpha(3) & \beta(3) & \alpha(3) \end{vmatrix}$$

However, we can recognize that this determinant equals zero, since it has two columns that are the same.

The problem arises because we are trying to get an antisymmetric spin function for three electrons using only two spin functions. The determinant above will always vanish in cases with more than two electrons. This is why we didn't run into problems in out treatment of Helium.

In the case of helium, we were able to take the wavefunctions as independent functions of spatial coordinates and spin coordinates. However, for more than two electrons, this approach fails. Instead, we must consider each zeroth-order function as a combination of spatial and spin variables and then take linear combinations of these functions to get the proper symmetry.

For instance, we could take as our function

$$f(1) = 1s(1)\alpha(1)$$

A function such as this which is a product of a one electron spatial orbital and a one electron spin function is called a *spin-orbital.* Although we had only two different spin functions we can construct many different spin-orbitals by using different spatial parts. We can now construct our determinant to find the proper antisymmetric combination of such functions.

We can see, that if we let our function $g(1) = 1s(1)\alpha(1)$, then the determinant will equal zero. This is where the implications of the Pauli Exclusion Principle become important. The requirement that the total wave function for a system of electrons be antisymmetric is what has led us to using such a determinant in finding the proper wave function.

The properties of the determinant that gives us the proper symmetry behavior (mandated by the Pauli exclusion principle) indicate that *NO TWO ELECTRONS CAN OCCUPY THE SAME SPIN ORBITAL i.e.* have the same quantum numbers. If they do, it will violate the requirement that the total wavefunction be antisymmetric.

The proper determinant for a three electron system is then

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}$$

Note that if 3rd column were to contain a 1*s* orbital, the determinant would equal zero.

If you work out this determinant, you will see that it is not a simple product of space and spin parts, but is a combination of terms, each of which is a product of space and spin parts. (NOTE: Such determinants of spin-orbital functions are called *Slater Determinants.* These determinants can be written for an *n*-electron atom, in which case the coefficient in front is $\frac{1}{\sqrt{n!}}$)

Two properties of determinants make these wave functions satisfy the Pauli Principle. Interchanging two rows multiplies the determinant by -1 and thus gives a properly antisymmetric wave function. A determinant with two identical rows will equal zero, thus fulfilling the requirement that no electrons occupy the same spin-orbital.

So the Pauli Exclusion principle has required us to put the third electron in a 2*s* orbital, making the ground state configuration:

$1s^2 2s^1$

Note that we could have equally well used the β function in the last column of our determinant. Thus this state is twofold degenerate:

1s 2s or 1s 2s

↑↓ ↑ ↑↓ ↓

So you can see that the Pauli Exclusion Principle ultimately requires that no two electrons have the same four quantum numbers.

We can trace this requirement back to the fact the electron is a spin 1/2 particle (*i.e*. a Fermion). If it were a Boson, the world would be a different place. If it were a spin 3/2 particle, *the world would be a different place as well.*

I would like to say a few brief words about Hartree-Fock calculations for atoms with more than two electrons. When we discussed the Hartree-Fock method a few lectures ago, we used helium as an example, although I commented on how one would treat a many electron system. Now that we have considered the topic of electron spin, there is just one point I would like to add to the previous discussion.

Recall that the basic Hartree-Fock approach was to start with a wave function that is a product of one electron functions and then calculate the average inter-electronic repulsion by using the one electron functions to calculate a probability density for the individual electrons. This average interaction potential was then used to

form a one electron Hamiltonian which was used to refine the one electron wave functions. This was done iteratively until the functions no longer change.

Our previous treatment neglected spin, and this was ok since the wave functions for a two-electron atom factor into a spatial part and a spin part and because the Hamiltonian is, to a high degree of approximation, independent of spin. Our treatment of spin and the Pauli Principle simply tells us that when we choose our one-electron functions for the Hartree-Fock procedure for atoms of more than two electrons, we need to use Slater determinants of spin-orbitals to insure the proper symmetry and indistinguishability.

Also, when we generalize the Hatree-Fock procedure to more than two electrons, we get a slightly different expression for the energy than we had for Helium. (Our result was a special case of this more general result). The approach is still the same: find the optimized orbitals and then use the variational principle to find the energy.

When we assign electrons in atoms into individual spin orbitals, we are assigning them each a set of quantum numbers, particularly spin and orbital angular momentum quantum numbers. A particular electronic configuration can have a variety of states with different energies depending on how the individual angular momenta couple together. A ***term symbol*** is a designation that indicates the total, orbital, and spin angular momenta for the whole atomic system.