Probability Distribution Functions

We are going to use the radial wave function to calculate probabilities:

$$dP = \psi^*(r,\theta,\varphi)\psi(r,\theta,\varphi)dV$$

gives the probability of finding the electron in the volume element dV.
We want to find the probability of finding the electron between r and r+dr. The differential volume element in spherical coordinates is:

$$dV = r^2 \sin\theta\, dr\, d\theta\, d\varphi$$

The angular and azimuthal equations are properly normalized so that the integral over these portions will equal 1. We thus have remaining:

$$P(r)dr = r^2 \left|R(r)\right|^2 dr$$

Here are some of the radial functions for hydrogen:

n	ℓ	$R_{n,\ell}(r)$
1	0	$\frac{2}{a_0^{\frac{3}{2}}} e^{-\frac{r}{a_0}}$
2	0	$\left(2-\frac{r}{a_0}\right)\frac{e^{-r/2a_0}}{(2a_0)^{\frac{3}{2}}}$
2	1	$\frac{r}{a_0}\frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$

The radial probability density is:

$$P(r) = r^2 \left|R(r)\right|^2$$

Example: Find the most probable radius for the electron of a hydrogen atom in the 1s and 2p states.

To find this, we take the derivative of the probability density with respect to r and set it equal to zero.

For the 1s state, we have:

$$\frac{d}{dr}P(r) = 0 \Rightarrow r = a_0$$

For the 2p state, we have:

$$\frac{d}{dr}P(r) = 0 \Rightarrow r = 4a_0$$

If you were so inclined, you could apply this to each of the states with the largest possible ℓ value which would give each of the Bohr radii. Thus we now do have that conclusion that the Bohr radii do correspond the states of maximum ℓ values for each quantum number n.

It's probably worthwhile to do this in class at least for the first one.

Now that you know the radial distribution functions, you can also use your knowledge of calculation of expectation values to make calculations of the average radii for the

various radial wave functions. Again, this is facilitated by the normalization of the angular and azimutal solutions:

$$\langle r \rangle = \int \psi^*(r,\theta,\varphi)\, r\, \psi(r,\theta,\varphi)\, dV = \int r\, P(r)\, dr$$

Finally (although, this is not really finally ... the possibilities here are endless), we can calculate the probability for an electron to be in a certain region of space, for example, at a radius beyond the Bohr orbit. For the 1s state of hydrogen, we can do this by:

$$\text{Probability} = \int_{a_0}^{\infty} P(r)\, dr$$

which would correspond to 50%. It's really a pretty amazing result when you think about it ... It is highly likely that the electron is confined in a very small region.
In fact, you might consider this problem: what is the probability that the electron is confined to a radius less than or equal to the radius of the proton for the 1s state of hydrogen? I think I'll show you this.
The radius of the proton is about $1\text{x}10^{-15}$m which is much less than the Bohr radius of $5\text{x}10^{-11}$m. One way to calculate this approximately is to not do the integration.

$$\text{probability} \approx r^2 \left|R(r)\right|^2 \Delta r \approx \left[2\text{x}10^{-5} a_0\right]^3 \left[\frac{2}{a_0^{3/2}}\right]^2 \approx 3.2\text{x}10^{-14}$$

This is indeed quite a small probability but not zero. In fact, when the electron gets close enough to the proton there is another force that must take over (the strong nuclear force) which increases the probability considerably.

Chapter 8: Many Electron Atoms

We want to understand this because it explains much of nature and also provides a model for understanding how nuclei are constructed.

Ultimately Dmitri Mendeleev produced the periodic table for the elements in 1869 ... for us it is hard to believe this table never existed, but indeed it did not before that date.
With the advent of QM, there were many attempts to extend the QM theory to more fully explain this table. Wolfgang Pauli helped greatly in this attempt with the Pauli Exclusion principle:

No two electrons in an atom may have the same set of (n, ℓ, m_ℓ, m_s).

This principle applies to all particles of ½ integer spin (fermions), a set which includes particles in the nucleus (neutrons and protons are also fermions).

The atomic electron structure which leads to the ordering of the periodic table can be understood with two rules:
(1) the electrons in an atom tend to occupy the lowest energy levels available to them
(2) only one electron can be in a state with a given set of 4 quantum numbers.

For multi-electron atoms, the principle quantum number n has been given letter codes:
(1,2,3,4,...)=(K,L,M,N,...)

Mostly the binding energies depend upon n and within a shell these energies are almost the same.

Let's make a helium atom. The lowest energy state would correspond to the K shell. Within this n=1 shell, we then have the 1s subshell. This subshell can contain 2 electrons which are paired (their spins are pointed in opposite directions).
The hydrogen atom designation would be $1s^1$
Helium would be $1s^2$
For the next element (lithium) we need to move to the next higher shell, the L shell. For the L shell, n=2 and there are the following possibilities:
2s (2 states) or 2p (6 states) to give a total of 8 states.
According to rule 1, the electrons will go in with the lowest energy. Your author argues that the electron in the p states will see less effective charge because the two earlier electrons tend to shield it from some of this charge. This would mean that the 2p states will be further out from the nucleus and thus at a higher energy level than the 2s states. This then gives the structure for lithium:
$Li:1s^2 2s^1 = H2s^1$
The filling of shells within an atom will continue filling subshells till they are full and then go to the next subshell. Of course, you can expect that there will be exceptions to this.

Notice (looking at table 8.1) up till n=4, the s shells are filled before the p shells. Also notice that the 4s shell is filled before the 3d shell and the 4p shell is filled before the 5s shell. We are able using this model to work up pretty simply the configuration of the atomic structure for the lower-lying elements:
after Li, we have
$Be:=H:2s^2$

$B:=Be:2p^1$
$C:=Be:2p^2$
$N:=Be:2p^3$
$O:=Be:2p^4$
$F:=Be:2p^5$
$Ne:=Be:2p^6$

$Na=Ne:3s^1$
$Mg=Na:3s^2$

$Al=Mg:3p^1$
$Si=Mg:3p^2$
$P=Mg:3p^3$
$S=Mg:3p^4$
$Cl=Mg:3p^5$
$Ar=Mg:3p^6$

$K=Ar:4s^1$

$$Ca = Ar:4s^2$$

After this things begin to get a bit more complicated. However, up to about element 56, it can be observed that the (n-1)d shells have a lower energy than the (n)p shells. This allows us to insert electrons up till the point (at element 58) where the (n-1)f shells become lower in energy than the (n)d shells, which must be filled before filling the (n+1) p shells. Fortunately by element 112, we run out of elements to stick into the table.

Ok, that's how you fill the atomic chart. But we have said nothing about how the electrons pair up in the subshells. This is particularly important if you want to understand things about the magnetic behavior of the elements.

We thus need to investigate section **8.2 Total Angular Momentum.**

Single electron atoms

We define the total angular momentum as:

$$\vec{J} = \vec{L} + \vec{S}$$

The eigenvalues of the total angular momentum are given by:

$$J = \sqrt{j(j+1)}\hbar$$

$$J_z = m_z\hbar$$

I've introduced a new quantum number here:

$$j = \ell \pm s$$

For example, if l=1 then j can be ½ or 3/2.

The notation used to describe these states of total angular momentum is:

$$nL_j$$

with n the principle quantum number, j the total angular momentum quantum number and L represents the orbital angular momentum quantum number.

Now let's think about things from the point of view of the electron: The electron sees the proton circulating about it (classically) which is effectively going to result in a magnetic field to which the electron must respond since, after all, the electron is a tiny magnet in a single package.

The effect of this is to couple the spin and orbital angular momentum. The potential energy associated with this is given by:

$$V_{s\ell} = -\vec{\mu}_s \bullet \vec{B}_{internal}$$

The magnetic field produced internally will be proportional to L while the spin magnetic moment will be proportional to –S. The effect of this is that we have:

$$V_{s\ell} \sim \vec{S} \bullet \vec{L} = SL\cos(\alpha)$$

with the angle being the angle between S and L vectors. This will result in the state: J=l-1/2 being slightly lower in energy than the state J=l+1/2.

The result of this is that we accept j and m_j as "better quantum numbers" than m_L and m_s, even for single-electron atoms like hydrogen. The "better" means that it leads to more directly observable quantities. This better actually means that a state having a definite energy can no longer be assigned a definite L_z and S_z but it can have a definite J_z. The wave functions will now depend upon (n, ℓ, j, m_j). The spin-orbit interaction splits the 2P level into two states: $2P_{3/2}$ and $2P_{1/2}$ with $2P_{1/2}$ being lower in energy.

There are also relativistic effects that come into play here.

In the absence of an external magnetic field, the total angular momentum is conserved in magnitude and direction. The effect of the internal magnetic field is to cause L and S to precess about J. In an external magnetic field, however, J will precess about $B_{external}$. while L and S still precess about J. As you can imagine, the motion of L and S then becomes pretty complicated.

For single electron atoms, we can also add some additional selection rules:

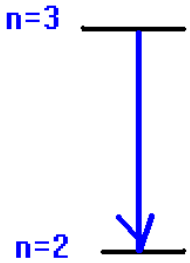
$$\Delta n = \text{anything}$$

$$\Delta m_j = 0, \pm 1$$

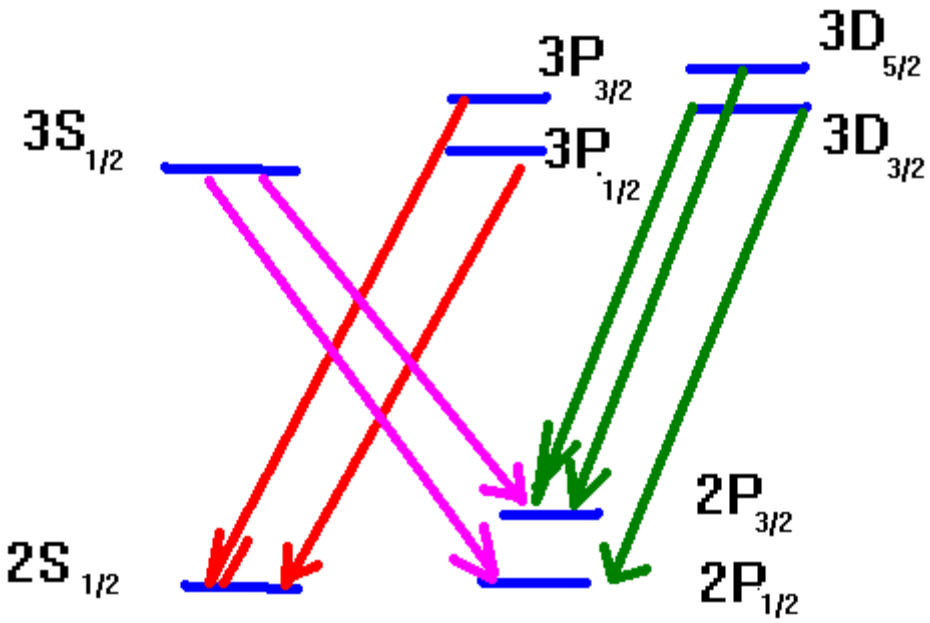
$$\Delta \ell = \pm 1$$

$$\Delta j = 0, \pm 1$$

We can apply this to a relatively "simple" situation of the n=3 – n=2 states of hydrogen:
notice, although it is probably obvious, that the spin-orbit interaction will not become involved with l=0 states since the internal magnetic field is proportional to the orbital angular momentum.



Unperturbed hydrogen spectra transitions



optical fine structure observed from hydrogen. The spin-orbit interaction splits each of the $\ell \neq 0$ states.