

### LECTURE 3. THE ORIGIN OF THE ATOMIC ORBITAL: WHERE THE ELECTRONS ARE

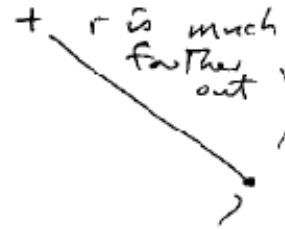
In one sentence I will tell you the most important idea in this lecture:

**Wave equation solutions generate atomic orbitals that define the electron distribution around an atom.**

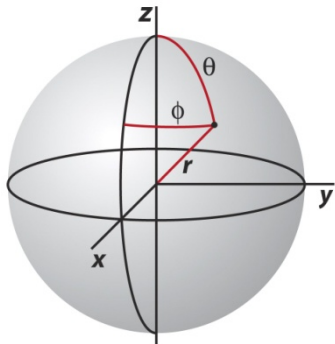
To start we need to simplify the math by switching to spherical polar coordinates (everything = spherical) rather than Cartesian coordinates (everything = at right angles). So the wave equations generated will now be of the form  $\psi(r, \theta, \Phi) = R(r)Y(\theta, \Phi)$  where  $R(r)$  describes how far out on a radial trajectory from the nucleus you are.



r is a little way out and is small



Now that we are extended radially on  $\psi$ , we need to ask where we are on the sphere carved out by  $R(r)$ . Think of blowing up a balloon and asking what is going on at the surface of each new  $R(r)$ . To cover the entire surface at projection  $R(r)$ , we need two angles  $\theta, \Phi$  that get us around the sphere in a manner similar to knowing the latitude & longitude on the earth.



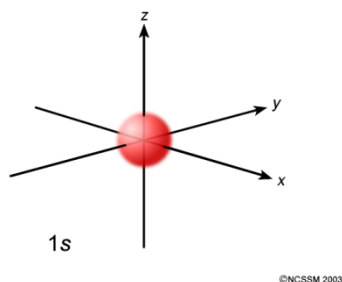
These two angles yield  $Y(\theta, \Phi)$  which is the angular wave function

### A first solution: generating the 1s orbit

So what answers did Schrodinger get for  $\psi(r, \theta, \Phi)$ ? It depended on the four quantum numbers that bounded the system  $n, l, m_l$  and  $m_s$ . So when  $n = 1$  and  $l = 0$  the solution he calculated was:

$$R(r) = 2(Z/a_0)^{1/2} * e^{-Zr/a_0} \text{ and } Y(\theta, \Phi) = (1/4\pi)^{1/2}.$$

This combination is the wave function for a ground state electron in a 1s hydrogen orbit and has the famous spherical shape that was described in the Bohr atom and in elementary school Styrofoam models across the world.



### Angular Momentum Happens

Things get a lot more complicated for  $\psi$  mathematically, at even the next principal energy level,  $n=2$ . This is shown in the table below. Specifically note that while  $l = 0$ , there was no  $\theta$  or  $\Phi$  component, when  $l = 1$ , there is a  $\sin\theta\cos\Phi$  term.  $Y(\theta, \Phi)$  describes the angular momentum of an electron. When  $l = 0$  there is no angular momentum (no dependence of  $\theta, \Phi$ ) and we have a simple blob-like distribution of aimless electrons. But for  $l = 1$  and higher,  $\theta$  and  $\Phi$  define an angular momentum that is the acceleration of electrons around a p, d, or f orbit.

**TABLE 1.2** Hydrogen Wavefunctions (Atomic Orbitals),  $\psi = RY$

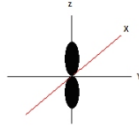
(a) Radial wavefunctions, $R_{nl}(r)$			(b) Angular wavefunctions, $Y_{lm_l}(\theta, \phi)$		
$n$	$l$	$R_{nl}(r)$	$l$	" $m_l$ "*	$Y_{lm_l}(\theta, \phi)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right)e^{-Zr/2a_0}$	1	$x$	$\left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \cos \phi$
	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$		$y$	$\left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \sin \phi$
3	0	$\frac{1}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(3 - \frac{2Zr}{a_0} + \frac{2Z^2r^2}{9a_0^2}\right)e^{-Zr/3a_0}$	2	$z$	$\left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$
	1	$\frac{2}{27\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{3a_0}\right)e^{-Zr/3a_0}$		$xy$	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2 \theta \cos 2\phi$
	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$		$yz$	$\left(\frac{15}{4\pi}\right)^{1/2} \cos \theta \sin \theta \sin \phi$
				$zx$	$\left(\frac{15}{4\pi}\right)^{1/2} \cos \theta \sin \theta \cos \phi$
				$x^2 - y^2$	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2 \theta \sin 2\phi$
				$z^2$	$\left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$

Note: In each case,  $a_0 = 4\pi\epsilon_0^2/m_e e^2$ , or close to 52.9 pm; for hydrogen itself,  $Z = 1$ .

\*In all cases except  $m_l = 0$ , the orbitals are sums and differences of orbitals with specific values of  $m_l$ .

**$\psi^2$  is what we're after.**

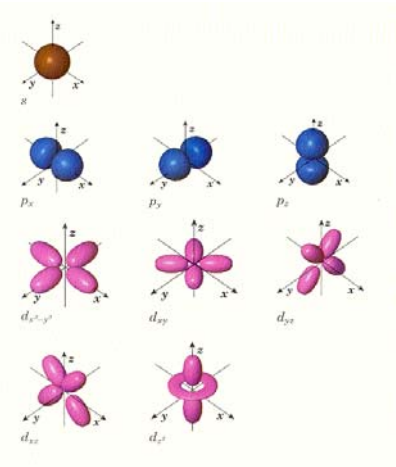
While it's great to have a table of wave functions,  $\psi$ , what we are really after is  $\psi^2(r, \theta, \Phi)$  which tells us the probability of finding an electron in a small volume,  $\Delta V$ , defined by  $r, \theta, \Phi$ . For example,  $\psi^2(r, \theta, \Phi)$  for  $n=2, \ell=1$  generates the famous p orbital shape that has a nodal plane at the nucleus.



$\psi^2$  tells us the density of  $e^-$  probability for any volume we carve how around the nucleus. Simply stick in  $\psi^2(r, \theta, \Phi)$  and it tells you the probability of  $e^-$  at each of those volumes. Thus for example, for the quantum numbers that describe the dumbbell shape above, most of the electron density lies along the z axis.

**Azimuthal quantum number,  $\ell$ , describes the shape.**

The azimuthal quantum number,  $\ell$ , tell us the shape of orbits with the boundaries,  $\ell=0,1,2,\dots,n-1$ . If we calculate  $\psi^2$  for various values of  $\ell$ , the orbital angular momentum, you end up with shapes like:



Note that any time you have  $\ell = 0$ , you get something that looks spherical (though if you look closely it isn't that simple.) and is labeled as an "s orbital." If you have  $\ell = 1$ , you create a shape that looks like a dumbbell and is labeled as a "p orbital." For  $\ell = 2$ , you create a shape that often looks like two overlapping dumbbells, and is labeled as a "d orbital." These are the famous shapes that we will draw over and over again to represent "where the electrons are" around a nucleus.

## A Third Quantum Number, $m_l$ , Describes the Direction or Orientation of the Orbital

Falling out of the wave equations for  $\psi(r, \theta, \Phi)$  is another quantum number defining the direction or orientation of wave function. The number of directions is determined from the boundary condition.

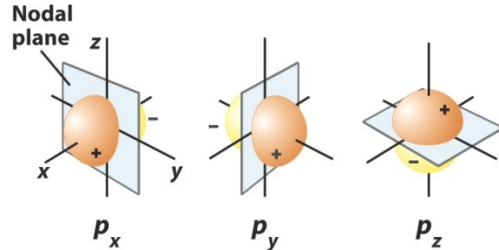
$l = 0, 1, \dots$  yielding  $m_l$  from  $-l, \dots, 0, \dots, +l$  so when

$l = 0$  there is one orientation (because a sphere looks the same from every direction.)

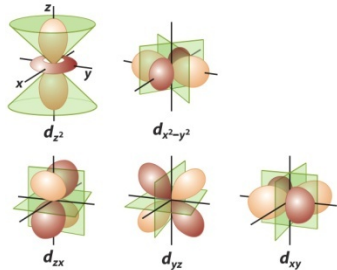
$l = 1$  there are three orientations  $-1, 0, 1$

$l = 2$  there are five orientations  $-2, -1, 0, 1, 2$

The directions usually are not easy to define given the unfamiliarity of spherical polar coordinates. But fortunately we can easily identify the 3 directions of p orbits for  $l = 1$  in Cartesian system



As you look at the d orientations for the d orbitals it is apparent that a lot more is going on that you will be taught in this course.



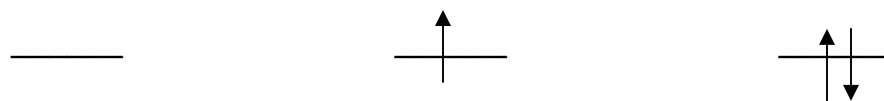
## A Fourth Quantum Number, $m_s$ , Defines the Spin of the Electron

The  $m_s$  quantum number for an electron describes the direction of spin of an electron. The really good news is that there are only two ways an electron can spin: up and down. They are assigned the values of plus and minus  $\frac{1}{2}$ , but we don't need to be concerned with that value. Just the fact that there are two directions. We can show off these two directions using a cheerleader who does head stands and spins while I stay upright and spin--or we can do it with an electron.



## Creating Orbital Shorthand to Define the Possible $m_s$ conditions

This last quantum number is actually the one that gets depicted most often as we start to build up our electron configurations. Rather than the pretty pictures above, we simply draw a line which represents an orbital. An "orbital" is what you get when you combine a value for  $n$  and a value for  $l$  to produce orbitals like 1s or 3p or 4d. The boundary conditions established by the  $m_s$  quantum number are that you can only have two possible electron spins, up and down. So putting these ideas together we end up having just three possible allowed states for an orbital: empty, half filled, and filled, as depicted below.



### Putting it all together—the boundary conditions that define the appearance of the periodic table

The end result of Scrodinger's solution to the wave equations for a multi-electron system surrounding a positive nucleus is the set of four boundary conditions in the table below. It is these allowed combinations of these quantum numbers that determine the distribution of electron density around atoms and consequently the basis for chemical bonding that define matter in the universe. Learn to apply these boundary conditions and then compare them to what you see in the periodic table. They are the same. Wow. Summarizing:

**TABLE 1.3** Quantum Numbers for Electrons in Atoms

Name	Symbol	Values	Specifies	Indicates
principal	$n$	$1, 2, \dots$	shell	size
orbital angular momentum*	$l$	$0, 1, \dots, n - 1$	subshell: $l = 0, 1, 2, 3, 4, \dots$ $s, p, d, f, g, \dots$	shape
magnetic	$m_l$	$l, l - 1, \dots, -l$	orbitals of subshell	orientation
spin magnetic	$m_s$	$+\frac{1}{2}, -\frac{1}{2}$	spin state	spin direction

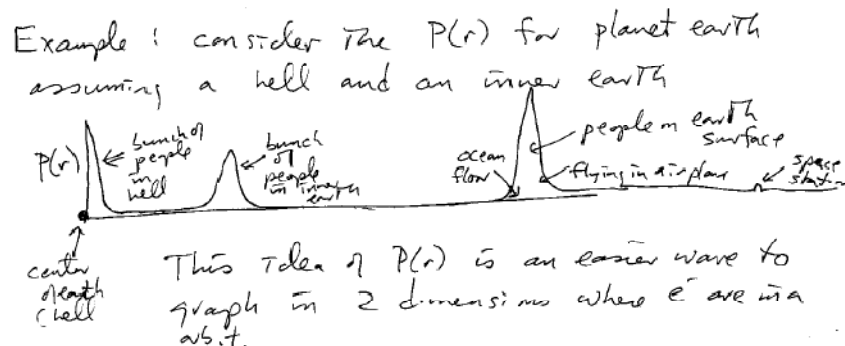
\*Also called the *azimuthal quantum number*.

## Radial Distribution Function.

One final idea before we leave quantum mechanics and start building electronic configurations. There is a different way for expressing electron density without having to draw the complicated three-dimensional pictures using  $\psi^2$  which is a probability of  $e^-$  in a small volume of space. Instead, why not consider  $P(r)$  which is a radial distribution along a single axis..

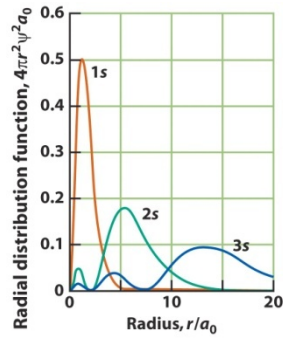
$P(r) \equiv$  radial distribution  $\equiv$  probability of finding an  $e^-$  at any location on the sphere carved out along  $r$

As an example,  $P(r)$  just for fun, starting at the center of the earth (assuming there is a hell with people in it), let's draw  $P(r)$  for number of people as we extend outward radially into space. Here is a crude drawing of what it would look like.



Why are  $P(r)$  distributions valuable? Well we all think s orbitals are pretty spheres but actually the radial distributions indicate layers of electron density within the larger s orbitals.





By looking at the radial distribution for the s orbits we can uncover that there are a lot of complexities we might not have seen otherwise. For example, the larger s orbits are not single uniform spheres but actually have waves of increased spherical density extending out from the nucleus.