6 The Hydrogen Atom

We are now ready to move on to a slightly more difficult quantum mechanical problem whose solution pervades much of the way we think about chemistry -- ***the hydrogen atom***. As we will see, the eigenfunctions of the hydrogen atom Hamiltonian serve as prototypes for more complex atoms and for molecules. The concepts we will develop will be familiar from first year chemistry, in that it provides the basis for talking about orbitals and their properties.

We will consider the hydrogen atom as a proton fixed at the origin and an electron with mass m_e interacting with the proton through a coulomb potential

$$U(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

Here, e is the electron charge, ε_0, the permittivity of free space, and r the distance between the proton and electron.

Recall that we can reduce a two-particle problem to a single particle problem with a reduced mass of μ by separating off the center of mass motion. In this case, the electron is so light compared to the proton, that the reduced mass of the system is not very different from the mass of the electron.

$$\mu = \frac{m_p m_e}{m_p + m_e} \cong \frac{m_p m_e}{m_p} = m_e$$

Nevertheless, one can calculate the reduced mass simply enough that we will use it.

The spherical symmetry of the system (*i.e.* the fact that the potential depends only upon the proton-electron distance and not the angles θ and φ) suggests that we should use spherical polar coordinates.

We can write down the Schrödinger equation for a hydrogen atom as

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\theta,\varphi) + U(r)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi)$$

If we substitute ∇^2 in spherical polar coordinates we get

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\varphi^2}\right)\right]\psi(r,\theta,\varphi) + U(r)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi)$$

Let's multiply through by $2\mu r^2$ and bring everything over to the left hand side:

$$-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\varphi)}{\partial r}\right) - \hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi(r,\theta,\varphi)}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2\psi(r,\theta,\varphi)}{\partial\varphi^2}\right)\right] + 2\mu r^2\left[U(r) - E\right]\psi(r,\theta,\varphi) = 0$$

The second term here depends only upon θ and φ, and if you compare it to the expression we had for the $\hat{L}^2$ operator, you can see that we can write

$$-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\varphi)}{\partial r}\right) + \hat{L}^2\psi(r,\theta,\varphi) + 2\mu r^2\left[U(r) - E\right]\psi(r,\theta,\varphi) = 0$$

Since all the θ and φ dependence is carried by the $\hat{L}^2$ term, we can use the method of separation of variables once again. We can let the wave function be a function of r times a function of θ and φ.

Because the θ and φ part of the equation is simply an eigenvalue equation for $\hat{L}^2$, then we know what the θ and φ part of the wave function will be, the eigenfunctions of the $\hat{L}^2$ operator.

$$\hat{L}^2 Y_l^m(\theta,\varphi) = \hbar^2 l(l+1) Y_l^m(\theta,\varphi) \qquad l = 0,1,2,3,\ldots$$

The total wave function can be written

$$\psi(r,\theta,\varphi) = R(r) Y_l^m(\theta,\varphi)$$

So we had already solved the angular part of the hydrogen atom when we found the eigenfunctions of the $\hat{L}^2$ operator.

Notice that this result is perfectly general for any case when the potential U is spherically symmetrical (that is only a function of *r*). We saw this in the case of the rigid rotor where *U*(*r*)=0 since *r* was constant.

If we substitute this form for the wave function back into the differential equation, divide by $2\mu r^2$ and use the fact that we know the eigenvalues of $\hat{L}^2$ we get the following equation for *R*(*r*):

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\left[\frac{\hbar^2 l(l+1)}{2\mu r^2}+U(r)-E\right]R(r)=0$$

This is called the radial equation for the hydrogen atom because its solutions yield *R*(*r*), the radial part of the wavefunction. Solving this equation is the only new part of the hydrogen atom problem, since we already know the solution to the angular part.

It is important to have some feel for the meaning of the terms in this equation.

- The first term represents the radial kinetic energy of the hydrogen atom system, *i.e*. the energy due to the change in *r*.
- The second term is the angular kinetic energy term (recall that it originates from the $\hat{L}^2$ term).
- The third is the potential energy.

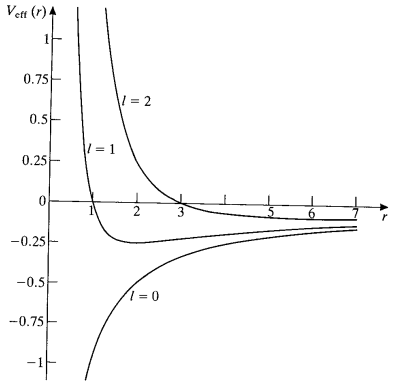
The angular kinetic energy term $\frac{l(l+1)\hbar^2}{2\mu r^2}$ is called the centrifugal potential. It is frequently grouped together with the coulomb potential term to yield an effective potential

$$U_{eff}(r) = U(r) + \frac{l(l+1)\hbar^2}{2\mu r^2} = -\frac{e^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

Let's take a look at this potential

The coulomb potential alone is purely attractive (and hence negative), going to -∞ at *r*=0. The centrifugal term is purely repulsive (positive). The positive $1/r^2$ term wins out over the negative $1/r$ term at *r*=0, and hence the effective potential goes to ∞ at *r*=0 for nonzero *l*.

The radial equation for the hydrogen atom must be solved by the series method similar to our solution for the Harmonic Oscillator. I will not repeat this treatment, but trust that you recall the general approach.



In a manner similar to these previous problems, when one forces to the wave functions to obey the boundary conditions, quantization of the energy arises. In this case, the quantization condition is

$$E_n = -\frac{\mu e^4}{8\varepsilon_0^2 h^2 n^2} \qquad n = 1,2,3,\ldots$$

This is often written in terms of the Bohr radius, a_0

$$a_0 = \frac{\varepsilon_0 h^2}{\pi \mu e^2} \qquad \text{(Recall the Bohr planetary model)}$$

The energy equation then becomes

$$E_n = -\frac{e^2}{8\pi\varepsilon_0 a_0 n^2} \qquad n = 1,2,3,\ldots$$

Notice that although the quantum number *l* appeared in the radial equation, the energy does not directly depend upon *l* (although we will see that the wave function certainly does). Rather, the energy depends inversely upon the square of a total quantum number *n*.

The restrictions on the quantum number *n* that arises in solving the radial equation is $n \geq l + 1$. Since , as we saw previously, the smallest value of $l = 0$, this is usually written as

$$0 \leq l \leq n-1 \qquad n = 1,2,3,\ldots$$

Note that the levels get closer together due to the $1/n^2$ dependence as one approaches zero energy. For positive values of the energy (as measured relative to the energy of the electron at infinite separation) the energies of the hydrogen atom are no longer quantized but continuous. This is because there is no boundary condition to keep the electron from going to $r=\infty$.

The Hamiltonian for any one-electron atom (such as He^+, Li^{2+}, Be^{3+}) is exactly the same as for the hydrogen atom, except that the nuclear charge changes. If we had solved the problem for the more general case of one-electron atoms, we would have had a factor of *Z* in the numerator of the Hamiltonian. In this case the energy is given by:

$$E_n = -\frac{\mu e^4 Z^2}{8\varepsilon_0^2 h^2 n^2} = -\frac{RZ^2}{n^2} \qquad n = 1,2,3,\ldots$$

where $R = R_H = 109{,}677.4212\ \text{cm}^{-1}$ for the hydrogen atom. (It is very slightly different for other nuclei because μ, the reduced mass of the electron changes as the mass of the nucleus changes). This is simply the Rydberg expression that we discussed in the early part of the course. Using this expression, one can therefore predict the spectra of one-electron atoms.

Let us now look at the hydrogen atom wavefunctions. Recall that because the potential energy term in the Hamiltonian, $U(r)$, is spherically symmetric, the wave function will be of the form

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_l^m(\theta,\varphi)$$

	l=0	l=1	l=2
m=0	$Y_0^0 = \frac{1}{\sqrt{4\pi}}$	$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$	$Y_2^0 = \sqrt{\frac{5}{16\pi}}\left(3\cos\theta - 1\right)$
m=+1		$Y_1^1 = \sqrt{\frac{3}{8\pi}}\sin\theta e^{i\varphi}$	$Y_2^1 = \sqrt{\frac{15}{8\pi}}\cos\theta\sin\theta e^{i\varphi}$
m=-1		$Y_1^{-1} = \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}$	$Y_2^{-1} = \sqrt{\frac{15}{8\pi}}\cos\theta\sin\theta e^{-i\varphi}$
m=+2			$Y_2^2 = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{i2\varphi}$
m=-2			$Y_2^{-2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-i2\varphi}$

where the $Y_l^m(\theta,\varphi)$ are the spherical harmonics. These were the angular solutions to the rigid rotor problem as well. The first few are shown in the table above.

Recall that the radial equation (given a few pages back) can be solved by using a power series solution similar to our approach for the harmonic oscillator.

The radial wave functions for the hydrogen atom can be given in terms of well-known polynomials called the **associated Laguerre functions**.

The general formula for the radial wave function is

$$R_{nl}(r) = \left[\frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}\right]^{\frac{1}{2}}\left(\frac{2}{na_0}\right)^{l+\frac{3}{2}} r^l e^{-\frac{r}{na_0}} L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$$

where the $L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$ are the associated Laguerre functions and $a_0 = \frac{\varepsilon_0 h^2}{\pi\mu e^2}$ is called the Bohr radius.

The first few Laguerre functions are:

n=1	l=0	$L_1^1(x) = -1$	$x = \frac{2r}{a_0}$
n=2	l=0	$L_2^1(x) = -2!\left(2 - x\right)$	$x = \frac{r}{a_0}$
	l=1	$L_3^3(x) = -3!$	
n=3	l=0	$L_3^1(x) = -3!\left(3 - 3x + \frac{1}{2}x^2\right)$	$x = \frac{2r}{3a_0}$
	l=1	$L_4^3(x) = -4!\left(4 - x\right)$	
	l=2	$L_5^5(x) = -5!$	

The total wave function, $\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_l^m(\theta,\varphi)$, depends upon three quantum numbers. Note that the radial wave function depends both upon *n* and *l*, and the angular part of the wave function depends upon *l* and *m*.

***n* - the total quantum number** (note that *n* alone determines the energy)

This comes from the solution of the radial part of the wave function. Recall that the energy of the hydrogen atom is determined by the total quantum number *n*.

$$E_n = -\frac{\mu e^4}{8\varepsilon_0^2 h^2 n^2} \qquad n = 1,2,3,\ldots$$

***l* - the azimuthal quantum number or angular momentum quantum number**

The *l* quantum number arose from solving the θ part of the angular equations. It is related to the magnitude of the angular momentum vector.

l can take on the values $0 \le l \le n-1$ $\qquad n = 1,2,3,\ldots$

All the functions with the same value of *n* but different *l* have the same energy.

***m* - the magnetic quantum number**

It gets its name from the fact that in a magnetic field, states of different *m* which are degenerate split. It represents the projection of the angular momentum vector on the *z*-axis.

m can take on any of the 2*l*+1 values ranging from

-*l*, -*l*+1, -*l*+2, . . , 0, . . , *l* -2, *l* -1, *l*

Each *n*, *l* state is 2 *l* +1 degenerate.

For historical reasons, the *l* quantum number is usually denoted by letters instead of numbers.

l = 0 1 2 3 4 5 6 7 (after *f* they go alphabetically except for *j*)
s p d f g h i k

Also, when *l*=0 and *m*=0, *m* is dropped as a subscript of ψ, since if *l*=0, *m* must equal zero. Thus the first few wavefunctions are designated

ψ_{1s}	*n*=1	*l* =0	*m*=0
ψ_{2s}	*n*=2	*l* =0	*m*=0
ψ_{2p-1}	*n*=2	*l* =1	*m*=-1
ψ_{2p0}	*n*=2	*l* =1	*m*=0
ψ_{2p1}	*n*=2	*l* =1	*m*=1

Let us put everything together and look at the first few total wave functions.

$$\psi_{1s}(r,\theta,\varphi) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$$

$$\psi_{2s}(r,\theta,\varphi)=\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(2-\frac{Z}{a_0}r\right)e^{-\frac{Zr}{2a_0}}$$

$$\psi_{2p\pm1}(r,\theta,\varphi)=\frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}}re^{-\frac{Zr}{2a_0}}\sin\theta e^{\pm i\varphi}$$

$$\psi_{2p0}(r,\theta,\varphi)=\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}}re^{-\frac{Zr}{2a_0}}\cos\theta$$

The parameter *Z* in these functions is the charge of the nucleus. These equations are valid not only for the hydrogen atom, but for any one electron atom such as He^{+} or Li^{2+}. Only *Z* will differ.

Recall that the energy of the H atom is independent of *l* and *m*, so all the levels *n*=2 levels have the same energy. For a given *n* and *l*, the (2 *l* +1) *m* levels are degenerate, but as we will see, this degeneracy can be broken by a magnetic field.

There are several things I would like us to consider regarding these wave functions. First note that since the wave functions are the eigenfunctions of a Hermitian operator, they are orthogonal.

This is expressed by the following integral.

$$\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi}\psi^{*}_{nlm}(r,\theta,\varphi)\psi_{n'l'm'}(r,\theta,\varphi)d\tau=\delta_{nn'}\delta_{ll'}\delta m_{mm'}$$

where $d\tau$ is the volume element in spherical polar coordinates.

This says unless *n*, *l*, and *m* quantum numbers are all the same the functions with be orthogonal.

The wave functions as I have given them to you are normalized and thus one can calculate the probability of finding the electron in any range of *r* or θ or φ, however one must be careful to do this properly.

The normalization integral is:

$$\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi}\left(R_{nl}(r)Y_l^m(\theta,\varphi)\right)^{*}\left(R_{nl}(r)Y_l^m(\theta,\varphi)\right)d\tau=1$$

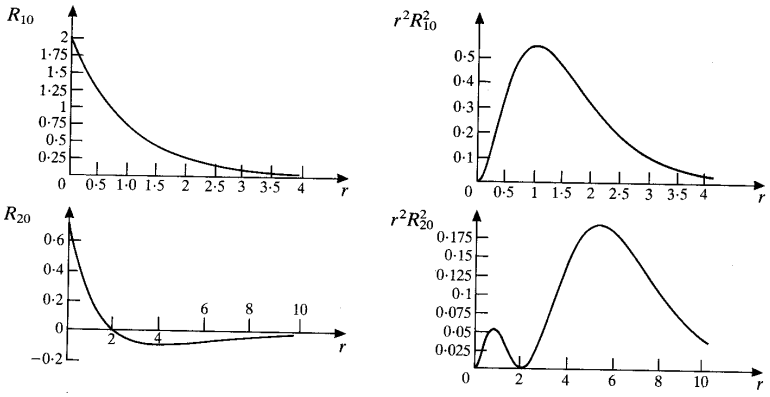
We can normalize each part separately, since the probability of finding the system with *r*=0 to ∞ must = 1, and similarly for finding θ between 0 and π and for φ between 0 and 2π.
However you must be careful to include the proper terms in the volume element for each coordinate.

$$\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi}\left(R_{nl}(r)Y_l^m(\theta,\varphi)\right)^{*}\left(R_{nl}(r)Y_l^m(\theta,\varphi)\right)r^2\sin\theta dr\,d\theta d\varphi=\int_0^{\infty}R^{*}_{nl}(r)R_{nl}(r)r^2dr\int_0^{\pi}\int_0^{2\pi}Y_l^{m*}(\theta,\varphi)Y_l^m(\theta,\varphi)\sin\theta d\theta d\varphi$$

The probability of finding the electron between *r* and *r*+*dr* $\left|R_{nl}(r)\right|^2r^2dr$ since the functions $Y_l^m(\theta,\varphi)$ are normalized.

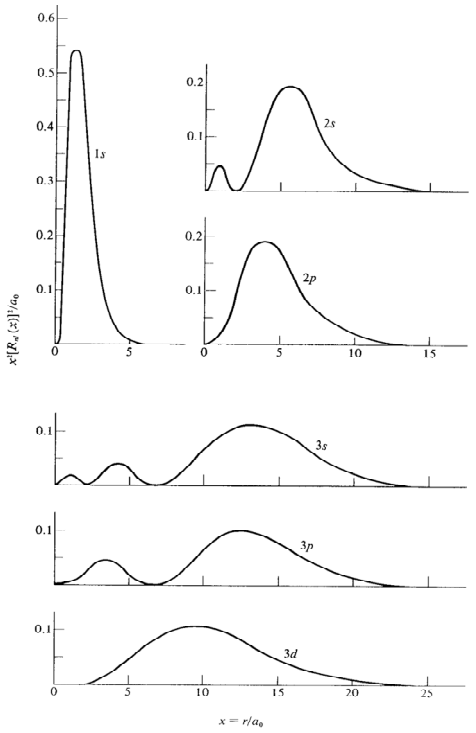
So to find the electron between r_1 and r_2 one must integrate $\left|R_{nl}(r)\right|^2r^2dr$ between these limits. Physically, the r^2 comes in that we are calculating the probability of finding the electron in a spherical shell between *r* and *r*+*dr.* The volume of that shell gets smaller as *r* gets smaller, so even though the 1*s* wave function is exponentially

decaying and peaks at r = 0, the probability density function $\left|R_{nl}(r)\right|^2 r^2$ peaks at some non-zero value of r and is zero at the origin.



Because the wave functions are three dimensional, it is difficult to visualize them and have physical intuition into their meaning. One way to do that is to plot the radial part of the wave function separately. What is probably more informative than the wave function itself is the radial probability distribution (as shown above for the 1*s* function), since that has a physical interpretation.

The radial probability distribution for the first functions is shown below.

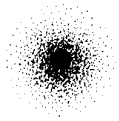


Note that the higher the energy, the larger the average r of the electron. Also note that there are n- l-1 nodes.

The angular parts of the wave functions are more difficult to display. However the wave functions with l=0 are somewhat easier to display. The angular part of the wave function for l=0, m=0 is

$$Y_0^0(\theta,\varphi) = \frac{1}{\sqrt{4\pi}}$$

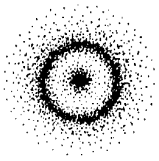
You can see that there is no explicit dependence upon θ and φ. Therefore, the wave function is spherically symmetric. Combining this angular dependence with the radial probability distribution we showed earlier, the picture is something like



$1s$

where the probability density is shown by the density of the dots.

A 2*s* wavefunction has the same angular part but with a different radial distribution

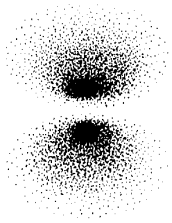


$2s$

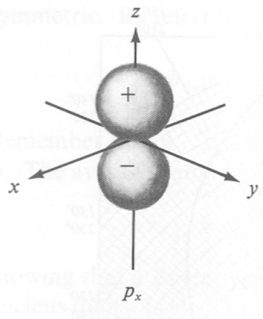
The wave function with *n*=2, *l*=1, *m*=0, that is the ψ_{2p0} function has somewhat of a different angular dependence.

$$\psi_{2p0}(r,\theta,\varphi) = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a_0}} \cos\theta$$

It looks something like this



$2p_0$



Note that the type of figure on the right which one commonly sees in textbooks only shows the angular part of the wavefunction. A shell is drawn containing a certain percentage of the probability density. One must combine this with the radial portion to get a good view of the electron density.

One way to help visualize this function is to make a substitution for the term *r* cosθ. If we realize that the Cartesian coordinate *z* in polar coordinates is $z = r\cos\theta$ we could write the ψ_{2p0} wave function as

$$\psi_{2p0}(r,\theta,\varphi) = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} z e^{-\frac{Zr}{2a_0}}$$

Even though it is a little awkward to mix coordinates here, this serves to emphasize the fact that the wave function has a ***nodal plane***, which in this case is the *xy* plane. The *z* in the wave function emphasizes this since when *z*=0 then the wave function and the probability equal zero. Because of this, ψ_{2p0} is usually called ψ_{2pz}

The wave functions corresponding to $m \neq 0$ (for example $m = \pm 1$) are somewhat more difficult to visualize because they are imaginary (due to the $e^{i\varphi}$ factor). We would like to work with real wave functions so we can easily plot them.
We can use the imaginary wave functions to construct real wave functions by taking linear combinations of the degenerate imaginary solutions. Remember, if two wavefunctions are solutions to the Schrödinger equation with the same eigenvalue (*i.e*. they are degenerate), any linear combination of them is also a solution with the same eigenvalue.

We can take an equally weighted linear combination of the *m*=±1 orbitals:

$$\psi_{2px}(r,\theta,\varphi) = \frac{1}{\sqrt{2}}\left(\psi_{2p-1}(r,\theta,\varphi) + \psi_{2p+1}(r,\theta,\varphi)\right)$$

You will see why we call it ψ_{2px} in a moment

Recall that $$\psi_{2p\pm1}(r,\theta,\varphi) = \frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a_0}} \sin\theta e^{\pm i\varphi}$$

Thus, $$\psi_{2px}(r,\theta,\varphi) = \frac{1}{\sqrt{2}}\frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a_0}} \sin\theta\left(e^{-i\varphi} + e^{+i\varphi}\right)$$

By manipulating Euler's formula we can see that

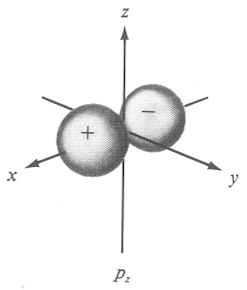
$$\cos\varphi = \frac{e^{-i\varphi} + e^{+i\varphi}}{2}$$

So, $$\psi_{2px}(r,\theta,\varphi) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a_0}} \sin\theta\cos\varphi$$

But recall the conversion from the Cartesian coordinate *x*, to spherical polar coordinates:

$$x = r\sin\theta\cos\varphi$$

Thus $$\psi_{2px}(r,\theta,\varphi) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} x e^{-\frac{Zr}{2a_0}}$$



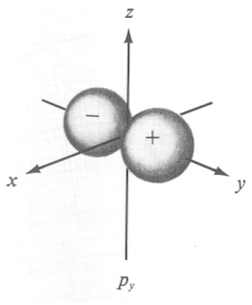
You can see that the *yz*-plane (*x*=0) is a nodal plane

One can similarly show that if we take the linear combination:

$$\psi_{2py}(r,\theta,\varphi)=\frac{1}{i\sqrt{2}}\left(\psi_{2p+1}(r,\theta,\varphi)-\psi_{2p-1}(r,\theta,\varphi)\right)$$

$$=\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} y e^{-\frac{Zr}{2a_0}}$$

the nodal plane is the *xz*-plane (*y*=0).



So we now have three 2*p* functions, $\psi_{2px},\psi_{2py},\psi_{2pz}$ which are all real. We could demonstrate that $\psi_{2px},\psi_{2py},\psi_{2pz}$ are mutually orthogonal. Now, because $\psi_{2p-1},\psi_{2p0},\psi_{2p+1}$ all have the same energy eigenvalue, any linear combination will also have the same energy eigenvalue. The same holds true with respect to the $\hat{L}^2$ operator. $\psi_{2p-1},\psi_{2p0},\psi_{2p+1}$ all have the same eigenvalues when operated on by $\hat{L}^2$, hence their linear combinations will also. Hence $\psi_{2px},\psi_{2py},\psi_{2pz}$ are eigenfunctions of $\hat{L}^2$.

However, $\psi_{2p\pm1}$ have different eigenvalues ***with respect to*** $\hat{L}_z$ (different *m*'s), *thus their linear combinations are not eigenfunctions of* $\hat{L}_z$ (in general). The *m*=0 function will be since we didn't change it. Hence ψ_{2px},ψ_{2py} are not eigenfunctions of $\hat{L}_z$ (that is, *m* is not a good quantum number for these wave functions). It turns out that ψ_{2px} and ψ_{2py} are eigenfunctions of the $\hat{L}_x$ and $\hat{L}_y$ operators respectively. By looking at the functions you can see this intuitively. They have the exact same form as ψ_{2pz} but with different axis labels.

We can also take linear combinations of degenerate eigenfunctions for states of higher *l* to get real wavefunctions.

For a given *l*, *m* ranges from -*l* . . . .*l*

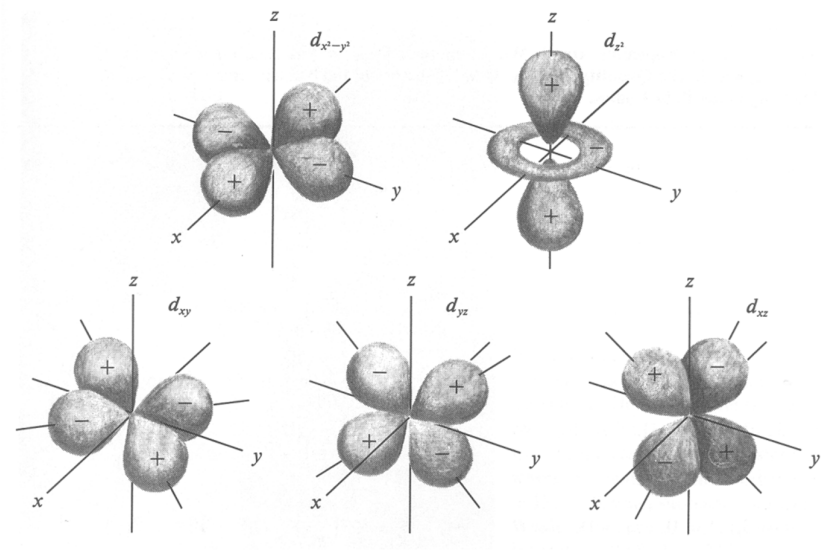
One will find that for every function containing an $e^{im\varphi}$, there is a corresponding one containing $e^{-im\varphi}$. Addition and subtraction of these functions will give two real functions. The subscripts on these new functions come from substituting Cartesian coordinates as we did with the ψ_{2px} and ψ_{2py} functions.

For example, for *n*=3, *l*=2, *m*=±2

$$\psi_{3d_{x^2-y^2}}(r,\theta,\varphi)=\frac{1}{\sqrt{2}}\left(\psi_{3d2}(r,\theta,\varphi)+\psi_{3d-2}(r,\theta,\varphi)\right)$$

$$=\frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}}e^{-\frac{Zr}{3a_0}}\left(x^2-y^2\right)$$

Hence, this is called a $3d_{x^2-y^2}$ function.



Hydrogen-like wavefunctions are also called ***hydrogen-like orbitals.***

In first year chemistry you may have wondered where the strange labels for these hydrogen atom orbitals came from. It is precisely from the mathematical form of the wave functions after we take linear combinations of the imaginary functions with ±*m*.

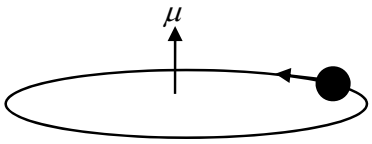
These hydrogen atom wave functions derive additional importance because when we get to many electron atoms, products of hydrogen atom functions are used as a first approximation to the eigenfunctions.

Also, linear combinations of hydrogen-like orbitals are used to understand molecular bonding. The terms *sp*, sp^2, and sp^3 hybridization originates from linear combinations of *s* and *p* orbitals. Remember the energy depends only upon *n*. So for example, a 2*s* and 2*p* have the same energy to first order.

6.1 The Zeeman effect

I would briefly like to consider how the hydrogen atom energy levels change when the atom is placed in a magnetic field. This will give you a bit more insight into the meaning of the magnetic quantum number, *m*. This effect is called the **Zeeman Effect**.

We must first consider the nature of the interaction of a moving charge with a magnetic field.



The motion of an electric charge around a closed loop produces a magnetic dipole μ whose magnitude is

$$\mu = iA$$

where i is the current in amps/sec and A is the area of the loop in m^2.

For a circular loop,

$$i = \frac{q\mathrm{v}}{2\pi r}$$

where q is the charge, v is the linear velocity and r is the radius of the loop.

The area of a circular loop $A = \pi r^2$ so

$$\mu = \frac{q\mathrm{v}r}{2}$$

However we must consider the fact that the magnetic dipole moment is a vector property with both magnitude and direction. This tells us the magnitude but not the direction of the magnetic dipole.

In general,

$$\boldsymbol{\mu} = \frac{q(\mathbf{r}\times\mathbf{v})}{2}$$

This is true whether or not you have a circular loop. You can show that if the loop is circular, then you will get the result we had previously.

This says that the direction of the magnetic moment is perpendicular to the plane of rotation as I have drawn above. Remember when doing a cross product you use the right hand rule to determine the direction of the resultant vector.

Note that

$$\mathbf{p} = m\mathbf{v},$$

so

$$\boldsymbol{\mu} = \frac{q(\mathbf{r}\times\mathbf{p})}{2m} = \frac{q}{2m}\mathbf{L}$$

Since $\mathbf{L} = \mathbf{r}\times\mathbf{p}$

For an electron q = -|e|, so

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

Even though we cannot think about the electron in a hydrogen atom moving in a circular orbit, we know that it does have angular momentum and hence will have a magnetic moment. To understand how the magnetic field affects the energy levels of the hydrogen atom, we must add the energy of interaction between a magnetic field and a magnetic dipole into the Hamiltonian and solve the Schrödinger equation. The potential energy of interaction between a magnetic dipole and a magnetic field is given by

$$U = -\boldsymbol{\mu}\cdot\mathbf{B}$$

where **B** is the magnetic field. If we choose the magnetic field to be aligned along the *z*-direction, we have

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

We can therefore write the Hamiltonian for the H atom in a magnetic field as

$$\hat{H} = \hat{H}_0 + \frac{|e|B_z}{2m_e}\hat{L}_z$$

where $\hat{H}_0$, is the Hamiltonian in the absence of the field and $\hat{L}_z$ is the operator corresponding to the *z*-component of the angular momentum.

The Schrödinger equation is therefore

$$\hat{H}_0\psi + \frac{|e|B_z}{2m_e}\hat{L}_z\psi = E\psi$$

Recall that the hydrogen atom wavefunctions are eigenfunctions of both the $\hat{H}_0$, and the $\hat{L}_z$ operators. That is, we can write separate eigenvalue equations:

$$\hat{H}_0 R_{nl}(r)Y_l^m(\theta,\varphi) = -\frac{\mu e^4}{8\varepsilon_0^2 h^2 n^2}R_{nl}(r)Y_l^m(\theta,\varphi)$$

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

You can use these relations to see that:

$$E = -\frac{\mu e^4}{8\varepsilon_0^2 h^2 n^2} + \frac{|e|B_z}{2m_e}m\hbar \qquad n = 1,2,3,\ldots \qquad m = 0,\pm1,\pm2,\ldots\pm l$$

Let's consider the implications of this.

In the absence of the field the hydrogen atom energies are just as we had previously calculated. However in the presence of the field, an extra term is added which depends on the value of *m*.

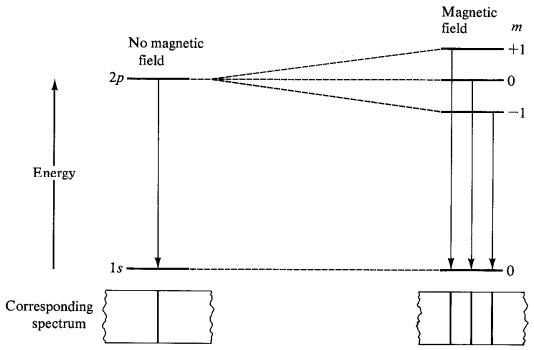
Consider the 2*p* level for example. *m* can take on the values *m* = -1, 0, 1

For *m*=0 there is no energy due to the magnetic field.

For *m*=1 there is a positive term added to the energy.

For *m* = -1 there is a negative term.

The energy that is added to each level is directly proportional to the magnetic field. Schematically this looks like the following:



The 2*p* level is a single level in the absence of the field splits up into three different levels in the absence of the field. The magnitude and direction of the shift depends upon the value of *m* and the magnetic field strength.

The splitting can be observed experimentally by looking at the transitions of the hydrogen atom. In the absence of the field, there will be a single transition from 1*s* to 2*p*, whereas in the presence of the field, the single line will be split into a triplet.

The splitting is relatively small relative to the 1*s*→2*p* transition energy. If we were considering a 3*d* level rather than a 2*p*, the level would be split into a quintet, since *m* can range from -2 to +2. One can use this effect to determine the value of *l* in the terminal level.

Pieter Zeeman