

Lectures 16-17

We now turn to our first quantum mechanical problems that represent real, as opposed to idealized, systems. These problems are the **structures of atoms**. We will begin first with **hydrogen-like atoms**, atoms and ions that have only one electron. This problem is of importance because the hydrogen-like atom has certain features that will be common to all atomic systems. In addition, it is important because **it is the last problem that we can solve exactly**. All other problems will involve both approximations and correction factors.

As always, when beginning to consider a new quantum mechanical problem we need to write down the Hamiltonian. The **hydrogen-like atom is an atom with atomic number  $Z$  and one electron**. The charge on the nucleus is  $+Ze$ , where  $e$  is the magnitude of the charge of the electron,  $1.602 \times 10^{-19}$  C and the charge on the electron is  $-e$ . The **potential energy of attraction between the electron and the nucleus is given by the Coulomb potential**,

$$V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r},$$

where  $r$  is the distance between the electron and the nucleus, and  $\epsilon_0$  is the permittivity of free space. The potential is negative to indicate that the interaction between the electron and the nucleus is attractive. In addition, when we write the Hamiltonian for this problem,

we will use the reduced mass,  $\mu = \frac{m_e m_n}{m_e + m_n}$ , for the mass of the system. In this equation,

$m_n$  is the mass of the nucleus and  $m_e$  is the electron mass. Since the nucleus is orders of magnitude more massive than the electron, the reduced mass will be slightly less than the mass of an electron,  $9.11 \times 10^{-31}$  kg. Thus our Hamiltonian for the hydrogen-like atom is

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The Schrödinger equation for the hydrogen like atom will not be separable unless the Hamiltonian is expressed in one of a number of non-Cartesian coordinates. (Write  $r$  as function of  $x, y, z$  and ask if separable.) The simplest of these are spherical coordinates. This implies that our wavefunction will be a function of  $r, \theta$  and  $\phi$  so our Schrödinger equation becomes

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right)\psi(r, \theta, \phi) = E\psi(r, \theta, \phi).$$

Writing this out in full gives us

$$\left(-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] - \frac{Ze^2}{4\pi\epsilon_0 r}\right)\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

First, notice that all of the terms in this operator are terms involving only radii or angles.

This suggests that we can **apply separation of variables**, and write

$$\psi(r, \theta, \phi) = R(r) f(\theta, \phi).$$

Second, notice that if we multiply through by  $-\frac{\hbar^2}{2\mu r^2}$ , that the angular terms are identical

to  $\frac{\hat{L}^2}{2\mu r^2}$ , which was the Hamiltonian for the rigid rotor. This suggests that  $f(\theta, \phi) =$

$Y_l^m(\theta, \phi)$ , the spherical harmonics which were our solutions to the rigid rotor.

If we now take  $\psi(r, \theta, \phi) = R(r)Y_l^m(\theta, \phi)$ , and plug it into our Schrödinger equation, it results in the separation of our Schrödinger equation into an angular equation whose eigenfunctions are indeed the spherical harmonics, and a radial equation,

$$\left(-\frac{\hbar^2}{2\mu r^2} \left(\frac{d}{dr} \left(r^2 \frac{d}{dr}\right) - l(l+1)\right) - \frac{Ze^2}{4\pi\epsilon_0 r}\right)R(r) = ER(r)$$

Notice that the angular momentum quantum number  $l$  is part of our radial Hamiltonian, so we expect that our solution  $R(r)$  will depend in part on  $l$ . Just as the spherical harmonics will give us the angular probability distribution for finding the electron, **the radial function  $R(r)$  will give us the probability distribution for finding the electron at various distances from the nucleus.**

When we solve the radial equation we obtain a set of functions called **Laguerre polynomials,  $R_{nl}(r)$** . The first few Laguerre polynomials are

$$R_{10}(r) = 2^{-1/2} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}$$

$$R_{20} = 8^{-1/2} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$$

$$R_{21} = 24^{-1/2} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}},$$

where  $a_0$  is 52.918 pm, the radius of the first orbit of a Bohr hydrogen atom and is called the Bohr radius.

**Thus our solution for the hydrogen atom is a product of two functions,**

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

One of these functions, the radial function, depends on two quantum numbers,  $n$  and  $l$ , while the other function depends on both  $l$  and  $m$ . The overall wavefunctions are labeled with all three quantum numbers  $n$ ,  $l$ , and  $m$ .

The eigenvalues of hydrogen-like atoms are given by the equation

$$E_n = -\frac{\mu e^4 Z^2}{2(4\pi\epsilon_0)^2 \hbar^2 n^2}$$

and thus depend only on the quantum number  $n$ , called the **principle quantum number**, which takes on any value from 1 to  $\infty$ . As usual the negative sign indicates that the electron is bound to the nucleus, i.e., the negative energy  $E_n$  is the energy it would take to remove an electron in state  $n$  completely from the hydrogen like atom. This energy is called the binding energy, because it is the amount of energy necessary to ionize the atom. Increasing the atomic number  $Z$  has the effect of increasing this **binding energy**. For example, the binding energy of the hydrogen electron in its ground state is -13.605 eV, while the binding energy for the  $\text{Li}^{+2}$  electron in its electronic ground state is -122.4 eV. To embellish this point with a rather absurd example, the binding energy in the ground electronic state of  $\text{U}^{+91} = -1.127 \times 10^5$  eV. To perhaps put this on a more familiar basis for comparison, 1 eV = 96.5 kJ/mol.

Notice also that **the binding energy is reduced for a given atom as  $n$  increases**. Again for a couple of examples, hydrogen in its ground  $n = 1$  state has a binding energy of -13.605 eV, while in the  $n = 2$  state the energy is -3.401 eV, and in the  $n = 3$  state it is -1.512 eV. These numbers show us that the stablest state of the atom is  $n = 1$ . This stablest state is often referred to as the ground state.

As we showed for the Bohr atom, **these energies can account for the spectra of the hydrogen atom**. Absorption spectra arise when an electron is promoted from a state with  $n = n_1$  to a higher state  $n_2$ , while emission spectra arise when an electron drops from an initial state with  $n = n_1$  to a lower state  $n_2$ . The photon energy is equal to the difference between the energies of these states, i.e., for absorption  $h\nu = E_2 - E_1$ . The wavenumber of

the absorption is related to the energy by  $\Delta E = hc\bar{\nu}$ , so for the hydrogen atom the wavenumber is given by

$$\bar{\nu} = \frac{1}{hc}(E_{n_2} - E_{n_1}) = \frac{1}{hc} \left( -\frac{\mu e^4 Z^2}{2(4\pi\epsilon_0)^2 \hbar^2} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \right).$$

If we calculate our reduced mass carefully, this equation will reproduce experimental measurements of hydrogen atom spectral lines to seven significant figures.

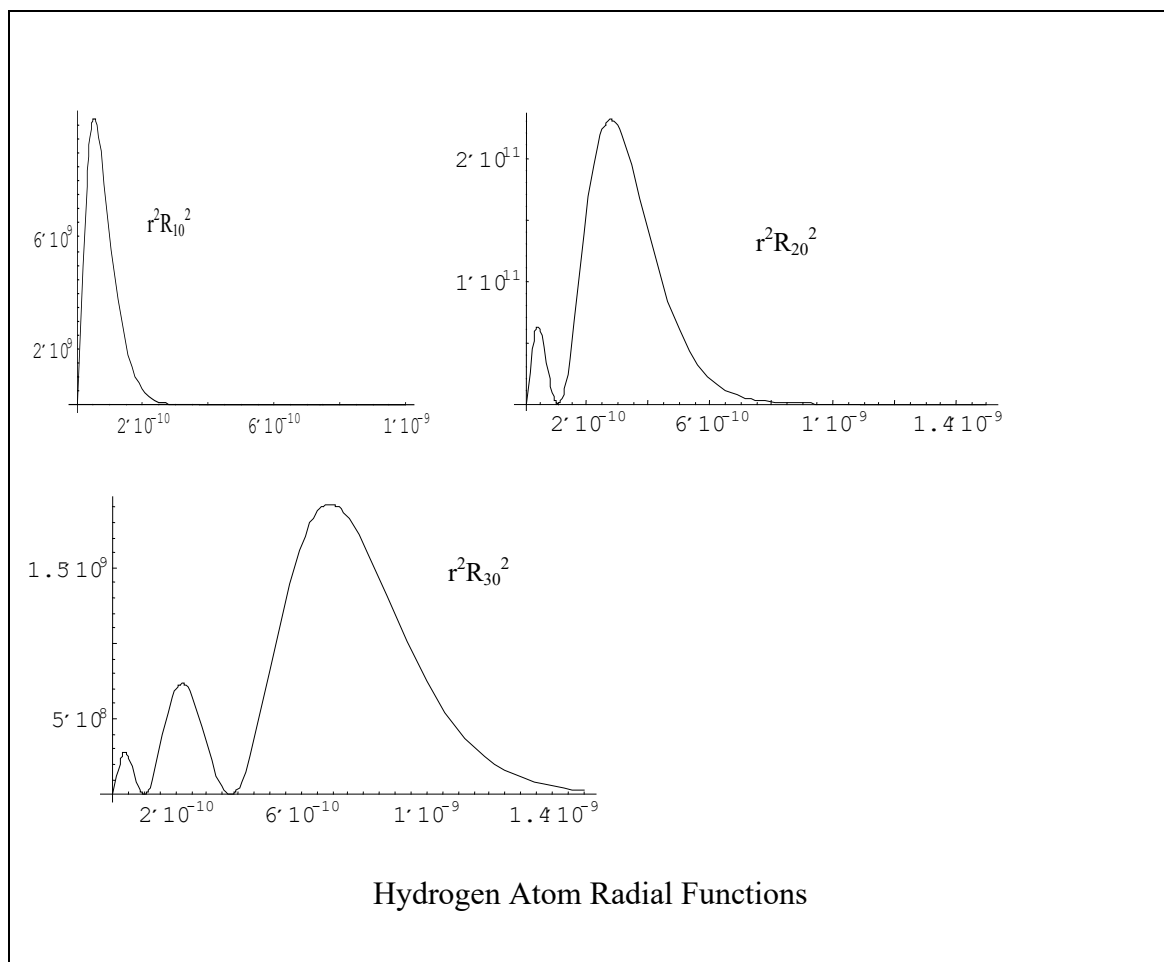
It is important to realize that **there are several eigenstates of hydrogen with the same energy for each  $n > 1$** . This is because even though the energies depend only on  $n$ , the eigenfunctions depend on  $n$ ,  $l$ , and  $m$ . **The values of these quantum numbers are not independent but are interrelated.** As just stated,  **$n$  can vary from 1 to  $\infty$ .  $l$ , the angular momentum quantum number, can take on only values from 0 to  $n-1$ , and  $m$ , the magnetic quantum number, can vary from  $-l$  to  $l$ .** Thus when  $n = 1$ , there is only one eigenfunction  $\psi_{100} = R_{10}(r)Y_0^0(\theta, \phi)$ , while for  $n = 2$ , there are four,  $\psi_{200} = R_{20}(r)Y_0^0(\theta, \phi)$ ,  $\psi_{21-1} = R_{21}(r)Y_1^{-1}(\theta, \phi)$ ,  $\psi_{210} = R_{21}(r)Y_1^0(\theta, \phi)$ , and  $\psi_{211} = R_{21}(r)Y_1^1(\theta, \phi)$ . Thus the degeneracy of  $n = 1$  is one, for  $n = 2$  the degeneracy is four and for a level with principle quantum number  $n$  the degeneracy is given by  $n^2$ .

What do these eigenfunctions look like? It is important to realize that **both the radial function and the angular function contribute to the probability density of the wavefunction**. Typically when the hydrogen atom is treated at the freshman level, only the angular portion of the wavefunction is considered. We will look at both the angular and radial parts of the wavefunction, first separately and then together.

Let's begin with a quick review of the **angular parts**. The spherical harmonics are exactly the solutions we calculated for the rigid rotor. When  $l = 0$  and  $m = 0$ , the angular

solution is spherical, i.e., the angular probability distribution is completely uniform, and there are no angular nodes. This is called an s orbital. If  $l = 1$ , the distribution is a double bowling ball shape, with a single angular node and pointing along the x, y or z axis, and is called a p orbital. **The value of m indicates the direction in which the orbital is pointing.** If  $l = 2$ , a d orbital, the distribution is one of two shapes. [Draw] Here m indicates the direction in which the x shaped orbitals are pointing, and also determines the unique shape of the fifth orbital. A d orbital has two angular nodes.

Let's look at our **radial functions**,  $R_{nl}(r)$ . First let's plot the **radial probability density**,  $R_{nl}^*(r)R_{nl}(r)r^2 dr$ , for a series of s orbitals with increasing n. The  $r^2 dr$  appears



because when we convert from Cartesian coordinates to spherical coordinates, the volume

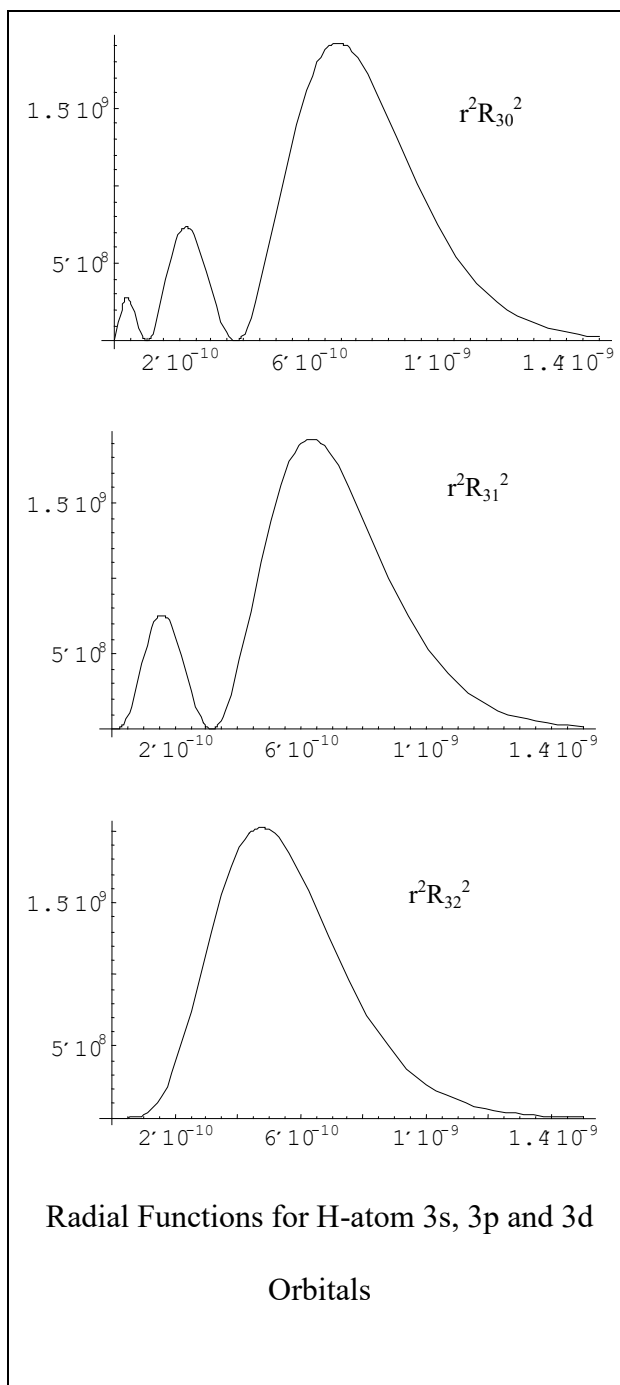
element  $dx dy dz$  becomes  $r^2 \sin \theta dr d\theta d\phi$ .  $r^2 dr$  is the differential element for  $r$ . Notice two things that change with increasing  $n$  and the same value of  $l$ . First **the number of radial nodes increases with increasing  $n$** .  $n=1$  has no radial nodes,  $n=2$  has one,  $n=3$  has two, etc. Second, notice that **as  $n$  increases, the probability of finding the electron farther from the nucleus increases**. This should make sense since as  $n$  increases energy increases, and a greater energy allows the electron to overcome some of the coulomb attraction. We can quantify this increase in radius by calculating the average radius between the nucleus and the electron, also called the expectation value of the radius. HOW DO WE CALCULATE THE AVERAGE OF A QUANTUM MECHANICAL QUANTITY? Thus

$$\langle r \rangle = \int_0^{\infty} R_{nl}^*(r)rR_{nl}(r)r^2 dr$$

WHY DIDN'T I INCLUDE THE ANGULAR PARTS? If we use this to calculate the average radius for a 1s and 2s orbital we find that  $\langle r \rangle$  for 1s is  $3/2 a_0$ , and  $\langle r \rangle$  for the 2s orbital is  $6a_0$ , where  **$a_0$  is the Bohr radius**. It is interesting to note that the Bohr radius corresponds to the most probable radius for the 1s orbital, but is smaller than the average radius of the orbital.

Now let's plot the **radial probability distribution for three states with the same principle quantum number but different values of  $l$** . Notice that **as  $l$  increases the number of radial nodes decreases**. For  $R_{30}(r)$ , we have two radial nodes,  $R_{31}(r)$  has one radial node, and  $R_{32}(r)$  has no radial nodes. So you see that **the number of radial nodes depends on both  $n$  and  $l$ , with the formula, # nodes =  $n - l - 1$** . In addition, we see that **as  $l$  increases the probability of finding the electron at longer distances decreases slightly**.

This sequence of radial functions for  $n=3$  leads to a natural question: if the bulk of the electron density gets closer and closer to the nucleus as we go from 3s to 3p to 3d, why does the hydrogenic 3s orbital have the same energy as the 3d orbital? The answer lies in the small amounts of probability density at the distances comparable to what we would see for 1s and 2s orbitals. These small probabilities that are very close to the nucleus compensate for the slightly longer distance of the outermost lobe.





When we start considering multielectron atoms, these small probabilities will have a profound effect on the energies of the various atomic subshells.

Let's combine the radial and angular functions for 1s, 2s and 3s orbitals, and for 3s, 3p and 3d orbitals. The s orbitals are simple to treat. Notice that we still have the same independence of electron position on the angle, but now as n increases there are radii at which there is no electron density.

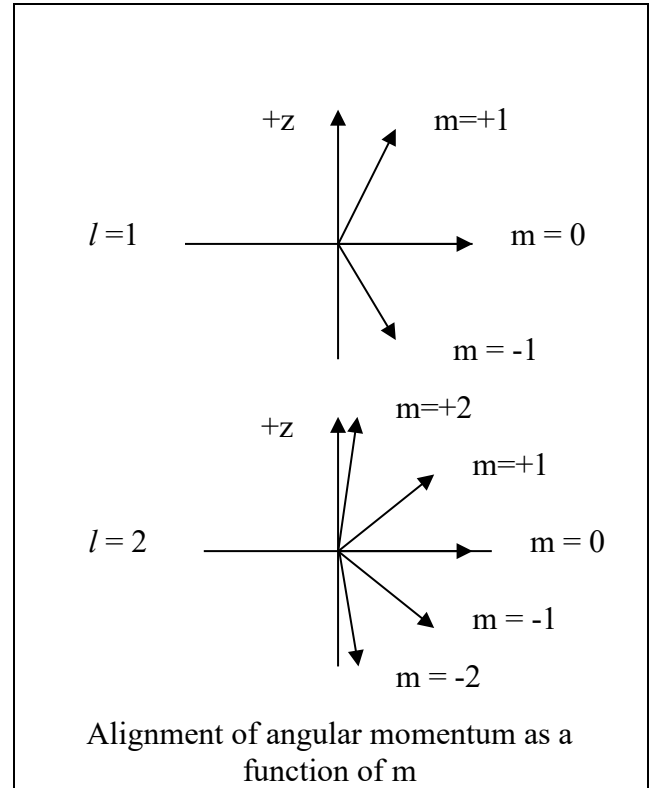
For the 3 different n = 3 orbitals note that while they all have the overall shapes that we expect for each type of orbital, the s and p orbitals are complicated by the presence of the radial nodes. Notice something else which I find interesting - that **the total number of nodes - angular + radial - is the same and equal to n - 1 for all of the orbitals with the same principle quantum number.**

Our solution to the Schrödinger equation for a hydrogen atom is  $\psi_{nlm} = R_{nl}(r) Y_l^m(\theta, \phi)$ . If we operate on this wavefunction with the operator for the angular momentum squared, we see that **this wavefunction is an eigenfunction of the angular momentum squared, with eigenvalue  $L^2 = \hbar^2 l(l + 1)$** . Therefore the magnitudes of the angular momentum for different states of the hydrogen electron are given by  $\hbar(l(l+1))^{1/2}$ .

For this reason we call the quantum number  $l$  for an atomic electron the angular momentum quantum number. For historical reasons it is also called the azimuthal quantum number, dating back to a time when Sommerfeld was trying to improve on Bohr's model by positing an elliptical orbit for electrons in atoms. We can show similarly that  **$L_z$ , the component of the angular momentum in the z direction, is given by  $L_z = m\hbar$** . For reasons that we will see shortly, m is often called the magnetic quantum number. Thus **the angular**

momenta of the hydrogen atom are identical to those of the rigid rotor with the same quantum numbers  $l$  and  $m$ .

The source of this angular momentum is the orbital motion of the electron around the nucleus. Since  $l$  can vary from zero to infinity, a hydrogen atom can have any angular momentum from zero on up. Note that this is the case even when the overall energy  $n$  is high, since every set of orbitals with a given value of  $n$  contains one with  $l = 0$ . The  $m$  values, as in the case of the rigid rotator, give us the various orientations of the angular momentum vector with respect to the  $z$ -axis. In other words,  $m$  tells us how



closely the angular momentum is aligned with the  $z$ -axis. Notice that positive values of  $m$  are aligned in the positive  $z$  direction, and that when  $m = 0$ , the angular momentum is perpendicular to the  $z$ -axis. To reiterate our results from the rigid rotator, for each  $l$  there are  $2l + 1$  orientations of the angular momentum.

If we don't include the effect of electron spin, which we will treat shortly, and in the absence of an external magnetic field, there is no observable associated with these various  $L_z$  states. Remember that under these conditions, the energy, for example, depends only on the value of  $n$ . However, in the presence of an external magnetic field, the

energy of the hydrogen atom depends on the value of  $m$ , with each  $m$  yielding a different total energy.

Why is this? We know from physics that **any accelerating charge generates a magnetic field**. Remember that all objects moving in a circle are constantly accelerating, so **if an electron is moving in a circle with any angular momentum at all it will generate a magnetic field in the direction of the angular momentum vector**. The larger the angular momentum, the larger this generated field will be. **The magnetic field generated by the orbital angular momentum of the electron will interact with the external field to raise or lower the energy of the electron**. The amount and sign of the energy change depends on the alignment of the two fields with respect to each other.

The generated magnetic field is called the **magnetic dipole moment** of the electron and is given by

$$\boldsymbol{\mu} = \gamma_e \mathbf{L},$$

where  $\gamma_e$  is called the **gyromagnetic ratio** of the electron and is equal to  $-\frac{e}{2m_e}$ , where  $e$  is the charge on the electron, and  $m_e$  is the mass of the electron. The z component of the magnetic field is given by

$$\mu_z = -\frac{e}{2m_e} L_z = -\left(\frac{\hbar e}{2m_e}\right)m = -\mu_B m,$$

where  $\mu_B$ , the Bohr magneton, is equal to  $\frac{\hbar e}{2m_e} = 9.724 \times 10^{-24} \text{ J T}^{-1}$ . It is introduced because

**all our z components of the magnetic moment will be some integral multiple of this number**. The potential energy of interaction between a magnetic dipole and a magnetic field is given by

$$V' = -\boldsymbol{\mu} \cdot \mathbf{B}.$$

Since by convention, the direction of an external field is taken to be the positive z direction, this simplifies to

$$V' = \mu_z B = \frac{eB}{2m_e} L_z$$

If we want **to find the energy of a hydrogen atom in the presence of the magnetic field, we have to add the quantum operator version of this potential to the Hamiltonian** in the absence of the field. The quantum mechanical operator for this potential is obtained by substituting the operator  $\hat{L}_z$  for  $L_z$ . The new Hamiltonian now becomes

$$\hat{H} = \hat{H}^{(0)} + \frac{eB}{2m_e} \hat{L}_z$$

where

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

and is the Hamiltonian in the absence of the magnetic field. The Schrödinger equation which arises from this Hamiltonian,

$$\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \frac{eB}{2m_e} \hat{L}_z\right) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

is too difficult to be solved directly but can be treated with relative ease by a method called **perturbation theory**. We'll take a brief digression from the treatment of the angular momentum of the hydrogen atom to treat perturbation theory.

**The basic method of perturbation theory is to separate a Hamiltonian that is either too difficult to solve, or impossible to solve exactly, into two parts, one which**

can be solved either easily or exactly, and one containing the rest of the terms in the **Hamiltonian**. We write this as

$$\hat{H} = \hat{H}^{(0)} + \hat{H}',$$

where  $\hat{H}^{(0)}$ , **the unperturbed Hamiltonian, is the part of the Hamiltonian for which the Schrödinger equation can be solved exactly** (and in fact is usually has been), while  $\hat{H}'$ , **called the perturbation, is the remainder of the Hamiltonian**. Perturbation terms usually arise from two types of problems. One is like ours, where the addition of an external field adds new terms to the Hamiltonian whose effects on the energy and wavefunction we need to calculate. The other is a case where the problem that can be solved exactly is an oversimplification of a real physical problem, and the new terms serve the purpose of making the Hamiltonian more realistic. An example of the latter would be a rotating molecule. Our simplest model for a rotating molecule is the rigid rotor, which is a fairly good approximation, but is oversimplified because real molecules do not maintain a constant radius during rotation, but both vibrate continually and stretch as they rotate more and more. The effects of the vibration of the bond and of the stretching of the bond on the rotational energies can be treated by perturbation theory.

In our problem of a hydrogen atom in a magnetic field, the unperturbed Hamiltonian,  $\hat{H}^{(0)}$ , is the Hamiltonian for the hydrogen atom in the absence of a field,

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The perturbation is the potential energy of the magnetic dipole in a magnetic field,

$$\hat{H}' = \frac{eB}{2m_e}\hat{L}_z$$

It is assumed that we already know the solutions to the Schrödinger equation associated with  $\hat{H}^{(0)}$ , which are the solutions of the equation

$$\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$$

where  $\psi^{(0)}$  is the unperturbed wavefunction, and  $E^{(0)}$  is the unperturbed energy. For example, in our problem, the unperturbed wavefunctions are the eigenfunctions of the hydrogen atom,

$$\psi_{nlm}^{(0)} = R_{nl}(r)Y_l^m(\theta, \phi),$$

and our unperturbed eigenvalues are the hydrogen atom eigenvalues,

$$E_n^{(0)} = -\frac{\mu e^4 Z^2}{2(4\pi\epsilon_0)^2 \hbar^2 n^2}.$$

**Perturbation theory is based on the assumption that if the perturbation is small, then the eigenfunctions  $\psi$  of the complete Hamiltonian  $\hat{H}$ , will be close to the wavefunctions  $\psi^{(0)}$  of the unperturbed Hamiltonian, and the eigenvalues  $E$  of the complete Hamiltonian will be close to the eigenvalues  $E^{(0)}$  of the unperturbed Hamiltonian.** In other words, if  $\hat{H}'$  is a small correction to the Hamiltonian, and therefore  $\hat{H} = \hat{H}^{(0)} + \hat{H}'$  is close to  $\hat{H}^{(0)}$ , we can write our eigenfunction  $\psi$  as  $\psi = \psi^{(0)} + \Delta\psi$ , where  $\psi^{(0)}$  is our uncorrected eigenfunction, and  $\Delta\psi$  is a small correction, and we can write our eigenvalue  $E$  as  $E = E^{(0)} + \Delta E$ , where  $E$  is our unperturbed energy and  $\Delta E$  is a small correction to the energy. The Schrödinger Equation now becomes

$$\hat{H}(\psi^{(0)} + \Delta\psi) = (E^{(0)} + \Delta E)(\psi^{(0)} + \Delta\psi).$$

This method is only generally valid if  $\Delta E \ll E^{(0)}$ . In cases where  $\Delta E$  is not much smaller than  $E^{(0)}$  perturbation theory often works, although not in its simplest forms, but sometimes the results fail to converge to a solution at all.

In general, the corrections  $\Delta E$  and  $\Delta\psi$  are calculated as an infinite series of increasingly smaller corrections, i.e.,

$$\Delta\psi = \psi^{(1)} + \psi^{(2)} + \psi^{(3)} + \dots$$

and

$$\Delta E = E^{(1)} + E^{(2)} + E^{(3)} + \dots,$$

where  $\psi^{(1)}$  and  $E^{(1)}$  are called the first order corrections to the wavefunction and energy respectively,  $\psi^{(2)}$  and  $E^{(2)}$  are the second order corrections and so on. Since for many problems the size of the correction decreases drastically with order, i.e., the first order corrections are nearly equal to  $\Delta E$  or  $\Delta\psi$ , we will treat the first order corrections only.

The methods of obtaining the correction  $\psi^{(1)}$  are somewhat involved, but **the correction  $\Delta E$  can be obtained rather simply, so we will treat this first.** We limit ourselves, both for the energy correction and the correction to the wavefunction, to the case in which our energy levels are non-degenerate. After substituting  $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$  in our Schrödinger equation above, and going through some tedious calculations we obtain the following formula for the first order energy correction,

$$E^{(1)} = \int_{-\infty}^{\infty} \psi^{(0)*} \hat{H}^{(1)} \psi^{(0)} d\tau$$

DOES ANYBODY RECOGNIZE THE RIGHT SIDE OF THIS EQUATION? **The first order energy correction is just the expectation value or average of the perturbation.** This correction is a first approximation. The approximation is based on assuming that certain terms that

we get in expanding the equation above are sufficiently small to be neglected. If these so called second order (and higher order) terms are not too small to be neglected, then additional energy correction terms need to be calculated as well.

The treatment of the first order correction to the wavefunction,  $\psi^{(1)}$ , is more complicated. Once again, we take advantage of the fact the set of solutions to the unperturbed wavefunction,  $\{\psi_n^{(0)}\}$ , are a complete orthonormal set. While the actual formula is somewhat more complicated, it essentially amounts to writing  $\psi^{(1)}$  as a linear combination of the zero order solutions  $\{\psi_m^{(0)}\}$ . The formula obtained after following this procedure is

$$\psi_n^{(1)} = \sum_{m \neq n} \frac{\int_{-\infty}^{\infty} \psi_m^{*(0)} \hat{H}' \psi_n^{(0)} d\tau}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}.$$

In this equation, the symbol  $\sum_{m \neq n}$  indicates that the sum is over all the unperturbed states

except  $\psi_n$ . Note that the effect of the term in the denominator,  $E_n^{(0)} - E_m^{(0)}$ , is to give

greater weight to those states which are closest in energy to the state for which the

perturbation correction is being calculated. The term  $\int_{-\infty}^{\infty} \psi_m^{*(0)} \hat{H}' \psi_n^{(0)} d\tau$  tells us how much

the perturbation  $\hat{H}'$  makes the unperturbed wavefunction  $\psi_n^{(0)}$  like  $\psi_m^{(0)}$ . The more the

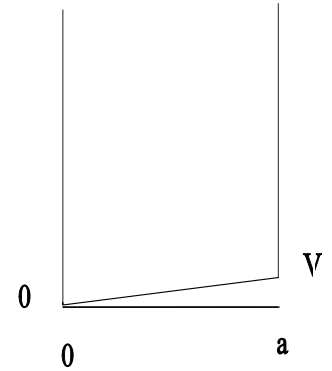
perturbation makes the two wavefunctions alike, the bigger  $\psi_m^{(0)}$ 's contribution to  $\psi_n^{(1)}$

will be.



Let's do a simple example. The first problem we solved in quantum mechanics was the particle in a box. The potential was written as  $V = 0, 0 \leq x \leq a; V = \infty$  elsewhere. The Hamiltonian for this problem was given as  $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$ , and the eigenfunctions

were given by  $\psi_n = \left(\frac{2}{a}\right)^{1/2} \sin \frac{n\pi x}{a}$ , with energies  $E_n = \frac{n^2 \hbar^2}{8ma^2}$ .



Suppose we change this slightly so that the bottom of the box is slightly slanted instead of flat. In this case the potential between 0 and a is given by

$$V(x) = Ux/a.$$

The Hamiltonian for this new problem is  $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{U}{a}x$ . We can break this into an unperturbed Hamiltonian and a perturbation. WHAT IS THE UNPERTURBED HAMILTONIAN? WHAT IS THE PERTURBATION? According to perturbation theory, the change in energy of our eigenvalues is given by

$$\begin{aligned} E^{(1)} &= \int_0^a \psi^{(0)*} \hat{H}^{(1)} \psi^{(0)} dx \\ &= \int_0^a \left(\frac{2}{a}\right)^{1/2} \sin \frac{n\pi x}{a} \frac{U}{a} x \left(\frac{2}{a}\right)^{1/2} \sin \frac{n\pi x}{a} dx = \frac{U}{2} \end{aligned}$$

This means that our total energy is  $E \approx E(0) + E^{(1)} = \frac{\hbar^2 n^2}{8ma^2} + \frac{U}{2}$ . Note that this result matches our qualitative interpretation of the energy correction being the average of the perturbation.

The correction to the wavefunction,  $\psi^{(1)}$ , is given by,

$$\psi_n^{(1)} = \sum_{m \neq n} \frac{\int_0^a \sin \frac{m\pi x}{a} \frac{Ux}{a} \sin \frac{n\pi x}{a} dx}{\frac{\hbar^2(n^2 - m^2)}{8ma^2}} \sin \frac{m\pi x}{a},$$

and the corrected wavefunction  $\psi$  is approximated by

$$\psi \approx \psi^{(0)} + \psi^{(1)}.$$

In conclusion, we see that first order perturbation theory is relatively easy to use. In fact, for the first order energy correction it requires no new techniques - just taking quantum mechanical averages, something we've already done more than once.

If we **apply perturbation theory to the H atom in a magnetic field**, our energy correction is

$$\Delta E = \int \psi_{nlm}^*(r, \theta, \phi) \frac{eB}{2m_e} \hat{L}_z \psi_{nlm}(r, \theta, \phi) d\tau = \mu_B mB.$$

Our total energy is therefore  $E^{(0)} + \Delta E$  and is equal to

$$E_{nlm} = -\frac{\mu e^4 Z^2}{2(4\pi\epsilon_0)^2 n^2 \hbar^2} + \mu_B mB$$

We can draw the following conclusions. First, **each of the  $(2l_{\max} - 1)$  m states in a given n shell will have a different energy in a magnetic field.** Second, **the energy difference increases as the strength of the magnetic field increases.** A similar effect is responsible for the increased resolution with increasing field strength in NMR. In addition, the magnetic dipoles that result from the orbital angular momentum of electrons are along with the magnetic moments due to electron spin, responsible for the magnetic susceptibilities of paramagnetic compounds, which some of you studied in Chem 317 lab. The orbital angular momentum makes a far weaker contribution to the paramagnetism of compounds than the electron spin, but still makes a measurable contribution.

## Lecture 18

We now turn to the helium atom, our first multielectron atom. The helium atom consists of two electrons moving in the field of a nucleus with charge +2. We call the distance between the nucleus and the first electron  $r_1$ , between the nucleus and the second electron  $r_2$ , and the distance between the two electrons  $r_{12}$ . As always, the Hamiltonian for this problem is the sum of the kinetic

energy and potential energy operators,

$\hat{H} = \hat{T} + \hat{V}$ . Since we have two electrons in this problem our kinetic energy operator will have one term for each of them,

$$\hat{T} = \frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2)$$

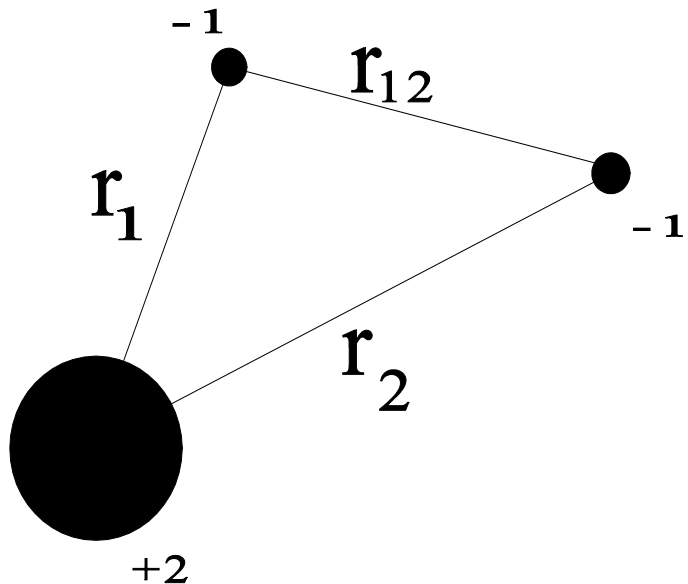
The potential energy operator has three terms, the potentials of interaction between each electron and the nucleus and the repulsion between the two electrons,

$$\hat{V} = \frac{1}{4\pi\epsilon_0} \left( -\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} \right),$$

where  $r_{12} = |r_1 - r_2|$ . Thus the overall Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) + \frac{1}{4\pi\epsilon_0} \left( -\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} \right)$$

The final term in the Hamiltonian, because of the term  $r_{12}$  in the denominator, prevents the Schrödinger equation from being separable, so we have to turn to approximation



**methods to solve the Schrödinger equation for the helium atom.** While this is a problem to which perturbation theory has been applied, we will turn to a new approximation method called the **variational method**, which is more generally useful in determining wavefunctions for multielectron atoms than perturbation theory.

The root of the variational method is the **variational principle**. We will first define the variational principle. Then we will show how this principle is incorporated into the variational method. The variational principle can be developed as follows. Consider the ground state for some arbitrary system for which we know the wavefunction  $\psi_0$  and the ground state energy  $E_0$ . The wavefunction and energy satisfy the Schrödinger equation

$$\hat{H} \psi_0 = E_0 \psi_0.$$

If we multiply both sides of this equation by  $\psi_0^*$  and integrate over all space, we get

$$\int \psi_0^* \hat{H} \psi_0 d\tau = E_0 \int \psi_0^* \psi_0 d\tau$$

Dividing by the integral on the right gives

$$\frac{\int \psi_0^* \hat{H} \psi_0 d\tau}{\int \psi_0^* \psi_0 d\tau} = E_0$$

The term in the denominator allows us to calculate energies for wavefunctions that are not yet normalized. Now suppose we use this equation to calculate the energy of some arbitrary function  $\phi$ . **The variational principle says that the energy of this arbitrary function  $\phi$  must be greater or equal to the energy  $E_0$  of the true ground state.** In other words,

$$E_\phi = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} \geq E_0.$$

This idea is sufficiently important that it bears repeating. The variational principle says that the energy of any arbitrary function, calculated using this equation, will always be greater than or equal to the energy of the ground state of the atom. In general, when people are told the variational principle, it is greeted with intense disbelief. However, it is not a postulate, but a derivable equation. I don't think that showing you the derivation is the best use of our class time, but I'd be happy to show it to anyone who would like to see it outside of class.

**How do we use the variational principle in an approximation method?** As always, the first step is to write our Hamiltonian. Second, we choose an arbitrary function, which we call a **trial function**, so that it depends on one or more arbitrary parameters, i.e.,

$$\phi = \phi(\alpha, \beta, \gamma, \dots)$$

where  $\alpha$ ,  $\beta$ , and  $\gamma$  are the arbitrary parameters, and are called **variational parameters**. Now we calculate the energy  $E_\phi$  of our trial function. This energy will also be a function of the arbitrary parameters,

$$E_\phi = E_\phi(\alpha, \beta, \gamma, \dots)$$

The next step is to take the derivative of this energy with respect to the first of these parameters and set it equal to zero. WHAT DO WE FIND OUT ABOUT A FUNCTION WHEN WE SET ITS DERIVATIVE EQUAL TO ZERO? Solving for the zero of this derivative allows us to find the value of  $\alpha$  which gives the lowest value of  $E_\phi$ . We now repeat this for each of the parameters. When we are done we have found the minimum value of  $E_\phi$  for this particular choice of trial function. The variational principle tells us that this will be greater than or equal to the energy of the true ground state eigenfunction of our Hamiltonian.

We can now modify our trial function and repeat the procedure. If our new  $E_\phi$  is higher in energy than our old one we know that our new wavefunction is worse than the old one. If our new  $E_\phi$  is lower in energy, we know that we have improved on the old one. In any case we know that whatever energy we calculate will be greater than or equal to the true ground state energy.

**Care must be taken to choose a trial function that is consistent with the known properties of the system, or it will be difficult to gain any physical insight from the solution.**

Let's look at an example of using the variational method. For the sake of comparison let's apply it to a system where we already know the answer, the radial function of the hydrogen atom. In the ground state  $l = 0$  and the Hamiltonian operator for the radial function is

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) - \frac{e^2}{4\pi\epsilon_0 r}.$$

Notice that we are only solving the radial equation. When we choose our trial function we want to try to match it to something we know about the system. We note that the Coulomb potential will tend to attract the electron to the nucleus, so we want a trial function which is high close to the nucleus, where  $r$  is small, and decreases at large  $r$ . As a guess we choose a Gaussian function,  $\phi = e^{-\alpha r^2}$ . [WHY COULDN'T WE USE  $\phi = e^{-\alpha r}$ , WHICH ALSO MATCHES OUR INITIAL INSIGHTS?] In this function  $\alpha$  is our variational parameter. The energy of this trial function is

$$E_\phi(\alpha) = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau}$$

$$= \frac{\int_0^\infty e^{-\alpha r^2} \left( -\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) \right) e^{-\alpha r^2} r^2 dr}{\int_0^\infty e^{-\alpha r^2} e^{-\alpha r^2} r^2 dr}$$

When this integral is carried out, we find that

$$E_\phi(\alpha) = \frac{3\hbar^2\alpha}{2\mu} - \frac{e^2\alpha^{1/2}}{2^{1/2}\epsilon_0\pi^{3/2}}$$

What we've done at this point is to obtain the energy as a function of  $\alpha$ . Now we want to minimize this energy by taking its derivative with respect to  $\alpha$  and setting it equal to zero.

When we do this, we find out that the value of  $\alpha$  for which the energy is minimized is

$$\alpha = \frac{\mu e^4}{18\hbar^4\epsilon_0^2\pi^3}$$

Substituting this in our equation for  $E_\phi$  yields

$$E_\phi = -.424 \frac{\mu e^4}{16\pi^2\epsilon_0^2\hbar^2}$$

Considering the crudeness of our trial function, this compares well with our actual ground state hydrogen energy,

$$E_0 = -.500 \left( \frac{\mu e^4}{16\pi^2\epsilon_0^2\hbar^2} \right)$$

Note that as expected the energy of our trial function is higher than the actual ground state energy.