

## 7. The Hydrogen Atom in Wave Mechanics

In this chapter we shall discuss :

- The Schrödinger equation in spherical coordinates
- Spherical harmonics
- Radial probability densities
- The hydrogen atom wavefunctions
- Angular momentum
- Intrinsic spin, Zeeman effect, Stern-Gerlach experiment
- Energy levels and spectroscopic notation, fine structure

# The Schrödinger equation in spherical coordinates ...

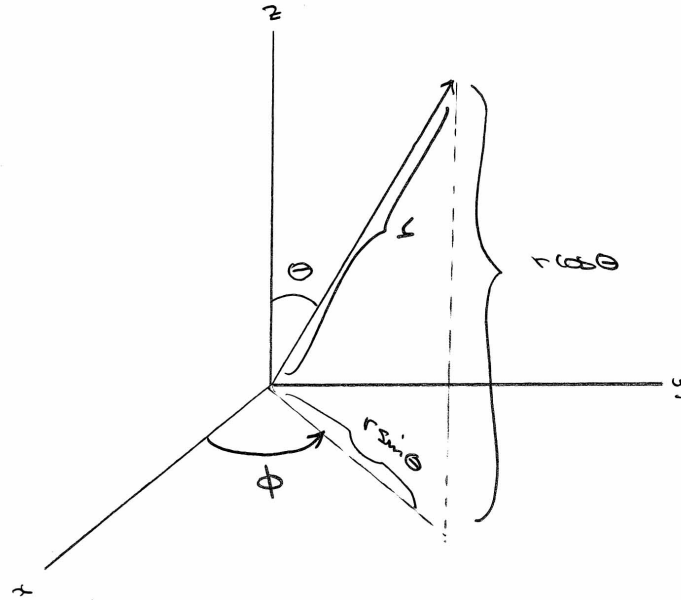
In 3D Cartesian  $(x, y, z)$  coordinates, the time-independent Schrödinger equation for a single particle bound by a potential,  $V(\vec{x})$ , is:

$$-\frac{\hbar^2}{2m}\nabla^2 u(\vec{x}) + V(\vec{x})u(\vec{x}) = Eu(\vec{x}) , \quad (7.1)$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} . \quad (7.2)$$

If the potential specialized to  $V(\vec{x}) = V(r)$ , where  $r$  is the distance to the origin, then, it is natural to use the spherical-polar coordinate system  $(r, \theta, \phi)$ .



## ... The Schrödinger equation in spherical coordinates ...

where:

$r$  is the distance from origin to the particle location

$\theta$  is the polar coordinate

$\phi$  is the azimuthal coordinate

Connection between Cartesian and spherical-polar:

$$x \rightarrow r \sin \theta \cos \phi, \quad y \rightarrow r \sin \theta \sin \phi, \quad z \rightarrow r \cos \theta \quad (7.3)$$

With  $dV = d\vec{x} = dx dy dz = r^2 dr \sin \theta d\theta d\phi$ , (volume element in both systems)

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz f(x, y, z) \longrightarrow \int_0^{2\pi} d\phi \int_0^{\pi} \sin \theta d\theta \int_0^{\infty} r^2 dr f(r, \theta, \phi) \quad (7.4)$$

The Laplacian operator of (7.2) becomes, in spherical-polar coordinates:

$$\nabla^2 = \mathcal{R} - \frac{\mathcal{L}^2}{r^2}, \quad \text{where} \quad (7.5)$$

$$\mathcal{R} = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}, \quad \text{and} \quad (7.6)$$

$$\mathcal{L}^2 = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (7.7)$$

## ... The Schrödinger equation in spherical coordinates ...

Since  $V(\vec{x}) = V(r)$ , a separation of variables occurs, and the most general solution of (7.1) in spherical-polar coordinates is given by:

$$u_{nlm_l}(r, \theta, \phi) = R_{nl}(r)Y_{l,m_l}(\theta, \phi) , \quad (7.8)$$

where

$$\mathcal{R} R_{nl}(r) = \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) R_{nl}(r) = E_{nl} R_{nl}(r) \quad (7.9)$$

and

$$\mathcal{L}^2 Y_{l,m_l}(\theta, \phi) = \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y_{l,m_l}(\theta, \phi) = l(l+1)Y_{l,m_l}(\theta, \phi) \quad (7.10)$$

The “radial” equation, (7.9) determines the energy of the system, since  $V(r)$  only involves the radial coordinate. The radial wavefunctions and the quantized energies are obtained by solving (7.10). Note that the radial eigenfunctions and energies may depend on two quantum numbers,  $n$  and  $l$ . We shall see several examples in due course.

The angular equation, (7.10), is a generic solution that applies for all the potentials of the form,  $V(\vec{x}) = V(r)$ . The  $Y_{l,m_l}(\theta, \phi)$ 's are the eigenfunctions of the angular part of the Laplacian operator,  $\mathcal{L}$ , with  $l(l+1)$  being its eigenvalue.

## ... The Schrödinger equation in spherical coordinates

We have 3 quantum numbers:

|       | name                            | range of values                                    |
|-------|---------------------------------|----------------------------------------------------|
| $n$   | principal                       | can be anything, depends on the specific of $V(r)$ |
| $l$   | orbital angular momentum        | positive integer or 0                              |
| $m_l$ | orbital magnetic quantum number | integer, $-l \leq m_l \leq l$                      |

Their meanings are:

|       |                                                                                                                                                         |
|-------|---------------------------------------------------------------------------------------------------------------------------------------------------------|
| $n$   | primary quantum number used to quantize $E$                                                                                                             |
| $l$   | quantized orbital angular momentum<br>may also have a role in determining the quantized $E$                                                             |
| $m_l$ | measures the $z$ -component of the angular momentum<br>plays no role in determining $E$<br>if $E$ depends on $n$ and $l$ , $D = \sum_{-l}^l 1 = 2l + 1$ |

# The Spherical Harmonics $Y_{l,m_l}(\theta, \phi) \dots$

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As evident in (7.10), the  $Y_{l,m_l}(\theta, \phi)$ 's are the eigenfunctions of the angular part of the Laplacian,

$$\mathcal{L}^2 Y_{l,m_l}(\theta, \phi) = l(l+1)Y_{l,m_l}(\theta, \phi) ,$$

with eigenvalue  $l(l+1)$ .

Low-order explicit forms:

| $l$      | $m_l$             | $Y_{l,m_l}(\theta, \phi)$                                                                                                                                                 |
|----------|-------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 0        | 0                 | $(\frac{1}{4\pi})^{1/2}$                                                                                                                                                  |
| 1        | 0, $\pm 1$        | $(\frac{3}{4\pi})^{1/2} \cos \theta, \mp (\frac{3}{8\pi})^{1/2} \sin \theta e^{\pm i\phi}$                                                                                |
| 2        | 0, $\pm 1, \pm 2$ | $(\frac{5}{16\pi})^{1/2} (3 \cos^2 \theta - 1), \mp (\frac{15}{8\pi})^{1/2} \sin \theta \cos \theta e^{\pm i\phi}, (\frac{15}{32\pi})^{1/2} \sin^2 \theta e^{\pm i2\phi}$ |
| $\vdots$ | $\vdots$          | $\vdots$                                                                                                                                                                  |

## ... The Spherical Harmonics $Y_{l,m_l}(\theta, \phi)$ ...

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The general form is:

$$Y_{l,m_l}(\theta, \phi) = (-1)^{m_l} \left[ \frac{2l+1}{4\pi} \frac{(l-m_l)!}{(l+m_l)!} \right]^{1/2} P_l^{m_l}(\cos \theta) e^{im_l \phi} \quad (7.11)$$

where the  $P_l^{m_l}$ 's are the “associated Legendre polynomials”. (You may be familiar with the usual Legendre polynomials, the  $P_l$ 's. They are a special case of the  $P_l^{m_l}$ 's obtained by setting  $m_l = 0$ .)

The most useful identities and recursion relationships for the generating all of the associated Legendre polynomials are:

$$P_{l+1}^{l+1}(\cos \theta) = -(2l+1) \sin \theta P_l^l(\cos \theta) \quad (7.12)$$

$$P_l^l(\cos \theta) = (-1)^l (2l-1)!! (1 - \cos^2 \theta)^{l/2} \quad (7.13)$$

$$P_{l+1}^l(\cos \theta) = \cos \theta (2l+1) P_l^l(\cos \theta) \quad (7.14)$$

$$(l - m_l + 1) P_{l+1}^{m_l}(\cos \theta) = (2l+1) \cos \theta P_l^{m_l}(\cos \theta) - (l + m_l) P_{l-1}^{m_l}(\cos \theta) \quad (7.15)$$

$$2m_l \cos \theta P_l^{m_l}(\cos \theta) = -\sin \theta \left[ P_l^{m_l+1}(\cos \theta) + (l + m_l)(l - m_l + 1) P_l^{m_l-1}(\cos \theta) \right] \quad (7.16)$$

## ... The Spherical Harmonics $Y_{l,m_l}(\theta, \phi)$ ...

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The relationship between the  $P_l^{m_l}$ 's for negative  $m_l$  is:

$$P_l^{-m_l}(\cos \theta) = (-1)^{m_l} \frac{(l - m_l)!}{(l + m_l)!} P_l^{m_l}(\cos \theta) . \quad (7.17)$$

The complex conjugate of  $Y_{l,m_l}(\theta, \phi)$  is given by:

$$Y_{l,m_l}^*(\theta, \phi) = Y_{l,-m_l}(\theta, \phi) \quad (7.18)$$

The statement of orthonormality is:

$$\delta_{l,l'} \delta_{m_l,m_{l'}} = \langle l, m_l | l', m_{l'} \rangle = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta Y_{l,m_l}^*(\theta, \phi) Y_{l',m_{l'}}(\theta, \phi) \quad (7.19)$$

Recalling that the parity operator has the effect:

$$\Pi[(\theta, \phi)] = (\pi - \theta, \phi + \pi) , \quad (7.20)$$

it follows that

$$\Pi[Y_{l,m_l}(\theta, \phi)] = (-1)^l Y_{l,m_l}(\theta, \phi) , \quad (7.21)$$

## ... The Spherical Harmonics $Y_{l,m_l}(\theta, \phi)$

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Finally, the  $m_l$ 's are the quantum number associated with the azimuthal component (equivalently, the  $z$  component of the angular momentum).

From the general form (7.11),

$$\mathcal{L}_z Y_{l,m_l}(\theta, \phi) = -i \left( \frac{\partial}{\partial \phi} \right) Y_{l,m_l}(\theta, \phi) = m_l Y_{l,m_l}(\theta, \phi) . \quad (7.22)$$

## Radial wave functions ...

As we have seen, for potentials of the form,  $V(\vec{x}) = V(r)$ , the angular part of the of the Laplacian in the Schrödinger equation, the  $\mathcal{L}$ , given in (7.7), is completely general.

In fact, it was discovered, and its solutions explored (eventually to become known as spherical harmonics) in a paper written by Laplace in 1783, well before Quantum Mechanics, by Pierre-Simon Laplace (1749—1827). It even predated Electromagnetism and Maxwell's equations. Laplace was an astronomer, as well as a Mathematician, and his application was in the classical mechanics of celestial bodies.

The applications are many! From Wikipedia: *“Spherical harmonics are important in many theoretical and practical applications, particularly in the computation of atomic orbital electron configurations, representation of gravitational fields, geoids, and the magnetic fields of planetary bodies and stars, and characterization of the cosmic microwave background radiation. In 3D computer graphics, spherical harmonics play a special role in a wide variety of topics including indirect lighting (ambient occlusion, global illumination, precomputed radiance transfer, etc.) and modeling of 3D shapes.*

You will encounter them in many applications in your technical career.

## Radial wave functions

Returning to quantum mechanics, we substitute the  $Y_{l,m_l}(\theta, \phi)$ 's into the Schrödinger equation

$$-\frac{\hbar^2}{2m} \left[ \mathcal{R} - \frac{\mathcal{L}^2}{r^2} \right] R_{nl}(r) Y_{l,m_l}(\theta, \phi) + V(r) R_{nl}(r) Y_{l,m_l}(\theta, \phi) = E_{nl} R_{nl}(r) Y_{l,m_l}(\theta, \phi) \quad (7.23)$$

operate using  $\mathcal{L}^2$  on  $Y_{l,m_l}(\theta, \phi)$ , and divide by  $Y_{l,m_l}(\theta, \phi)$  to obtain:

$$-\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right] R_{nl}(r) + \left[ V(r) + \frac{\hbar^2 l(l+1)}{2mr^2} \right] R_{nl}(r) = E_{nl} R_{nl}(r) , \quad (7.24)$$

that is known as the “radial wave equation”.

It is a second-order differential equation in the variable  $r$ , used to quantize the energies.

Note the role that the angular momentum part plays. It appears as a repulsive force that tends to push the particle away from the origin. This is the effect, quantum-mechanically speaking, of the effect of the centrifugal force.

We can anticipate that this will cause the probability density to be pushed away from the origin, with increasing effect as  $l$  increases, *i.e.* as angular momentum increases.

## The $l = 0$ radial wave functions, the “ $s$ -states” ...

When  $l = 0$  there is no angular distribution of the wavefunction.  $m_l$  can only assume the value  $m_l = 0$ . The angular solution contains no angular information and  $Y_{l,m_l}(\theta, \phi) = \sqrt{1/4\pi}$ . We are back to a one-dimensional problem!

Borrowing from spectroscopic notation, these are called “ $s$ -states”. (The  $s$  stands for “sharp”, because these spectroscopic lines tend to have very narrow distributions.)

There is a very nice analysis for this.

We define:

$$R_{n0}(r) = \frac{u_n(r)}{r} \quad \text{and} \quad E_{n0} = E_n, \quad (7.25)$$

(7.25)  $\rightarrow$  (7.24)  $\Rightarrow$

$$-\frac{\hbar^2}{2m} u_n''(r) + V(r)u_n(r) = E_n u_n(r) !!! \quad (7.26)$$

Since

$$\left[ \frac{f}{r} \right]'' + \frac{2}{r} \left[ \frac{f}{r} \right]' = \left[ \frac{f'}{r} - \frac{u}{r^2} \right]' + \frac{2}{r} \left[ \frac{f'}{r} - \frac{u}{r^2} \right] = \frac{f''}{r} - \cancel{\frac{f'}{r^2}} - \cancel{\frac{f'}{r^2}} + \cancel{\frac{2f}{r^3}} + \frac{2f}{r^2} - \cancel{\frac{2f}{r^3}} = \frac{f''}{r}$$

## ... The $l = 0$ radial wave functions, the “ $s$ -states” ...

(7.26) resembles the 1D Schrödinger equation!

∴ we can reuse much of the work we did in 1D.

There is, however, one subtle difference! We require that

$$u_n(0) = 0, \quad (7.27)$$

else the solution can not be continuous.

For example, consider the solutions to the harmonic oscillator, in 1 and 3 dimensions.

| $E$                      | Classical solutions for $V(r) = \frac{1}{2}kx^2$                                                  |          | Quantum solutions $V(r) = \frac{1}{2}kr^2$                                                        |          |
|--------------------------|---------------------------------------------------------------------------------------------------|----------|---------------------------------------------------------------------------------------------------|----------|
|                          | First four states $u_0(x), u_1(x), u_2(x), u_3(x)$                                                | $\Pi$    | First two $s$ -states $R_{10}(r), R_{20}(r)$                                                      | $\Pi$    |
| $\frac{1}{2}\hbar\omega$ | $\left(\frac{\alpha}{\sqrt{\pi}}\right)^{1/2} e^{-(\alpha x)^2/2}$                                | +1       | -                                                                                                 | -        |
| $\frac{3}{2}\hbar\omega$ | $(\alpha x) \left(\frac{2\alpha}{\sqrt{\pi}}\right)^{1/2} e^{-(\alpha x)^2/2}$                    | -1       | $(\alpha r) \left(\frac{2\alpha}{\sqrt{\pi}}\right)^{1/2} e^{-(\alpha r)^2/2}$                    | +1       |
| $\frac{5}{2}\hbar\omega$ | $[2(\alpha x)^2 - 1] \left(\frac{\alpha}{2\sqrt{\pi}}\right)^{1/2} e^{-(\alpha x)^2/2}$           | +1       | -                                                                                                 | -        |
| $\frac{7}{2}\hbar\omega$ | $[2(\alpha x)^3 - 3(\alpha x)] \left(\frac{\alpha}{3\sqrt{\pi}}\right)^{1/2} e^{-(\alpha x)^2/2}$ | -1       | $[2(\alpha r)^3 - 3(\alpha r)] \left(\frac{\alpha}{3\sqrt{\pi}}\right)^{1/2} e^{-(\alpha r)^2/2}$ | +1       |
| $\vdots$                 | $\vdots$                                                                                          | $\vdots$ | $\vdots$                                                                                          | $\vdots$ |

## ... The $l = 0$ radial wave functions, the “ $s$ -states” ...

- All the even parity 1D solutions are eliminated due to the boundary condition on  $u_n(0)$ , given in (7.27).
- All the odd parity states of the harmonic oscillator become  $l = 0$  solutions of the 3D spherical<sup>1</sup> harmonic oscillator.
- The eigenenergies of the 1D oscillator are given by  $E_n = \hbar\omega(n + 1/2)$ , where  $n = 1, 2, 3, \dots$ , while the 3D  $s$ -state eigenenergies are given by  $E_n = \hbar\omega(2n + 1/2)$ .<sup>2</sup>

Historically speaking, the spherical harmonic oscillator played an important role in the description of the first few bound states of the nucleus.

A slightly better approximation is given in the next example.

<sup>1</sup>The potential,  $V(r) = \frac{1}{2}kr^2$ , is called “spherical” because of its isotropic symmetry.

<sup>2</sup>“It can be shown” that if one includes angular momentum, the eigenenergies of the spherical harmonic oscillator are given by  $E_{nl} = \hbar\omega(2n + l + 1/2)$ , where  $n$  is the “principle” quantum number.

## ... The $l = 0$ radial wave functions, the “ $s$ -states” ...

### The finite spherical box potential ...

The finite spherical box potential is defined by:

$$V(r) = \begin{cases} 0 & \text{if } r \leq L \\ V_0 & \text{otherwise} \end{cases} \quad (7.28)$$

Since we are seeking  $l = 0$  solutions only, we employ (7.25)—(7.27) to solve this system.

Thus, the equation we must solve is:

$$\begin{aligned} \text{if } r \leq L & \quad u_n''(r) + k_n^2 u_n(r) = 0 \quad \text{where } k_n^2 = 2mE_n/\hbar^2 \\ \text{else} & \quad u_n''(r) - K_n^2 u_n(r) = 0 \quad \text{where } K_n^2 = 2m(V_0 - E_n)/\hbar^2 \end{aligned} \quad (7.29)$$

Due to the boundary condition (7.27), the solutions are of the form:

$$\begin{aligned} \text{if } r \leq L & \quad u_n(r) = A_n \sin k_n r \\ \text{else} & \quad u_n(r) = B_n e^{-K_n r} \end{aligned} \quad (7.30)$$

These equations are very familiar to us from our discussion of the finite 1D box potential ... with one essential difference ... there is no  $\cos k_n r$  because of the condition at the origin.

## ... The $l = 0$ radial wave functions, the “ $s$ -states” ...

The quantization condition is found by equating the logarithmic derivative at the edge of the potential, making the solution slope and value continuous.

The result was found in the 1D case to be

$$\beta_n = -\alpha_n \cot \alpha_n \quad (7.31)$$

where  $\alpha_n = kL$ , and  $\beta_n = K_n L$ , in this case. This is solved numerically, or graphically, as in Assignment 6.

However, the major result of this effort is that there must be a minimum, finite potential to bind at least one state, since  $\alpha_1^2 + \beta_1^2 = 2mV_0L^2/\hbar^2 > \pi^2/4$  to bind at least one state, or

$$V_0 > \frac{\hbar^2 \pi^2}{8mL^2} \quad (7.32)$$

Let us apply this knowledge to the most basic building block of nuclei, the deuteron.

# The only bound state of the deuteron ...

Going back to (7.24):

$$-\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right] R_{nl}(r) + \left[ V(r) + \frac{\hbar^2 l(l+1)}{2mr^2} \right] R_{nl}(r) = E_{nl} R_{nl}(r) ,$$

we note that the centrifugal force term, *i.e.*  $\hbar^2 l(l+1)/2mr^2$  is a repulsive force. Therefore, the minimum energy is expected to be obtained when  $l = 0$ .<sup>3</sup>

$\therefore$  we may attempt to characterise this nucleus with a single *s*-state solution, and use (7.25) and (7.26), where:

$$\begin{aligned} E_{n0} &= E_n \\ u_n(r) &= \frac{R_{n0}(r)}{r} \\ E_n u_n(r) &= -\frac{\hbar^2}{2m} u_n''(r) + V(r) u_n(r) \end{aligned} \tag{7.33}$$

<sup>3</sup>We shall be astonished to find out, in NERS 312, that the deuteron is about 96%  $l = 0$ , and 4%  $l = 2$ ! Let us ignore that 4% for the time being, and deal with it later, after we have talked about intrinsic spin.

## ... The only bound state of the deuteron ...

Essential facts of the deuteron for this discussion:

|                     |                                                                           |
|---------------------|---------------------------------------------------------------------------|
| name                | deuteron                                                                  |
| symbol              | $D$                                                                       |
| constituents        | $n, m_n c^2 = 939.6 \text{ [MeV]}$ and $p, m_p c^2 = 938.3 \text{ [MeV]}$ |
| lifetime            | stable                                                                    |
| reduced mass energy | $m_\mu c^2 = 469.5 \text{ [MeV]}$                                         |
| binding energy      | $E_b = 2.225 \text{ [MeV]}$                                               |
| RMS radius          | $\sqrt{\langle r_m^2 \rangle} = 1.975 \text{ [fm]}$                       |
| # of excited states | 0                                                                         |

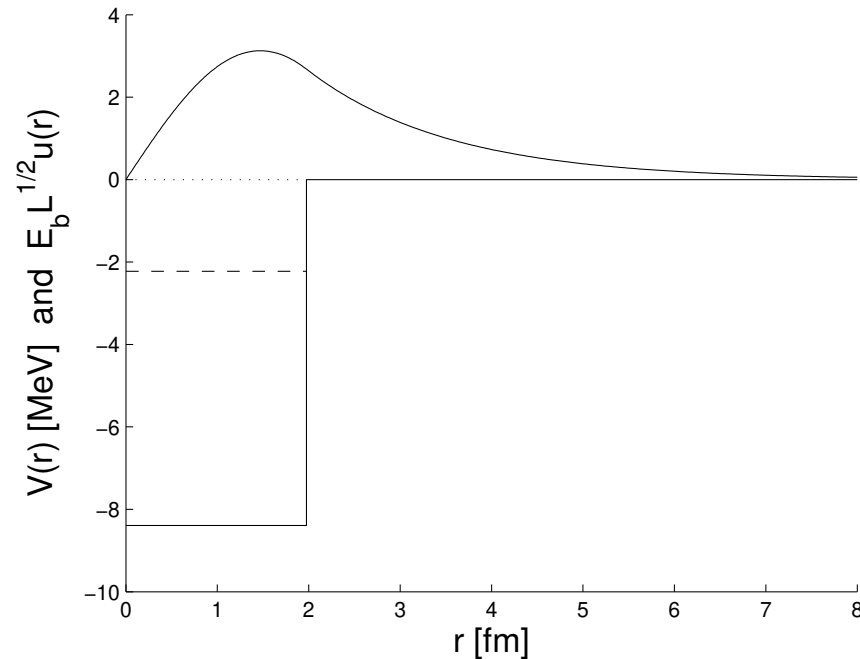
Using a spherical bounding box potential with the interior at  $V(r) = -V_0$  and the exterior at  $V(r) = 0$ , (7.33) may be solved in exactly the same fashion as the 1D case, except that the interior wavefunction can only be of the sine form to satisfy the boundary condition of (7.27). The result is that the wavefunction has the form:

$$u(r) = \sqrt{\frac{2}{L}} \sqrt{\frac{\beta}{1 + \beta}} \begin{cases} \sin(kr) & \alpha = kL, \quad k^2 = 2\mu(V_0 - E_b)/\hbar^2 \\ \sin(\alpha)e^\beta e^{-Kr} & \beta = KL, \quad K^2 = 2\mu E_b/\hbar^2 \end{cases} \begin{matrix} \text{if } r \leq L \\ \text{otherwise} \end{matrix} \quad (7.34)$$

## ... The only bound state of the deuteron

There are two unknowns in (7.34),  $V_0$  and  $L$ . However, we do know, from measurements the binding energy and the “root mean square” matter radius of the deuteron,  $\sqrt{\langle r_m^2 \rangle}$ , given in the previous table.

If we set  $L = \sqrt{\langle r_m^2 \rangle} = 1.975$ , we can find  $V_0 = 8.394$  MeV. The potential and the wavefunction as sketched below:



Note how much of the deuteron wavefunction is outside the potential!  
This is a result of the small binding energy of the neutron-proton pair.

## Radial probability density ...

Returning now, to our general considerations of solutions to the Schrödinger equation in central potentials, starting with (7.23), we define the “radial probability density”,  $P_{nl}$ :

$$P_{nl}(r) = r^2 R_{nl}^*(r) R_{nl}(r) \quad (7.35)$$

The radial probability density is used to quantify the locality of the wavefunction.

The “cumulative radial probability density”,  $C_{nl}$  is given by:

$$C_{nl}(r) = \int_0^r dr' (r')^2 R_{nl}^*(r') R_{nl}(r') , \quad (7.36)$$

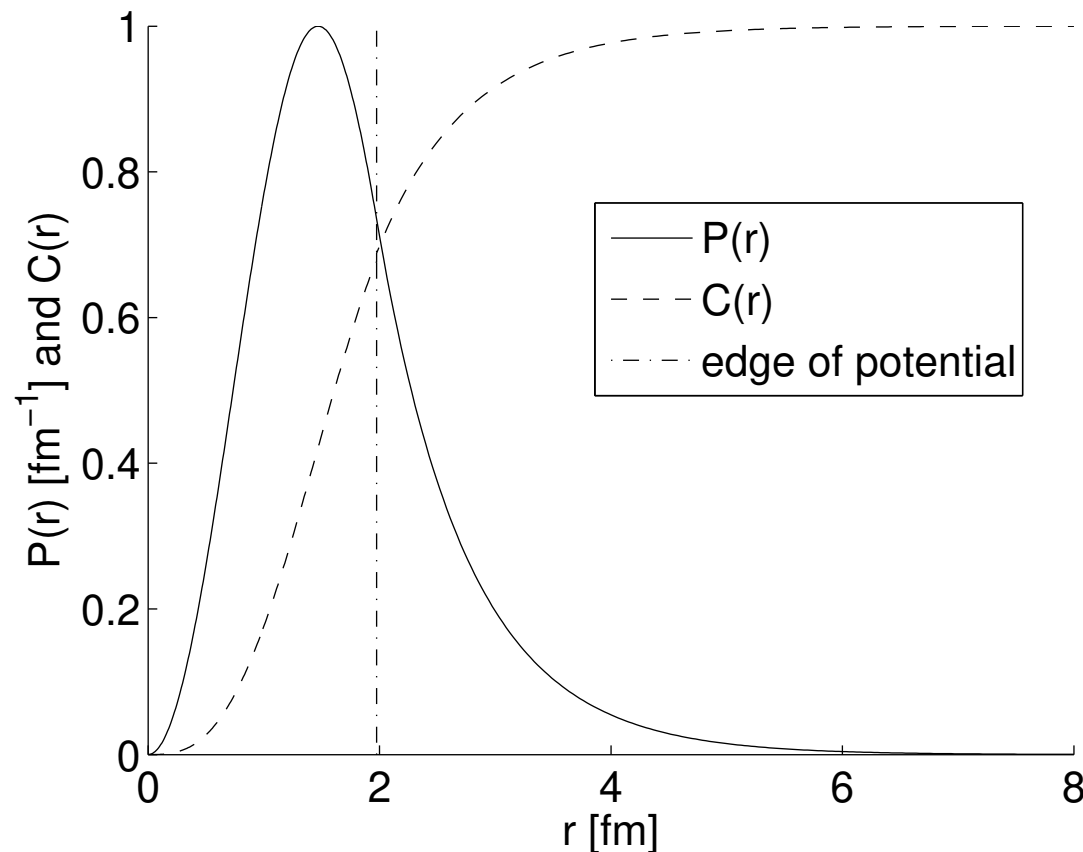
noting that, by definition:

$$C_{nl}(\infty) \equiv 1 . \quad (7.37)$$

## ... Radial probability density

For example, for the deuteron solution we have been describing, about 30% of the radial probability density is outside of the potential.

A graph of  $P(r)$  and  $C(r)$  for the deuteron is given below.



# The hydrogenic atom ...

A hydrogenic atom has  $Z$  protons and one electron.

The potential associated with this is:

$$V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r} . \quad (7.38)$$

For the hydrogenic atom, it can be shown that the wavefunctions are given by:

$$U(\vec{x}) = R_{nl}(r)Y_{l,m_l}(\theta, \phi) , \text{ where} \quad (7.39)$$

$$R_{nl}(r) = \sqrt{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \left(\frac{2Zr}{na_\mu}\right)^l \exp\left[\frac{-Zr}{na_\mu}\right] L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_\mu}\right) \quad (7.40)$$

$$n = 1, 2, 3 \cdots \infty \quad \text{principle quantum number} \quad (7.41)$$

$$l = 0, 1, 2 \cdots n-1 \quad \text{restricted by } n \quad (7.42)$$

$$E_{nl} = E_n \quad \text{does not depend on } l \quad (7.43)$$

$$E_n = -Z^2 \frac{\mu c^2 \alpha^2}{2} \frac{1}{n^2} \quad \text{exactly the same as Bohr's result!} \quad (7.44)$$

## ... The hydrogenic atom ...

Because the attractive force is central, the reduced mass,  $\mu$  was employed. This is a small effect even in the lightest atom, hydrogen. The reduced mass occurs in two places: in the energy constant, and in the revised Bohr radius, given by:

$$a_{\mu} = \left( \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \right) . \quad (7.45)$$

The degeneracy of the energy levels is given by:

$$D(n) = n^2 , \quad (7.46)$$

derived below:

## ... The hydrogenic atom ...

$$\begin{aligned} D(n) &= \sum_{l=0}^{n-1} \sum_{m_l=-l}^l (1) \quad [\# \text{ of } l \text{ for each } n \times \# \text{ of } m_l \text{ for each } l] \\ &= \sum_{l=0}^{n-1} (2l+1) \quad [\text{substituted for the degeneracy of each } l] \\ &= \sum_{l=1}^n (2l-1) \quad [l \hookrightarrow l+1] \\ &= 2 \sum_{l=1}^n l - \sum_{l=1}^n (1) \\ &= 2 \left( \frac{n(n+1)}{2} \right) - n \quad [\text{left summation is the Gaussian sum}] \\ &= n^2 + n - n \\ &= n^2 \quad [\mathcal{Q.E.D.}] \end{aligned}$$

Note that this derivation is specific to the hydrogenic atom only, because of the relationship between  $n$  and  $l$  for this potential.

## ... The hydrogenic atom ...

Some examples of hydrogenic radial wave functions:

$$\begin{aligned}R_{10}(r) &= \left(\frac{Z}{a_\mu}\right)^{3/2} 2e^{-Zr/a_\mu} \\R_{20}(r) &= \left(\frac{Z}{2a_\mu}\right)^{3/2} \left(2 - \frac{Zr}{a_\mu}\right) e^{-Zr/2a_\mu} \\R_{21}(r) &= \left(\frac{Z}{2a_\mu}\right)^{3/2} \left(\frac{1}{\sqrt{3}}\right) \left(\frac{Zr}{a_\mu}\right) e^{-Zr/2a_\mu} \\R_{30}(r) &= \left(\frac{Z}{3a_\mu}\right)^{3/2} 2 \left[1 - \frac{2}{3} \left(\frac{Zr}{a_\mu}\right) + \frac{2}{27} \left(\frac{Zr}{a_\mu}\right)^2\right] e^{-Zr/3a_\mu} \\R_{31}(r) &= \left(\frac{Z}{3a_\mu}\right)^{3/2} \frac{4\sqrt{2}}{3} \left(\frac{Zr}{a_\mu}\right) \left(1 - \frac{1}{6} \frac{Zr}{a_\mu}\right) e^{-Zr/3a_\mu} \\R_{32}(r) &= \left(\frac{Z}{3a_\mu}\right)^{3/2} \frac{2}{27} \sqrt{\frac{2}{5}} \left(\frac{Zr}{a_\mu}\right)^2 e^{-Zr/3a_\mu} \\&\vdots\end{aligned}\tag{7.47}$$

## ... The hydrogenic atom ...

### Systematics of the radial wave function (7.40) ...

$$R_{nl}(r) = \sqrt{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \left(\frac{2Zr}{na_\mu}\right)^l \exp\left[\frac{-Zr}{na_\mu}\right] L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_\mu}\right)$$

- The  $R_{nl}(r)$ 's are normalized via the normalization factor

$$A_{nl} = \sqrt{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}}$$

- The statement of orthonormality is:

$$\delta_{n'n} = \langle n'l|nl \rangle = \int_0^\infty dr r^2 R_{n'l}^*(r) R_{nl}(r) .$$

Several things to note in the above: 1) The  $l$ 's are the same in the orthonormality integral, 2) the  $r^2$  in the integral from spherical-polar coordinates, 3) though  $R_{nl}$  is usually real, one could, in principle include a complex phase in the normalization factor, 4) the  $\delta_{l'l}$  of the complete wavefunction comes from the spherical harmonics. The integral  $\int_0^\infty dr r^2 R_{n'l'}^*(r) R_{nl}(r)$  is, in general, non-zero when  $l \neq l'$  as demonstrated on the next page.

## ... The hydrogenic atom ...

This is a complete set of  $\langle nl|n'l' \rangle$  for  $n, n' = 0, 1, 2$  and  $l, l' = 0, 1$  for the radial wave-functions given on the previous page.

Note the orthonormality conditions  $\langle nl|nl \rangle = 1$  as well as the the orthogonality conditions for  $\langle nl|n'l \rangle = 0$ . For the cases where  $n \neq n'$  and  $l \neq l'$  the integrals are non-zero.

The values of  $\langle nl|n'l' \rangle$  for  $n \neq n'$  and  $l \neq l'$  are all non-zero in this case.

|              | $\langle 10 $     | $\langle 20 $          | $\langle 21 $        | $\langle 30 $        | $\langle 31 $      | $\langle 32 $          |
|--------------|-------------------|------------------------|----------------------|----------------------|--------------------|------------------------|
| $ 10\rangle$ | 1                 | 0                      | $16\sqrt{2/3}/27$    | 0                    | $3\sqrt{3/2}/16$   | $3\sqrt{3/10}/16$      |
| $ 20\rangle$ | 0                 | 1                      | $-\sqrt{3}/2$        | 0                    | $384\sqrt{3}/3125$ | $-3072\sqrt{3/5}/3125$ |
| $ 21\rangle$ | $16\sqrt{2/3}/27$ | $-\sqrt{3}/2$          | 1                    | $-144/\sqrt{2}/3125$ | 0                  | $4608/\sqrt{5}/3125$   |
| $ 30\rangle$ | 0                 | 0                      | $-144/\sqrt{2}/3125$ | 1                    | $-2\sqrt{2}/3$     | $\sqrt{2/5}$           |
| $ 31\rangle$ | $3\sqrt{3/2}/16$  | $384\sqrt{3}/3125$     | 0                    | $-2\sqrt{2}/3$       | 1                  | $-\sqrt{5}/3$          |
| $ 32\rangle$ | $3\sqrt{3/10}/16$ | $-3072\sqrt{3/5}/3125$ | $4608/\sqrt{5}/3125$ | $\sqrt{2/5}$         | $-\sqrt{5}/3$      | 1                      |

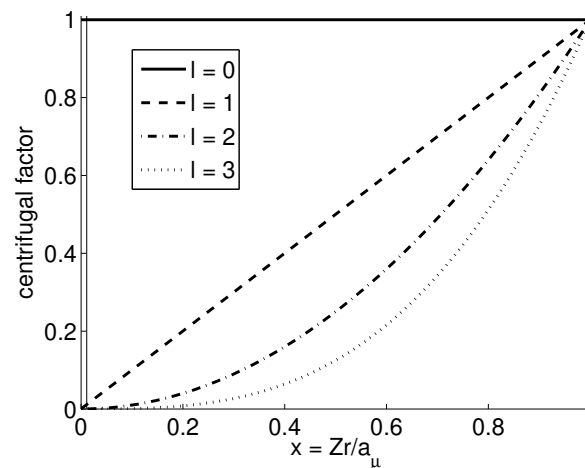
## ... The hydrogenic atom ...

### ... Systematics of the radial wave function (7.40) ...

$$R_{nl}(r) = \sqrt{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \left(\frac{2Zr}{na_\mu}\right)^l \exp\left[\frac{-Zr}{na_\mu}\right] L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_\mu}\right)$$

- As  $l$  increases, the wavefunction gets pushed further from the origin.  
(More centrifugal force.)

This comes from the centrifugal factor  $\left(\frac{2Zr}{na_\mu}\right)^l$ . Note the dependence as a power of  $l$ .



The narrow vertical line near zero is the radius of a lead nucleus.

The  $s$ -state electron wavefunctions have maximum overlap with the nucleus.

As  $l$  increases this overlap diminishes appreciably.

## ... The hydrogenic atom ...

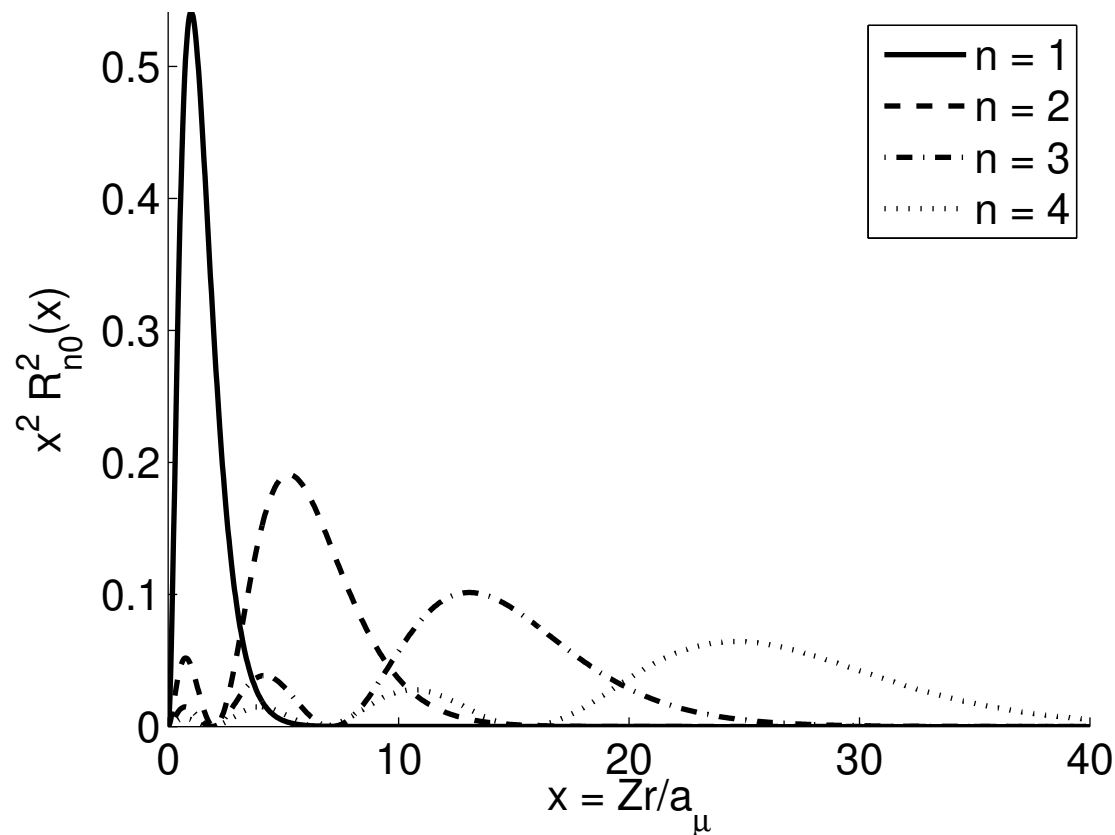
### ... Systematics of the radial wave function (7.40) ...

$$R_{nl}(r) = \sqrt{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \left(\frac{2Zr}{na_\mu}\right)^l \exp\left[\frac{-Zr}{na_\mu}\right] L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_\mu}\right)$$

- The radial wavefunction is localized by the exponential factor  $\exp\left[\frac{-Zr}{na_\mu}\right]$ .
- As  $n$  increases, the wavefunction gets more spread out.  
(Higher energy, greater “orbit”. Recall classically,  $r_n = a_0 n^2 / Z$ .)  
This is effected by the  $r/n$  scaling throughout the expression above.
- As  $Z$  increases, the wavefunction gets pulled into the origin. (More Coulomb attraction.) This is mostly due to the  $Z$  in the exponential factor  $\exp\left[\frac{-Zr}{na_\mu}\right]$ .
- The number of nodes is  $n - 1 - l$ .

## ... The hydrogenic atom ...

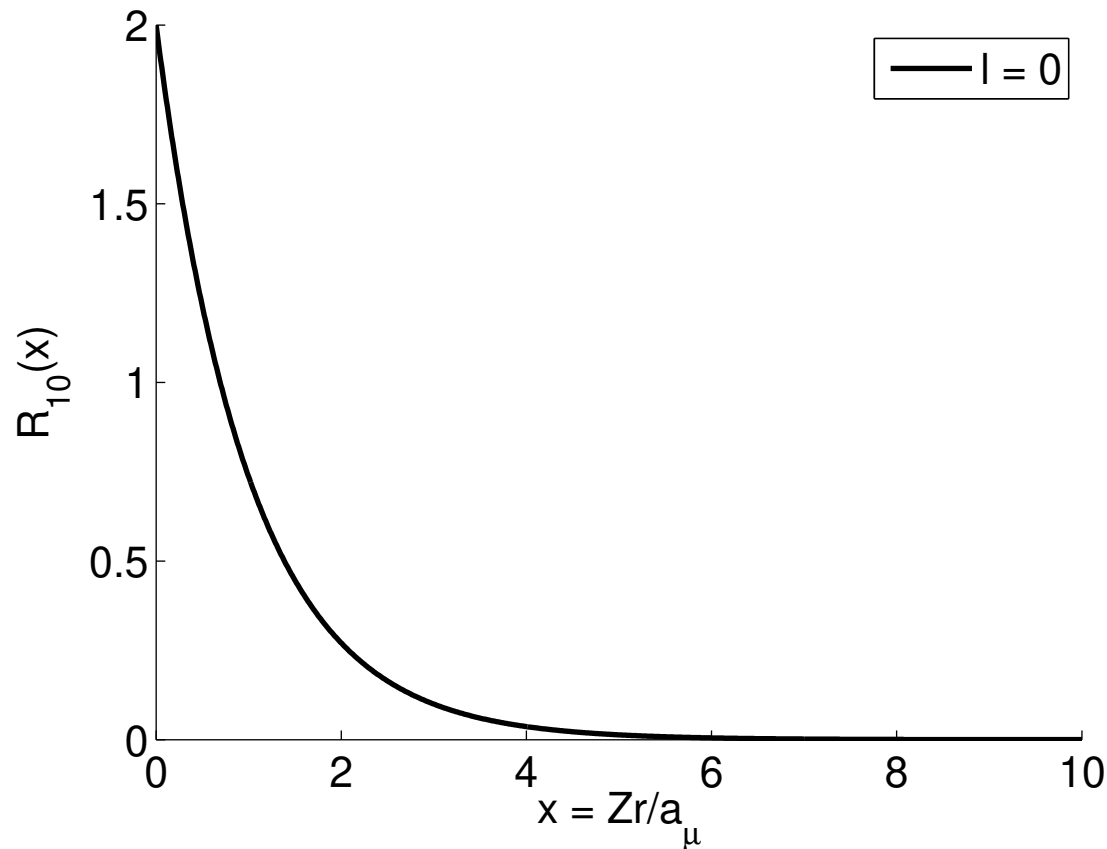
As  $n$  increases, the radial wavefunction gets spread out, as seen for the first 4  $s$ -state wave functions.



## ... The hydrogenic atom ...

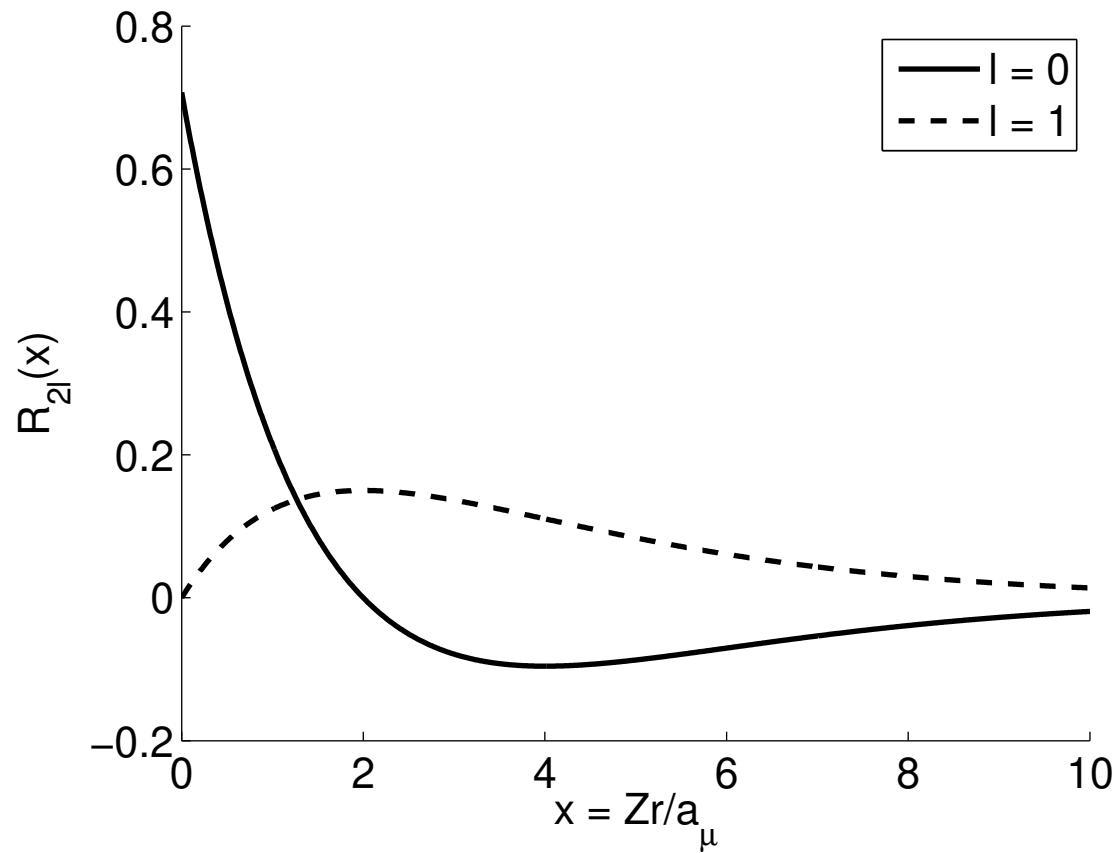
As  $l$  increases for a given  $n$ , the radial wavefunction gets pushed out from the origin, increasing in effect as  $l$  increases.

$n = 1, l = 0$  only



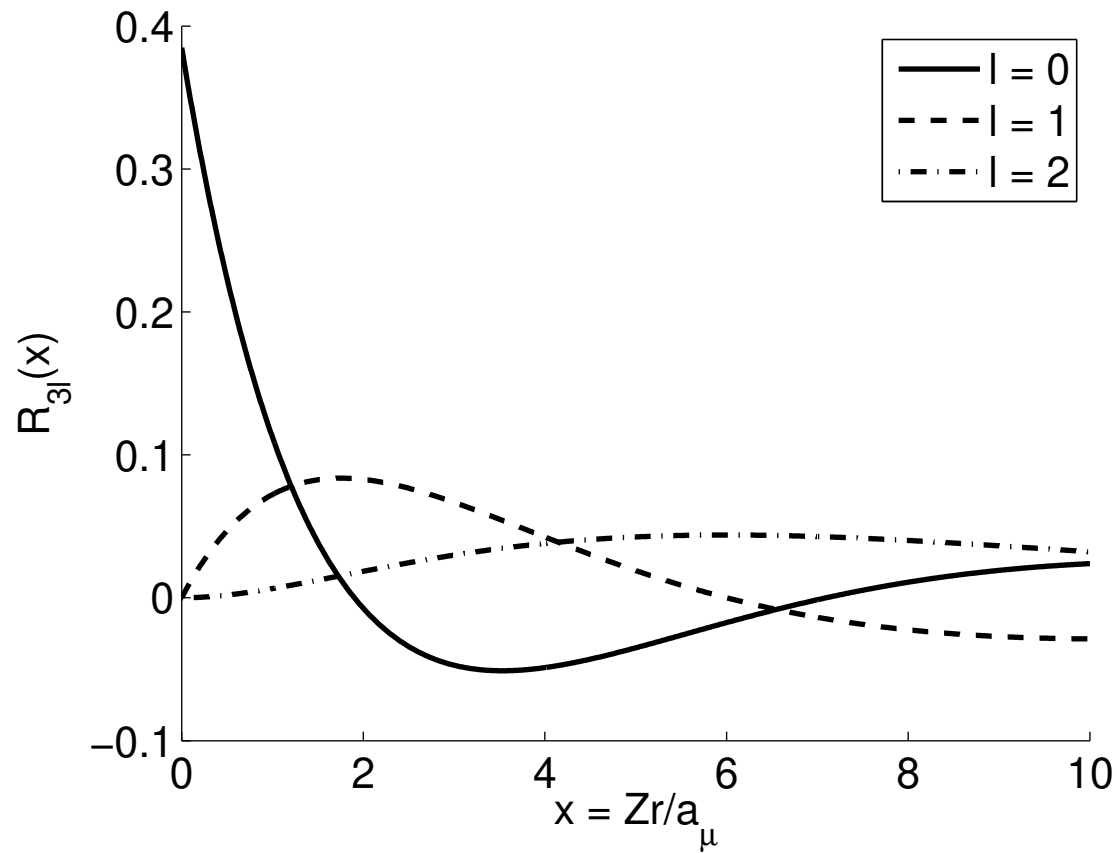
## ... The hydrogenic atom ...

$$\underline{n = 2}$$



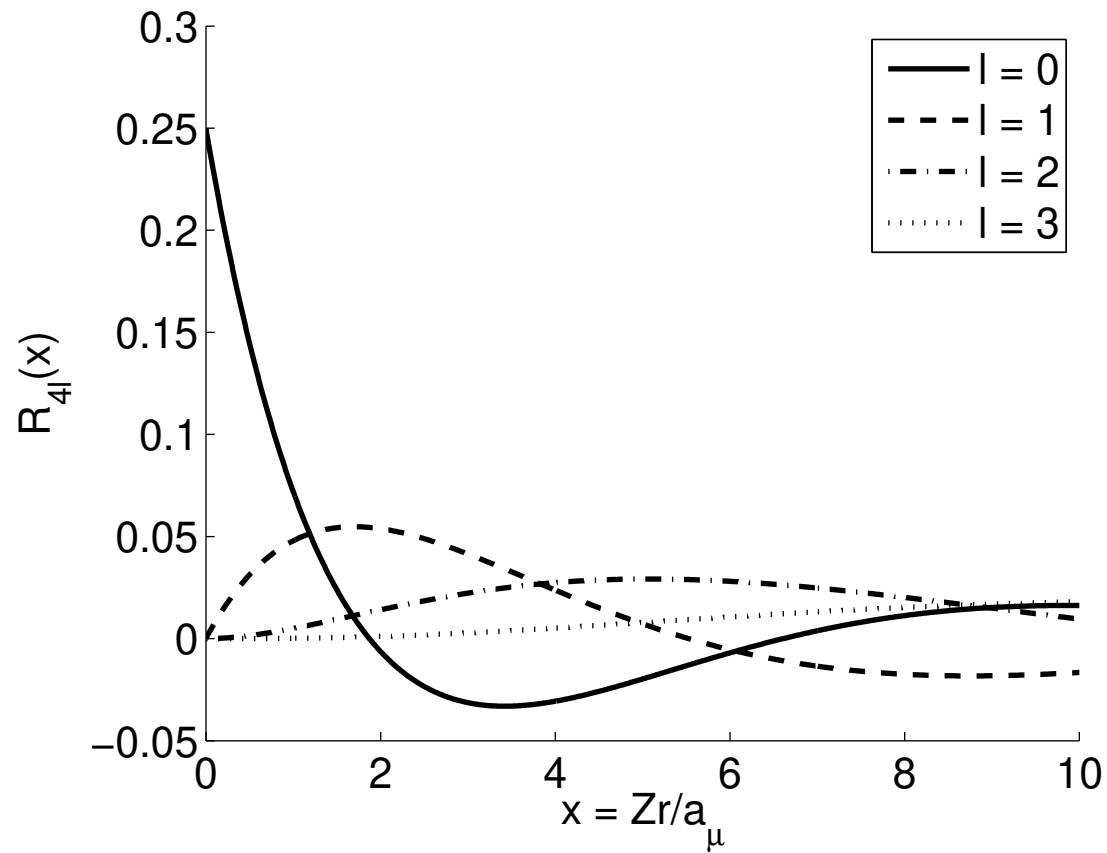
## ... The hydrogenic atom ...

$$\underline{n = 3}$$



## ... The hydrogenic atom ...

$$\underline{n = 4}$$



## ... The hydrogenic atom

$$\langle r \rangle, \langle r^2 \rangle, \text{ and } (\Delta r)^2$$

Recall the classical result from Bohr theory:

$$\langle r \rangle_{\text{cl}} = n^2 a_\mu / Z; \quad \langle r^2 \rangle_{\text{cl}} = \langle r \rangle_{\text{cl}}^2; \quad (\Delta r)_{\text{cl}}^2 = 0$$

It can be shown that the quantum mechanical result is:

$$\begin{aligned} \frac{\langle r \rangle}{\langle r \rangle_{\text{cl}}} &= 1 + \frac{1}{2} \left( 1 - \frac{l(l+1)}{n^2} \right) \\ \frac{\langle r^2 \rangle}{\langle r^2 \rangle_{\text{cl}}} &= 1 + \frac{3}{2} \left[ 1 - \frac{l(l+1) - \frac{1}{3}}{n^2} \right] \\ (\Delta r)^2 &= \frac{1}{4} \left( 1 - \frac{l(l+1)}{n^2} \right) \end{aligned} \tag{7.48}$$

This is a nice demonstration of the correspondence principle where the classical result is obtained with  $n \longrightarrow \infty, l(l+1) \longrightarrow n^2$ .

## Angular momentum ...

In Quantum Mechanics we define the angular momentum operators as follows:

$$L^2 = \hbar^2 \mathcal{L}^2 \quad (7.49)$$

$$L_z = \hbar \mathcal{L}_z \quad (7.50)$$

The most explicit form of the expectation values are:

$$\langle lm_l | L^2 | lm_l \rangle = \hbar^2 l(l+1) \quad (7.51)$$

$$\langle lm_l | L_z | lm_l \rangle = \hbar m_l \quad (7.52)$$

although the shorthand:

$$\langle L^2 \rangle = \hbar^2 l(l+1)$$

$$\langle L_z \rangle = \hbar m_l$$

or even

$$L^2 = \hbar^2 l(l+1)$$

$$L_z = \hbar m_l$$

are used.

## ... Angular momentum ...

Since  $\vec{L}$  is a vector,

$$\langle L^2 \rangle - \langle L_z^2 \rangle = \langle L_x^2 \rangle + \langle L_y^2 \rangle = \hbar^2[l(l+1) - m_l^2] , \quad (7.53)$$

The minimum value of  $\langle L_x^2 \rangle$  or  $\langle L_y^2 \rangle$  can not be zero!

This has an interesting “quantum mechanicsque” interpretation.

$L^2$  is a constant of the motion of an  $|lm_l\rangle$  state, since  $L^2 = \hbar^2 l(l+1)$ .

This has the consequence that  $\Delta L^2 = 0$ , since

$$\langle lm_l | L^4 | lm_l \rangle = \hbar^2 l(l+1) \langle lm_l | L^2 | lm_l \rangle = [\hbar^2 l(l+1)]^2$$

Hence

$$(\Delta L^2)^2 = \langle lm_l | L^4 | lm_l \rangle - \langle lm_l | L^2 | lm_l \rangle^2 = 0$$

The same argument may be made for  $\Delta L_z = 0$ .

Since  $\langle L_x^2 \rangle > 0$  and  $\langle L_y^2 \rangle > 0$ , they are not constants of the motion.

If there is no preferred azimuthal direction,

$$\langle L_x^2 \rangle = \langle L_y^2 \rangle = \hbar^2[l(l+1) - m_l^2]/2 \quad ; \quad \langle L_x \rangle = \langle L_y \rangle = 0 \quad (7.54)$$

## ... Angular momentum ...

This is a consequence of the Heisenberg uncertainty relationship for angular momenta.

$$\Delta L_z \Delta \phi \geq \hbar/2 \quad (7.55)$$

where  $\phi$  is the azimuthal angle associated with the particle's position.

This has the interpretation that the particle can be found at any azimuthal angle.

It is similar, for example, to the statement:

$$\Delta p_z \Delta z \geq \hbar/2$$

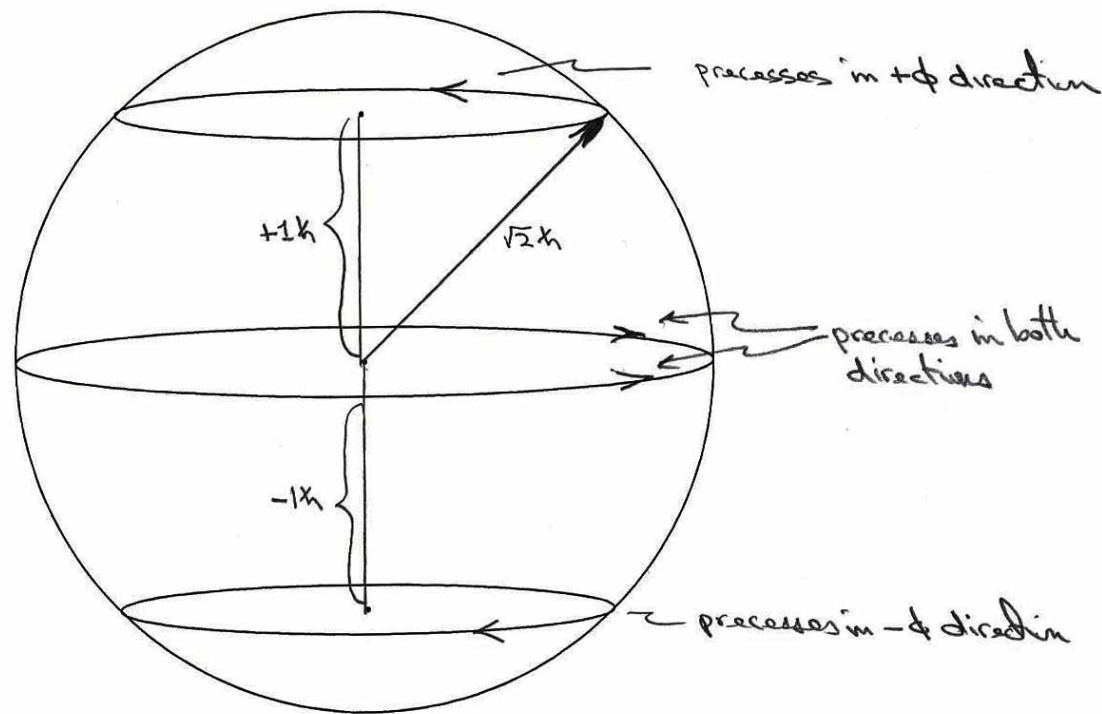
If the particle's momentum is known then the particle can be found at any angle.

The same is true for angular momentum, as it is for linear momentum.

## ... Angular momentum ...

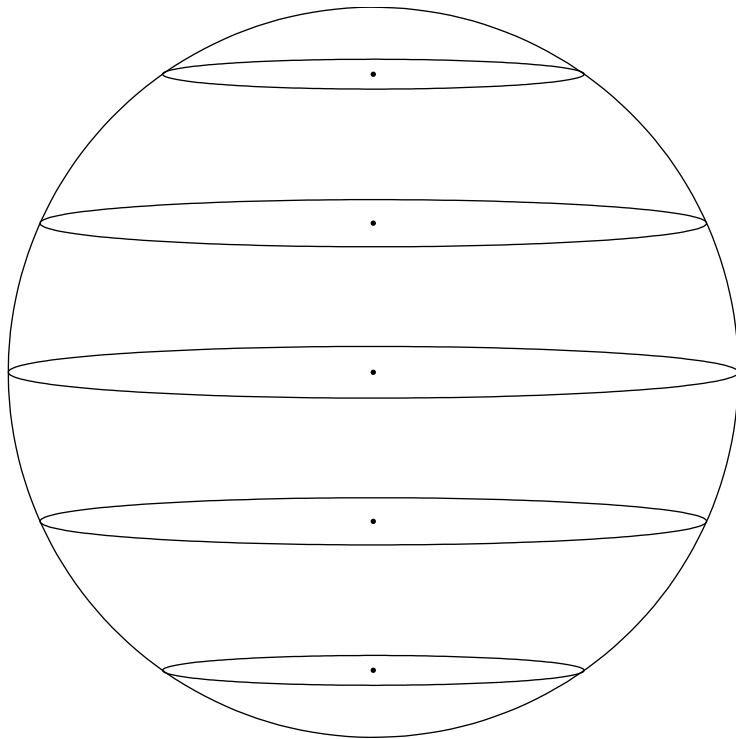
### Semi-classical picture of angular momentum

Consider the case when  $l = 1$ . We imagine that the particle is on a sphere of radius  $\sqrt{l(l+1)}\hbar$ . When  $m_l = \pm 1$ , the particle is “precessing” in the  $\pm\phi$  direction. When  $m_l = 0$ , it is precessing in both directions. This picture is called the “vector model” of angular momentum.

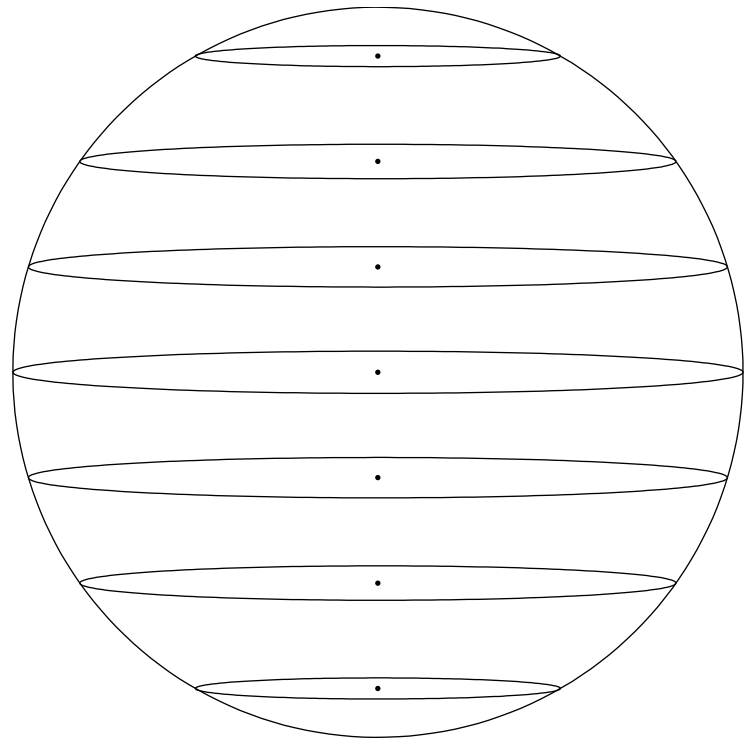


## ... Angular momentum ...

$$\underline{l = 2}$$



$$\underline{l = 3}$$



## ... Angular momentum ...

From the Mathematica website, the Spherical Harmonics look like:

$$|Y_0^0(\theta, \phi)|^2$$



$$|Y_1^0(\theta, \phi)|^2$$



$$|Y_1^1(\theta, \phi)|^2$$



$$|Y_2^0(\theta, \phi)|^2$$



$$|Y_2^1(\theta, \phi)|^2$$



$$|Y_2^2(\theta, \phi)|^2$$



$$|Y_3^0(\theta, \phi)|^2$$



$$|Y_3^1(\theta, \phi)|^2$$



$$|Y_3^2(\theta, \phi)|^2$$

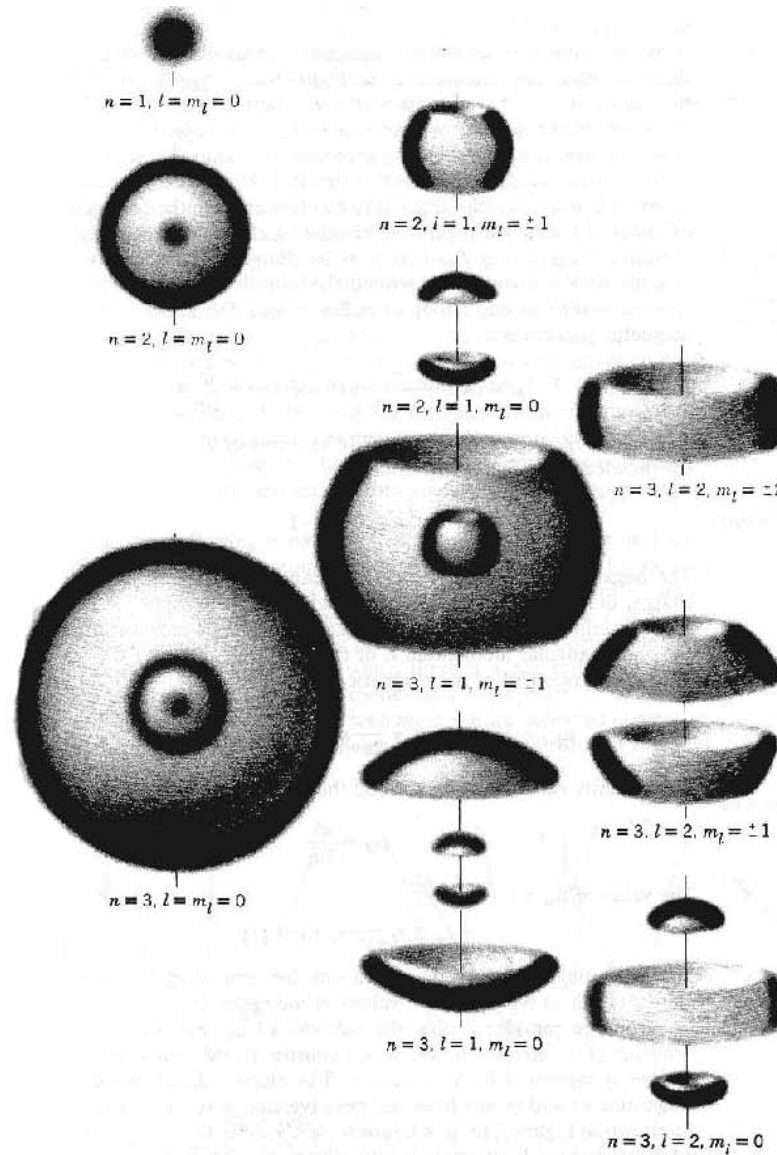


$$|Y_3^3(\theta, \phi)|^2$$



## ... Angular momentum

The hydrogenic radial wave functions look like:



## Intrinsic spin ...

When the hydrogenic wavefunctions were discovered, it occurred to the experimentalists of the time, that these wavefunctions must be explored, and tested. After all, theory without experimental validation, is just speculation. So, they subjected atoms to any apparatus that they had available at the time, to see if any behavior could be modified.

One thing they tried was putting the atoms in a magnetic field, and looking to see if they could see any changes.

The reason for using magnetic fields is that an additional force is exerted on the electrons that is different, for different values of the  $l$  quantum number.

The potential characterizing this force is:

$$V = -\vec{\mu}_L \cdot \vec{B} , \quad (7.56)$$

where  $\vec{\mu}_L$  is the magnetic moment associated with the electron's orbit. A moving charge creates a current, that generates a magnetic field. An external magnetic field exerts a force on the current loop to try and align the moving-charge-generated magnetic field into anti-alignment [hence the minus sign in (7.56)], the same force you feel when you bring two magnets together.

## ... Intrinsic spin ...

In classical physics, the magnetic moment of a point-like electron is given by:

$$\vec{\mu}_L = -\frac{e}{2m_e}\vec{L} , \quad (7.57)$$

where  $\vec{L}$  is the classical momentum vector. The minus sign arises from the negative charge of the electron.

In classical mechanics (Bohr model) it is clear how to contend with (7.56) and (7.57). In quantum mechanics, there are two approaches to evaluating the effect of this force, called the “Zeeman effect”, so named after Pieter Zeeman, the discoverer of this effect. (The discovery of this effect pre-dated quantum mechanics and even the Bohr model of the atom.)

One could put (7.57) into the Schrödinger equation along with the Coulomb potential, and solve the equation directly. This can only be done numerically. Or, one can estimate the effect using first-order perturbation theory<sup>4</sup> by combining (7.56) and (7.57) and using the expression:

$$\Delta E = \langle nlm_l | \frac{e\hbar}{2m_e}\vec{L} \cdot \vec{B} | nlm_l \rangle , \quad (7.58)$$

<sup>4</sup>Perturbation theory is an advanced topic in quantum mechanics. However, this first order expression is guaranteed to work quite well when the perturbation,  $V$  in this case, is small compared to the binding energy.

## ... Intrinsic spin ...

where

$$|nlm_l\rangle \equiv R_{nl}(r)Y_{l,m_l}(\theta, \phi) , \quad (7.59)$$

from (7.8).

Note that the quantum-mechanical operator for  $\vec{L}$ , namely  $\hbar\vec{\mathcal{L}}$  was used in (7.58).

The combination of constants on the right-hand side of the equation below,

$$\mu_B \equiv \frac{e\hbar}{2m_e} , \quad (7.60)$$

defines the “Bohr magneton”, a unit for describing the electron’s magnetic dipole moment, as a result of its motion.

If we define the  $z$ -axis, as the axis that the external magnetic field is aligned on, we may evaluate (7.58) directly:

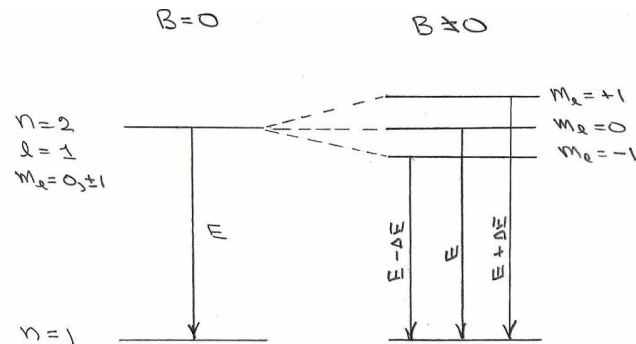
$$\Delta E = \mu_B m_l B . \quad (7.61)$$

This gives  $m_l$  its name as the magnetic quantum number.

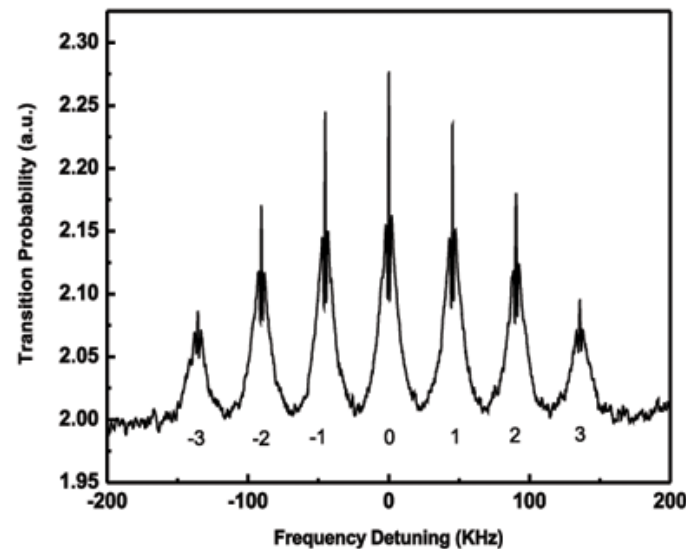
## ... Intrinsic spin ...

Thus the energy level degeneracy for a given  $l$ , gets split into  $2l + 1$  distinct lines.

Here is an illustration for the  $n = 2, l = 1$  to  $n = 1$  transition.

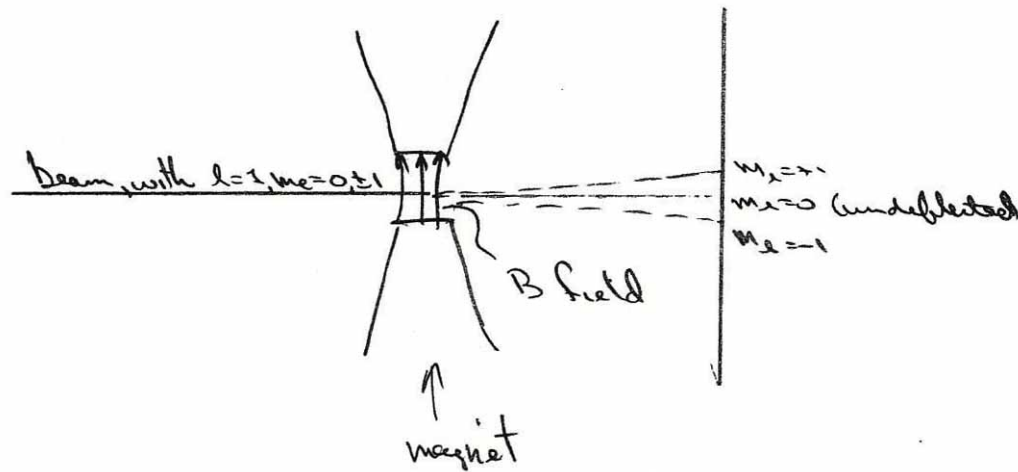


The Zeeman effect can be seen with modest magnetic fields using spectroscopy methods.



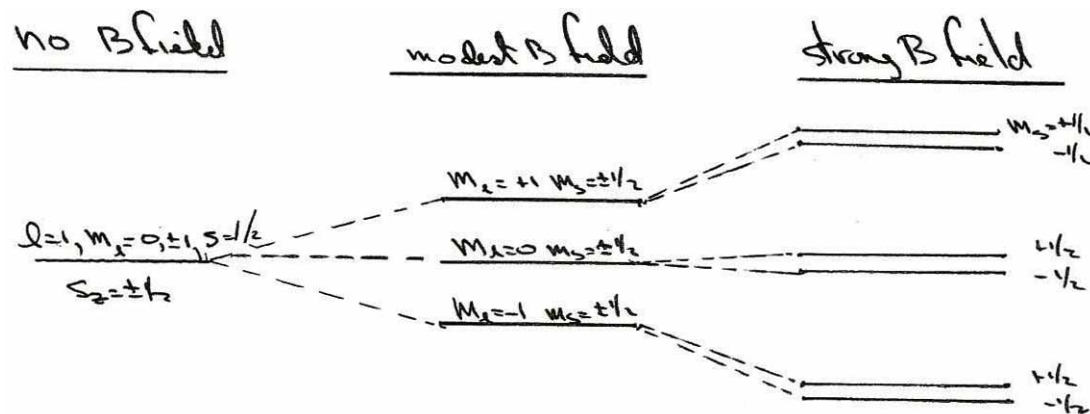
## ... Intrinsic spin ...

However, Otto Stern and Walther Gerlach, in 1922, decided to use much stronger magnetic fields, and see the actual deflection of the particle beam, a different way of measuring the same thing.



## ... Intrinsic spin ...

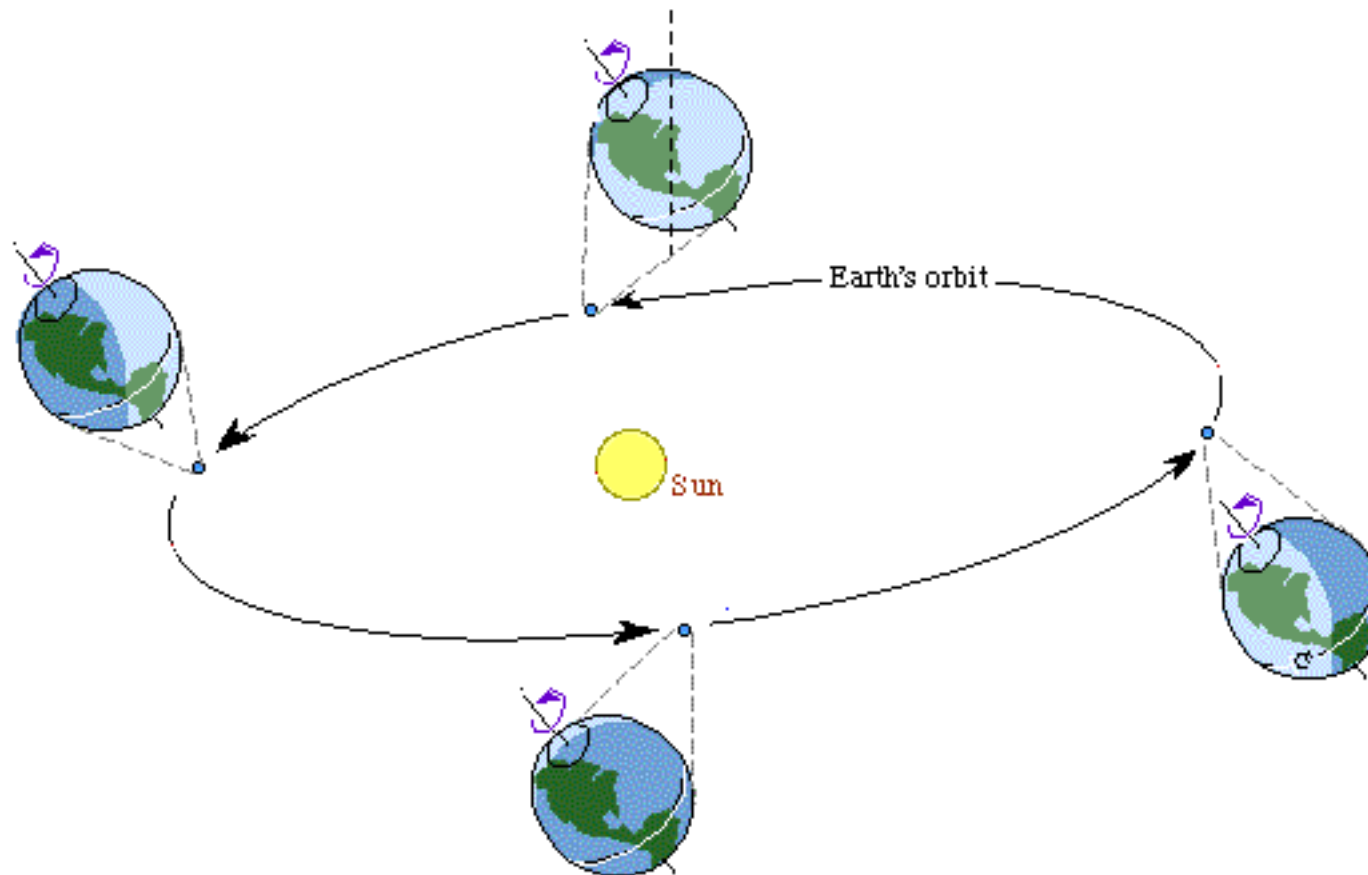
What they saw was surprising, and not predicted by any theory.  
There was an additional splitting, of each  $m_l$  line!



Samuel Goudsmit and Paul Ehrenfest, in 1925, suggested that the electron had an “intrinsic spin”, with a half-integral value of spin,  $s = \frac{1}{2}$ , with magnetic components  $m_s = \pm \frac{1}{2}$ . Orbital angular momenta, as we know, have only only integral values.

## ... Intrinsic spin ...

The concept of intrinsic spin is not uncommon.  
For example, the sun-earth system has intrinsic spin.



## ... Intrinsic spin ...

As the earth revolves around the sun, it has orbital angular momentum

$$\vec{L} = \vec{r} \times \vec{p} \quad (7.62)$$

where  $\vec{r}$  is the sun-earth distance, and  $\vec{p}$  is the earth's momentum.

The earth also has an intrinsic angular momentum that is given by

$$\vec{S} = I\omega\hat{n} \quad (7.63)$$

where  $\omega$  is the angular speed,  $\hat{n}$ , a unit vector, is the axis of rotation, and  $I$  is the moment of inertia about the axis of rotation.

The total angular momentum, is given by

$$\vec{J} = \vec{L} + \vec{S} \quad (7.64)$$

## ... Intrinsic spin

The equation for total angular momentum in quantum mechanics is similar to (7.64), except that  $\vec{S}$  is an operator, with the rules:

$$\langle S^2 \rangle = \hbar^2 s(s+1) = 3\hbar^2/4, \quad (7.65)$$

since  $s = \frac{1}{2}$ .

$$\langle S_z \rangle = \hbar m_s = \pm \frac{\hbar}{2}. \quad (7.66)$$

Lastly, the electron's intrinsic spin magnetic moment can be found to be:

$$\mu_s = \frac{e\hbar}{m_e} \quad (7.67)$$

which is exactly twice that of its orbital magnetic moment. The calculation comes from relativistic Quantum Electrodynamics, and is purely a relativistic effect.

## Fine structure

Quoting from Wikipedia, “In atomic physics, the fine structure describes the splitting of the spectral lines of atoms due to quantum-mechanical (electron spin) and relativistic corrections.”

The “gross structure” is given by the energy levels obtained from Bohr theory, later put on a firmer theoretical footing by the Schrödinger equation.

Part of the fine structure comes from the spin-orbit interaction of the electron’s magnetic moment interaction with the magnetic field induced by its own motion. This part of the fine structure in the H-atom is given by:

$$\Delta E = \frac{m_e c^2 \alpha^4}{n^5} . \quad (7.68)$$

In the frame of the moving electron, the electron sees the proton revolving around it. That moving charge induces a magnetic field that applies a torque to the electron’s magnetic moment, analogous to magnetic field attempting to align a magnet.

# Hyperfine structure

“Hyperfine structure” is a spin-spin interaction of the intrinsic spins of the electron and the proton. This is analogous to two magnets attempting to anti-align their poles. That energy shift is about:

$$\Delta E \approx \frac{m_e}{m_p} \frac{m_e c^2 \alpha^4}{n^5}, \quad (7.69)$$

several orders of magnitude less than the fine-structure shift.

# Spectroscopic notation

We conclude this Chapter with a discussion of spectroscopic notation, that we shall use in the rest of this course.

The various values of  $l$  have been given special names from the spectroscopists who studied them. They are:

| $l$    | 0     | 1         | 2       | 3           | 4 | 5 | 6 |
|--------|-------|-----------|---------|-------------|---|---|---|
| letter | s     | p         | d       | f           | g | h | i |
| name   | sharp | principle | diffuse | fundamental | - | - | - |