

# CH-4

## The Hydrogen Atom

# CONTENTS

- ❑ Schrödinger Equation to the Hydrogen Atom
- ❑ Solution of the Schrödinger Equation for Hydrogen
- ❑ Quantum Numbers
- ❑ Electron Probabilities

# QUANTUM THEORY OF HYDROGEN ATOM

- ❖ Hydrogen atom is a single proton nucleus surrounded by a solitary electron continuously revolving in an orbit .The force experienced by this electron due to proton is central and the field is spherically symmetric. As such potential is spherically symmetric.

# Schrödinger Equation to the Hydrogen Atom

The potential energy of the electron-proton system is electrostatic:

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

Use the three-dimensional time-independent Schrödinger Equation.

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(x, y, z)} \left[ \frac{\partial^2 \psi(x, y, z)}{\partial x^2} + \frac{\partial^2 \psi(x, y, z)}{\partial y^2} + \frac{\partial^2 \psi(x, y, z)}{\partial z^2} \right] = E - V(r)$$

For Hydrogen-like atoms ( $\text{He}^+$  or  $\text{Li}^{++}$ ), replace  $e^2$  with  $Ze^2$  ( $Z$  is the atomic number).

In all cases, for better accuracy, replace  $m$  with the reduced mass,  $\mu$ .

# Spherical Coordinates

The potential (central force)  
 $V(r)$  depends on the distance  
 $r$  between the proton and  
electron.

Transform to spherical polar  
coordinates because of the  
radial symmetry.

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

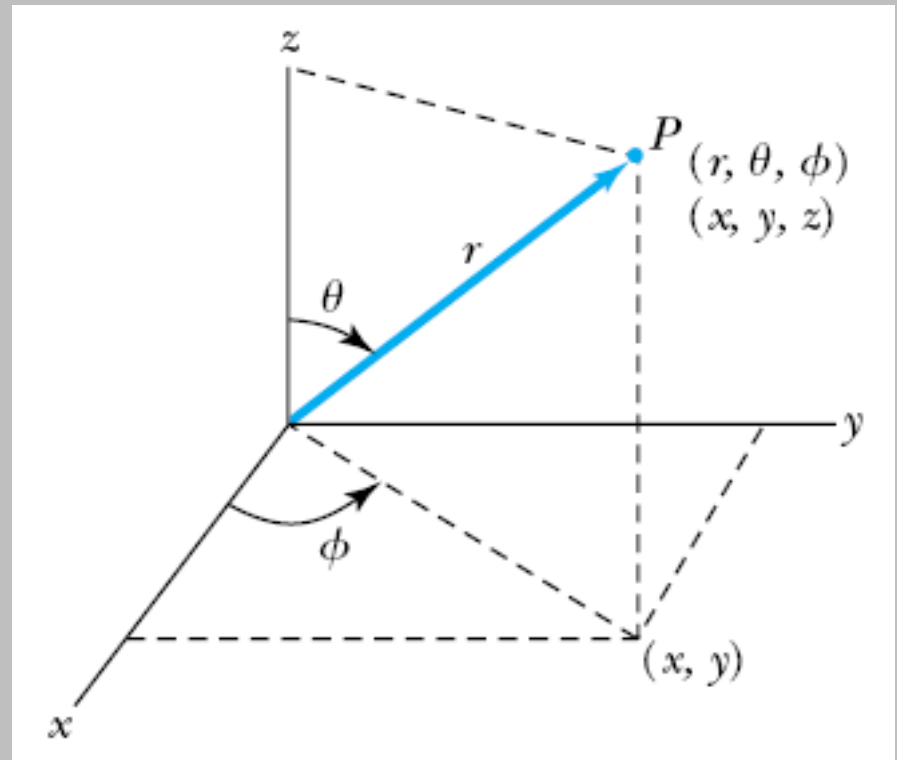
$$y = r \sin \theta \sin \varphi$$

$$z = r \cos \theta$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\theta = \cos^{-1} \frac{z}{r} \quad (\text{Polar angle})$$

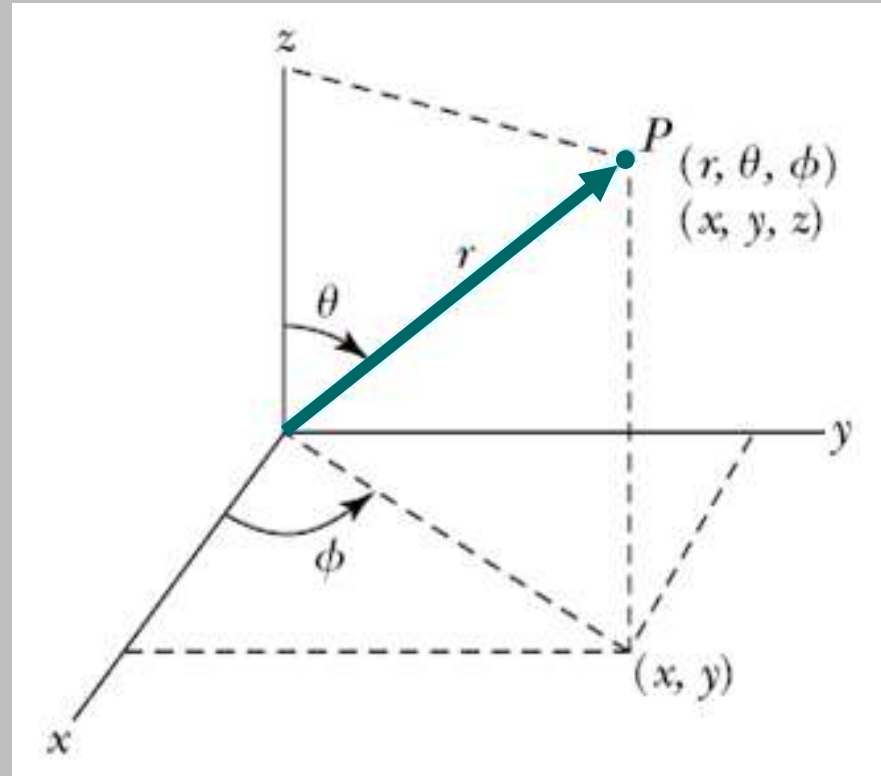
$$\varphi = \tan^{-1} \frac{y}{x} \quad (\text{Azimuthal angle})$$



# The Schrödinger Equation in Spherical Coordinates

Transformed into spherical coordinates, the Schrödinger equation becomes:

$$\frac{1}{r^2} \frac{\partial}{\partial t} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2} (E - V) \psi = 0$$



# Separable solution

The wave function  $\psi$  is a function of  $r$ ,  $\theta$ ,  $\phi$ . This is a potentially complicated function.

Assume optimistically that  $\psi$  is **separable**, that is, a product of three functions, each of one variable only:

$$\psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) = R \Theta \Phi$$

Let's assume

$$\psi(r, \theta, \phi) = R \Theta \Phi$$

This would make life much simpler—and it turns out to work!

With this assumption, the partial derivatives in Schrödinger's equation become

$$\frac{\partial \psi}{\partial r} = \Theta \Phi \frac{\partial R}{\partial r} = \Theta \Phi \frac{dR}{dr}$$

$$\frac{\partial \psi}{\partial \theta} = R \Phi \frac{\partial \Theta}{\partial \theta} = R \Phi \frac{d\Theta}{d\theta}$$

$$\frac{\partial \psi}{\partial \phi} = R \Theta \frac{\partial \Phi}{\partial \phi} = R \Theta \frac{d\Phi}{d\phi}$$

The partial derivatives become full derivatives because  $R$ ,  $\Theta$ , and  $\Phi$  depend on  $r$ ,  $\theta$ , and  $\phi$  only.



To separate variables, plug  $\psi = R\Theta\Phi$  into Schrödinger's equation and divide by  $R\Theta\Phi$ . The result is

$$\frac{\sin^2\theta}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left( \sin\theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} + \frac{2mr^2 \sin^2\theta}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) = 0.$$

We have separated out the  $\phi$  variable! The term

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2}$$

is a function of  $\phi$  only. Let's put it over on the right hand side of the equation. This gives us...

$$\frac{\sin^2\theta}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left( \sin\theta \frac{d\Theta}{d\theta} \right) + \frac{2mr^2 \sin^2\theta}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) = -\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2}.$$

This equation has the form

$$f(r, \theta) = g(\phi)$$

is a function of  $r$  and  $\theta$  only, and  $g$  is a function of  $\phi$  only.  $f$

Thus, we can write the RHS of this equation as

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = -m_l^2.$$

The LHS of our big Schrödinger equation also must equal  $m_\ell^2$ . If we set the LHS equal to  $m_\ell^2$ , divide by  $\sin^2\theta$ , and rearrange, we get

$$\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) = \frac{m_\ell^2}{\sin^2\theta} - \frac{1}{\Theta \sin\theta} \frac{d}{d\theta} \left( \sin\theta \frac{d\Theta}{d\theta} \right).$$

Once again we have separated variables. The LHS is a function of  $r$  only, and the RHS is a function of  $\theta$  only.

Again, the only way to satisfy this equation is for LHS=a constant=RHS.

Solution of the resulting differential equations will result in restrictions on this constant. In this case, the constant must equal an integer times the next larger integer:  $\ell(\ell+1)$ .

We have taken our initial differential equation and split into 3. Here are the pieces, rewritten slightly:

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\phi} = m_{\ell}^2$$

$$\frac{1}{\sin\theta} \frac{d}{d\theta} \left( \sin\theta \frac{d\Theta}{d\theta} \right) + \left[ \ell(\ell+1) - \frac{m_{\ell}^2}{\sin^2\theta} \right] \Theta = 0$$

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ \frac{2m}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{\ell(\ell+1)}{r^2} \right] R = 0$$

But in the “one” the variables were coupled, and in the “three” the variables are separated. Huge improvement!

We find the first quantum number by solving the differential equation for  $\Phi$ .

$$\frac{d^2\Phi}{d\phi^2} + m_\ell^2\Phi = 0$$

That equation should look familiar to you; you've seen it a number of times before. It has solutions which are sines and cosines, or complex exponentials. We write the general solution

$$\Phi(\phi) = A e^{jm_\ell\phi}.$$

We will get the constant  $A$  by normalization.

Now, because  $\phi$  and  $\phi+2\pi$  represent a single point in space, we must have

$$A e^{jm_\ell\phi} = A e^{jm_\ell(\phi+2\pi)}.$$

This happens only for  $m_\ell = 0, \pm 1, \pm 2, \pm 3, \dots$

$m_\ell$  is called the *magnetic quantum number*.

Our differential equation for  $\Theta$  is

$$\frac{1}{\sin\theta} \frac{d}{d\theta} \left( \sin\theta \frac{d\Theta}{d\theta} \right) + \left[ \ell(\ell+1) - \frac{m_{\ell}^2}{\sin^2\theta} \right] \Theta = 0$$

It involves the term

$$\left[ \ell(\ell+1) - \frac{m_{\ell}^2}{\sin^2\theta} \right]$$

It turns out that from differential equations that the equation for  $\Theta$  can be solved only if  $\ell$  is an integer greater than or equal to the absolute value of  $m_{\ell}$ .

$\ell$  is another quantum number, called the *orbital quantum number*, and the requirement on  $\ell$  can be restated as  $m_{\ell} = 0, \pm 1, \pm 2, \pm 3, \dots, \pm \ell$ .

# Normalized Spherical Harmonics

**Table 7.2** Normalized Spherical Harmonics  $Y(\theta, \phi)$

$\ell$	$m_\ell$	$Y_{\ell m_\ell}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}} \cos \theta$
1	$\pm 1$	$\mp \frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin \theta e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}} (3 \cos^2 \theta - 1)$
2	$\pm 1$	$\mp \frac{1}{2}\sqrt{\frac{15}{2\pi}} \sin \theta \cos \theta e^{\pm i\phi}$
2	$\pm 2$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}} (5 \cos^3 \theta - 3 \cos \theta)$
3	$\pm 1$	$\mp \frac{1}{8}\sqrt{\frac{21}{\pi}} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$
3	$\pm 2$	$\frac{1}{4}\sqrt{\frac{105}{2\pi}} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$
3	$\pm 3$	$\mp \frac{1}{8}\sqrt{\frac{35}{\pi}} \sin^3 \theta e^{\pm 3i\phi}$

Finally, the radial differential equation is

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ \frac{2m}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{\ell(\ell+1)}{r^2} \right] R = 0$$

It can be solved only for energies  $E$  which satisfy the same condition as we found on the energies for the Bohr atom:

$$E_n = - \frac{me^4}{32\pi^2 \epsilon_0 \hbar^2} \frac{1}{n^2} = \frac{E_1}{n^2}, \quad n=1, 2, 3, \dots$$

$n$  is called the *principal quantum number*.



# Hydrogen Atom Radial Wave Functions

First few radial wave functions  $R_{n\ell}$

Subscripts on  $R$  specify the values of  $n$  and  $\ell$ .

**Table 7.1** Hydrogen Atom Radial Wave Functions

$n$	$\ell$	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right) \frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0} \frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}} \frac{2}{81\sqrt{3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{6}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{30}} \frac{r^2}{a_0^2} e^{-r/3a_0}$

Here's the differential equation for R again:

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ \frac{2m}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{\ell(\ell+1)}{r^2} \right] R = 0$$

Note that the product  $\ell(\ell+1)$  shows up in the equation for R, and n comes out of solving this equation. Another math requirement for valid solutions is that  $n \geq (\ell+1)$ .

We can express the requirement that  $n=1,2,3,\dots$  and  $n \geq (\ell+1)$  as a condition on  $\ell$ :

$$\ell = 0, 1, 2, \dots, (n-1).$$

We summarize this section by noting that solutions to the Schrödinger equation for the hydrogen atom must be of the form

$$\Psi = R_{n\ell} \Theta_{\ell m_\ell} \Phi_{m_\ell},$$

with conditions on the quantum numbers  $n$ ,  $\ell$ , and  $m_\ell$

$$n = 1, 2, 3, \dots$$

$$\ell = 0, 1, 2, \dots, (n-1)$$

$$m_\ell = 0, \pm 1, \pm 2, \pm 3, \dots, \pm \ell$$

**Table 6.1** Normalized Wave Functions of the Hydrogen Atom for  $n = 1, 2,$  and  $3^*$ 

$n$	$l$	$m_l$	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
2	1	$\pm 1$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{\pm i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3} a_0^{3/2}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi} a_0^{3/2}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$
3	1	$\pm 1$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{\pm i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1)$
3	2	$\pm 1$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{\pm i\phi}$
3	2	$\pm 2$	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{\pm 2i\phi}$

\*The quantity  $a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2 = 5.292 \times 10^{-11}$  m is equal to the radius of the innermost Bohr orbit.

# Quantum Numbers

The three quantum numbers:

$n$ : Principal quantum number

$\ell$ : Orbital angular momentum quantum number

$m_\ell$ : Magnetic (azimuthal) quantum number

The restrictions for the quantum numbers:

$$n = 1, 2, 3, 4, \dots$$

$$\ell = 0, 1, 2, 3, \dots, n - 1$$

$$m_\ell = -\ell, -\ell + 1, \dots, 0, 1, \dots, \ell - 1, \ell$$

Equivalently:

$$n > 0$$

$$\ell < n$$

$$|m_\ell| \leq \ell$$

The energy levels are:

$$E_n = -\frac{E_0}{n^2}$$

# Principal Quantum Number $n$

- There are many solutions to the radial wave equation, one for each positive integer,  $n$ .
- The result for the quantized energy is:

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2\mu}{\hbar^2} \left( E + \frac{e^2}{4\pi\epsilon_0 r} \right) R = 0$$

$$E_n = -\frac{\mu}{2} \left( \frac{e^2}{4\pi\epsilon_0 \hbar} \right)^2 \frac{1}{n^2} = -\frac{E_0}{n^2}$$

A negative energy means that the electron and proton are bound together.

# Orbital Angular Momentum Quantum Number $\ell$

Energy levels are **degenerate** with respect to  $\ell$  (the energy is independent of  $\ell$ ).

Physicists use letter names for the various  $\ell$  values:

$\ell =$	0	1	2	3	4	5 ...
Letter =	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i> ...

Atomic states are usually referred to by their values of  $n$  and  $\ell$ .

A state with  $n = 2$  and  $\ell = 1$  is called a  $2p$  state.

# Orbital Angular Momentum Quantum Number $\ell$

It's associated with the  $R(r)$  and  $f(\theta)$  parts of the wave function.

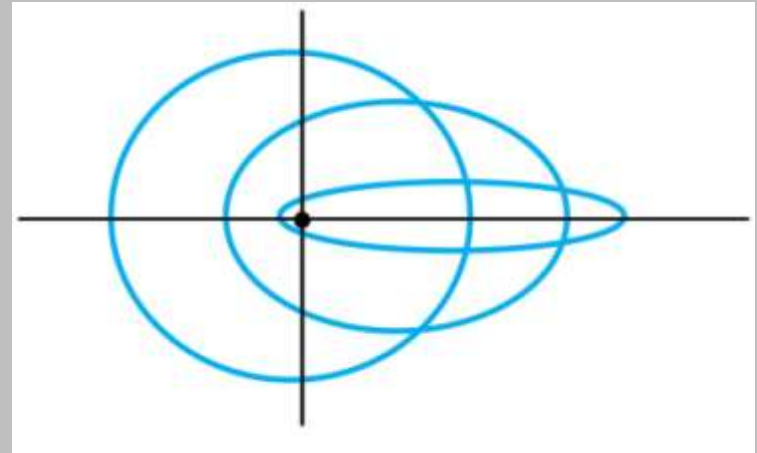
Classically, the orbital angular momentum is  $\vec{L} = \vec{r} \times \vec{p}$  with  $L = m v_{\text{orbital}} r$ .

But quantum-mechanically,  $L$  is related to  $\ell$  by:

$$L = \sqrt{\ell(\ell + 1)}\hbar$$

In an  $\ell = 0$  state,  $L = \sqrt{0(1)}\hbar = 0$

This disagrees with Bohr's semi-classical "planetary" model of electrons orbiting a nucleus  $L = n\hbar$ , where  $n = 1, 2, \dots$



Classical orbits—which do not exist in quantum mechanics



# Magnetic Quantum Number $m_\ell$

The solution for  $g(\phi)$  specifies that  $m_\ell$  is an integer and is related to the  $z$  component of  $L$ :

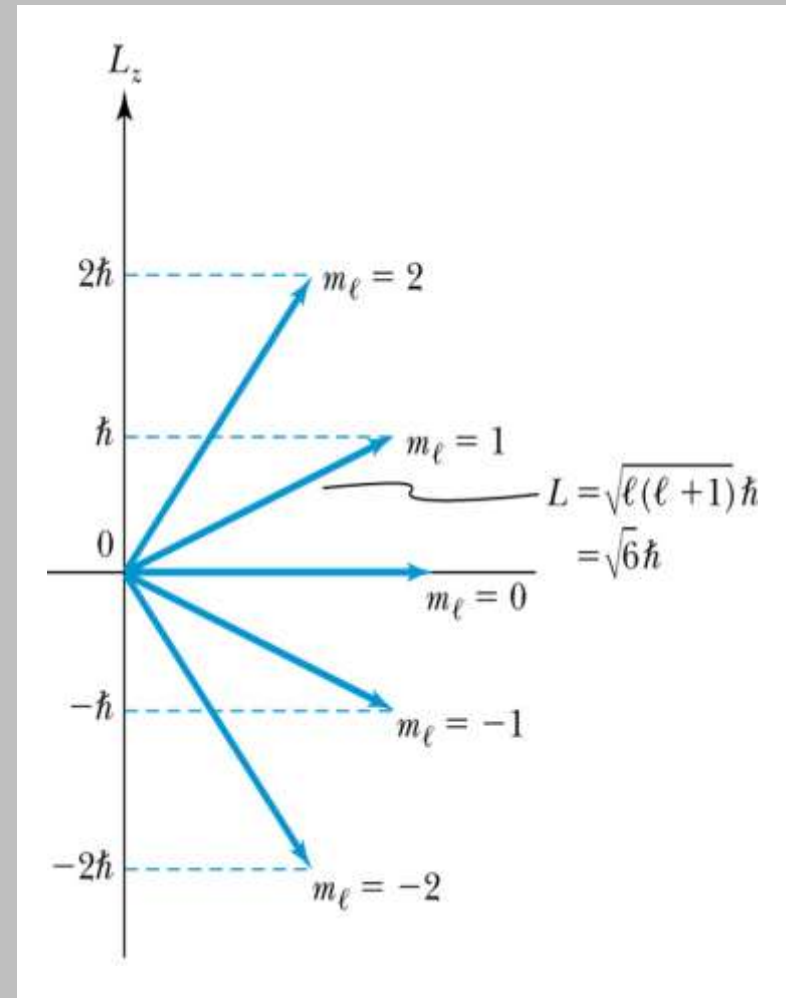
$$L_z = m_\ell \hbar$$

Example:  $\ell = 2$ :

$$L = \sqrt{\ell(\ell+1)}\hbar = \sqrt{6}\hbar$$

Only certain orientations of  $\vec{L}$  are possible.

And (except when  $\ell = 0$ ) we just don't know  $L_x$  and  $L_y$ !



# Electron Probability Density

Recall that the volume element in spherical polar coordinates is

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

Thus, the electron probability density in hydrogen is

$$P(r, \theta, \phi) dV = \psi^* \psi dV = R^* R \Theta^* \Theta \Phi^* \Phi r^2 \sin \theta \, dr \, d\theta \, d\phi$$

$$P(r, \theta, \phi) dV = [R^* R r^2 \, dr] [\Theta^* \Theta \sin \theta \, d\theta] [\Phi^* \Phi \, d\phi]$$

$$P(r, \theta, \phi) dV = [P(r) \, dr] [P(\theta) \, d\theta] [P(\phi) \, d\phi]$$

We often wish to calculate the probability of finding the electron in some volume element in space:

$$\text{Probability} = \iiint P(r, \theta, \phi) dV .$$

Because  $\psi$  is separable, and  $R$ ,  $\Theta$ , and  $\Phi$  are *orthonormal*,\* we can write the triple integral as three one-dimensional integrals.

$$\text{Probability}(r) = \int P(r) dr$$

$$\text{Probability}(\theta) = \int P(\theta) d\theta$$

$$\text{Probability}(\phi) = \int P(\phi) d\phi$$

## Important note:

In spherical polar coordinates,  $0 \leq r \leq \infty$ ,  $0 \leq \theta \leq \pi$ , and  $0 \leq \phi \leq 2\pi$ . It makes no sense to calculate probabilities outside these regions.

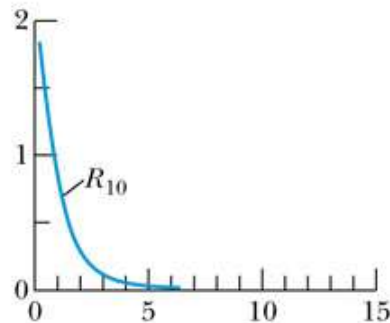
When you calculate  $\langle r \rangle$ , the integral goes from 0 to  $\infty$ , NOT from  $-\infty$  to  $\infty$ !

# Probability Distribution Functions

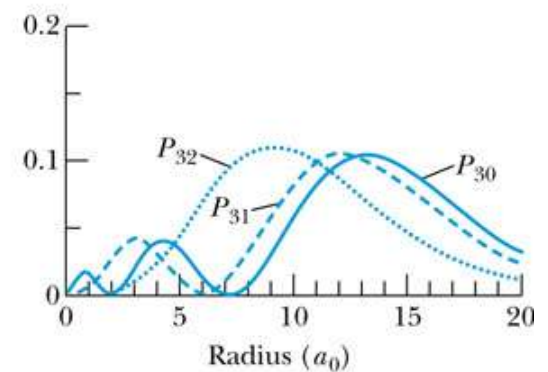
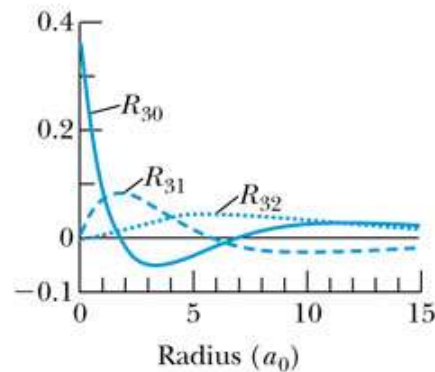
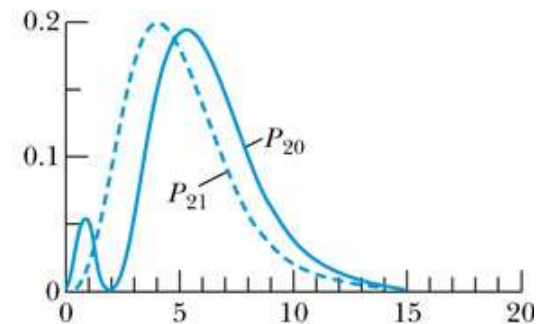
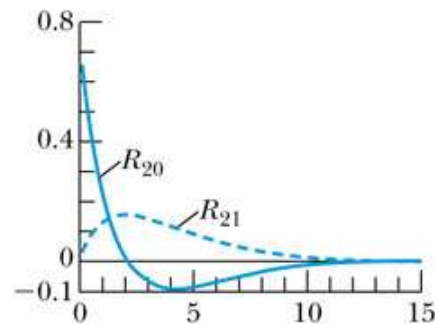
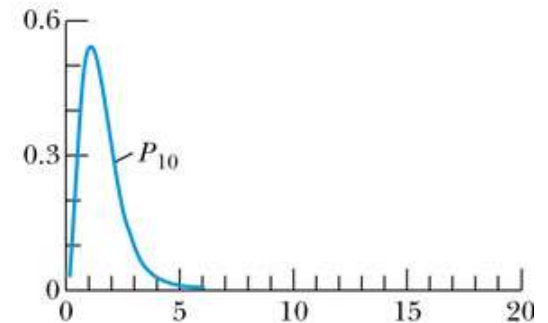
$R(r)$  and  $P(r)$  for the lowest-lying states of the hydrogen atom.

Note that  $R_{n0}$  is maximal at  $r = 0$ ! But the  $r^2$  factor reduces the probability there to 0. Nevertheless, there's a nonzero probability that the electron is inside the nucleus.

Radial wave functions ( $R_{nl}$ )

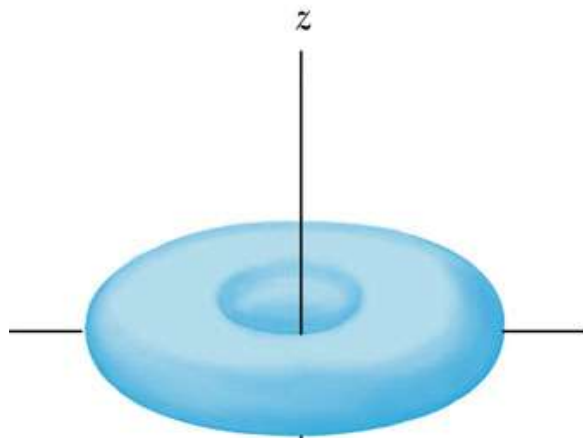


Radial probability distribution ( $P_{nl}$ )

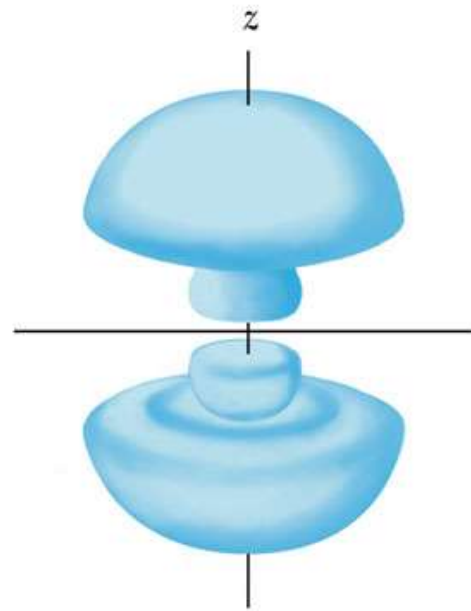


# Probability Distribution Functions

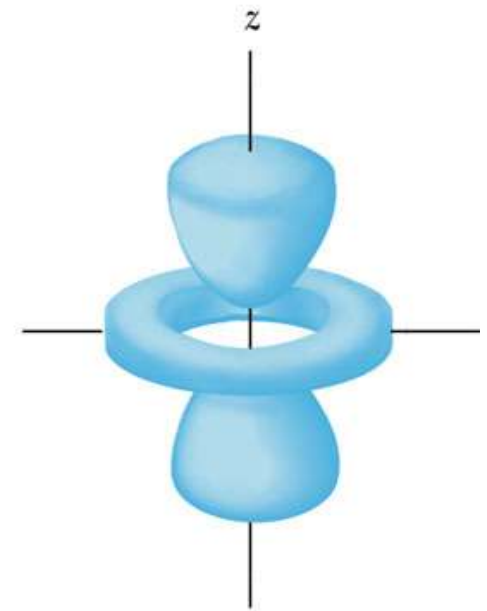
The probability density for the hydrogen atom for three different electron states.



$$\begin{aligned}n &= 2 \\ \ell &= 1 \\ m_\ell &= \pm 1\end{aligned}$$



$$\begin{aligned}n &= 3 \\ \ell &= 1 \\ m_\ell &= 0\end{aligned}$$



$$\begin{aligned}n &= 3 \\ \ell &= 2 \\ m_\ell &= 0\end{aligned}$$

# Ch-5

## Atoms with one valence electron

# CONTENTS

- ❑ BOHR'S MODEL
- ❑ SPECTRA LINES OF H-ATOM
- ❑ EXCITATION AND IONIZATION POTENTIAL
- ❑ CORRESPONDENCE PRINCIPLE
- ❑ ELECTRON SPIN
- ❑ MAGNETIC MOMENT
- ❑ TOTAL ANGULAR MOMENTUM
- ❑ STERN GERLACH EXPERIMENT
- ❑ SPIN ORBIT INTERACTION
- ❑ FINE STRUCTURE OF H-ATOM
- ❑ ZEEMAN EFFECT



# The Bohr Model

In 1913 Niels Bohr proposed a theory of the hydrogen atom that could account for its stability and for the frequencies of its spectral lines.

Bohr proposed that an electron can circle the nucleus without losing energy only in certain specific orbits.

The energy of the electron depends on which orbit it is in.

Thus Bohr suggested that atomic electrons can have only certain particular energies.

# Bohr's Model Of The Atom

Bohr in 1913 set down postulates to account for (1) the stability of the hydrogen atom and (2) the line spectrum of the atom

## Energy level postulate:

An electron can have only specific energy levels in an atom

## Transitions between energy levels:

An electron in an atom can change energy levels by undergoing a “transition” from one energy level ( $n_i$ ) to another ( $n_f$ ), the energy is emitted as a photon

$$\text{Energy of emitted photon} = h\nu = E_f - E_i = \Delta E$$

This is called Bohr's frequency condition

## quantize angular momentum of circular orbits

Only those orbits are permissible for which the angular momentum of electron is equal to an integral multiple of  $h/2\pi$

$$L = mvr + L_n = n \frac{h}{2\pi} = n\hbar$$

$$n \cdot \lambda_n = n \cdot \left( \frac{h}{mv_n} \right) = 2\pi r_n \Rightarrow mv_n r_n = \frac{nh}{2\pi}$$

This is called Bohr's quantum condition

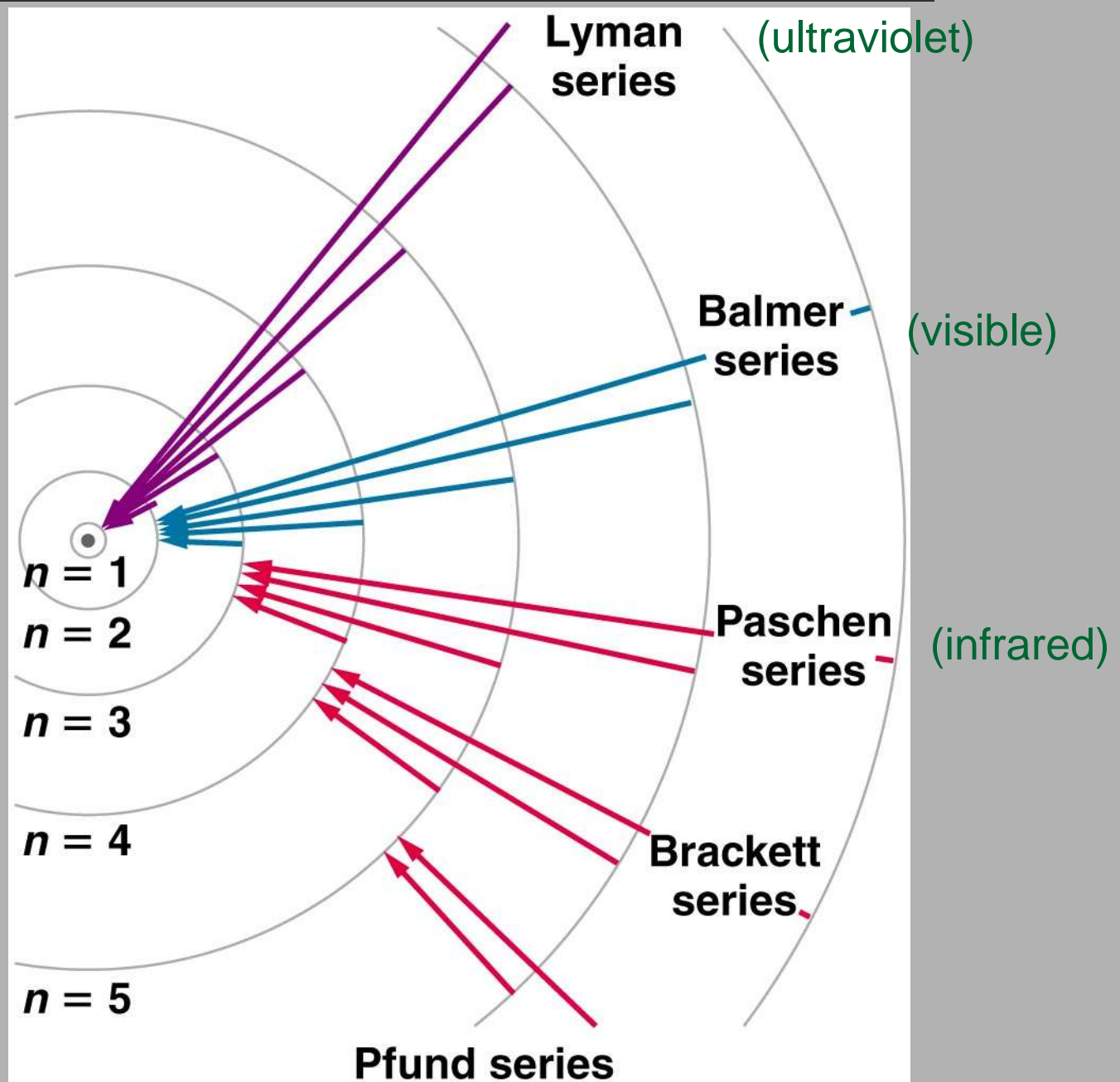
## Atomic electron follow certain orbits only

The de Broglie wavelength of the electron is exactly equal to the circumference of its ground state (the innermost orbit with  $n=1$ ).

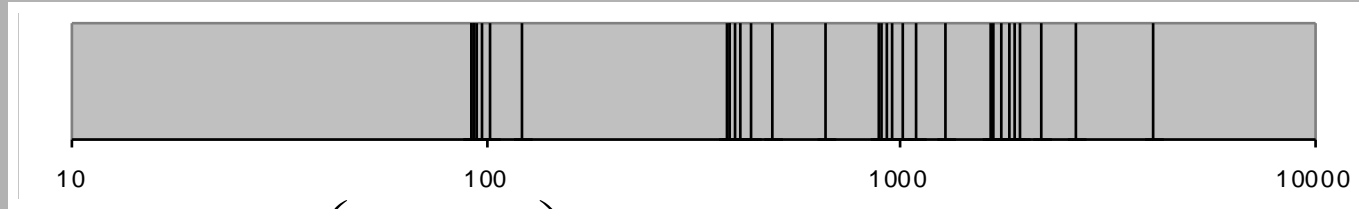
If we consider the vibrations of a wire loop, we find that their wavelengths always fit a whole number of times into the loop's circumference.

Thus, an electron can circle a nucleus only in orbits that contain a whole number of de Broglie wavelengths.

# HYDROGEN SPECTRAL LINES



# Hydrogen spectral series: patterns in the spectra



Balmer  $\frac{1}{\lambda_n} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \quad n = 3, 4, 5, \dots$  (visible light)

$$R = 0.01097 \text{ nm}^{-1}$$

Lyman  $\frac{1}{\lambda_n} = R \left( \frac{1}{1^2} - \frac{1}{n^2} \right) \quad n = 2, 3, 4, \dots$  (UV)

Paschen  $\frac{1}{\lambda_n} = R \left( \frac{1}{3^2} - \frac{1}{n^2} \right) \quad n = 4, 5, 6, \dots$  (IR)

Brackett  $\frac{1}{\lambda_n} = R \left( \frac{1}{4^2} - \frac{1}{n^2} \right) \quad n = 5, 6, 7, \dots$  (IR)

Pfund  $\frac{1}{\lambda_n} = R \left( \frac{1}{5^2} - \frac{1}{n^2} \right) \quad n = 6, 7, 8, \dots$  (IR)

## Energy levels for hydrogen atom

$$E_n = -\frac{me^4}{32\pi^2 \epsilon_0 \hbar^2} \frac{1}{n^2} = \frac{E_1}{n^2}, \quad n=1, 2, 3, \dots$$

$$E_1 = -13.6\text{eV}$$

called the ground state of hydrogen atom

$$\text{for } n=2, E_2 = -3.4\text{eV}$$

$$n=3, E_3 = -1.51\text{eV}$$

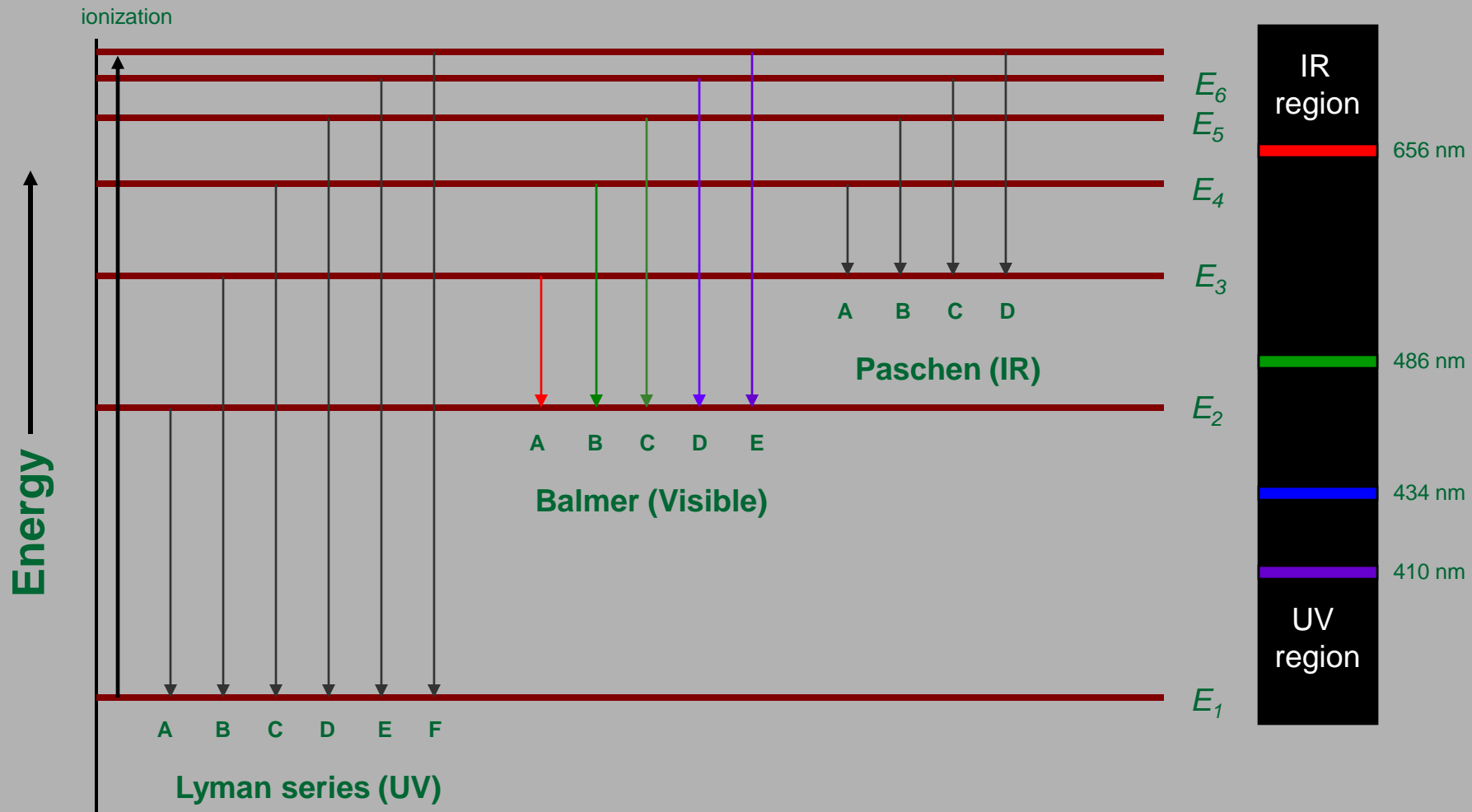
$$n=4, E_4 = -0.85\text{eV}$$

so on...

$$n=\infty, E_\infty = 0\text{eV}$$

# Hydrogen Spectral Lines

Bohr's model of the atom accounted mathematically for the energy of each of the transitions shown.





# The Correspondence Principle

A new theory should encompass an old theory where the old theory was successful.

Quantum theory approximates the results of classical mechanics when:

quantum numbers are large

$$h \rightarrow 0$$

Classical treatment of radiation from “planetary” hydrogen: frequency of emitted light = frequency of orbits (+ harmonics)

$$\left. \begin{aligned} f &= \frac{v}{2\pi r} \\ v &= \frac{e}{\sqrt{4\pi\epsilon_0 m r}} \end{aligned} \right\} \Rightarrow f = \frac{e}{2\pi\sqrt{4\pi\epsilon_0 m r^3}}$$

$$\text{with } r_n = \frac{n^2 h^2 \epsilon_0}{\pi m e^2} \Rightarrow f = \frac{m e^4}{8 \epsilon_0^2 h^3} \left( \frac{2}{n^3} \right) = \frac{-E_1}{h} \left( \frac{2}{n^3} \right)$$

Quantum transition from  $n \rightarrow n-p$  with  $p \ll n$

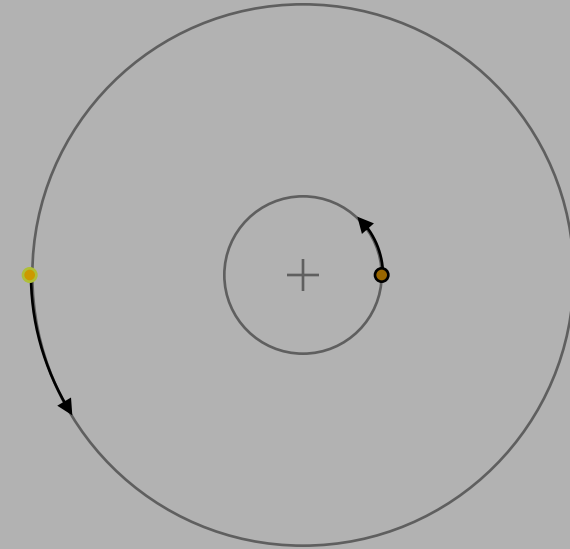
$$h\nu = -E_1 \left( \frac{1}{(n-p)^2} - \frac{1}{n^2} \right) \Rightarrow \nu = \frac{-E_1}{h} \frac{2np - p^2}{(n-p)^2 n^2}$$

$$\nu \cong \frac{-E_1}{h} \frac{2p}{n^3} = p \cdot f$$

## Refining the Bohr Atom

nuclear motion: electron and nucleus orbit each other (each orbit center of mass).

Two body problem => center of mass motion + relative motion (with reduced mass)



$$m' = \frac{mM}{m + M}$$

$$E'_n = -\frac{m'e^4}{8\varepsilon_0^2 h^2} \left( \frac{1}{n^2} \right) = \frac{m'}{m} \left( \frac{E_1}{n^2} \right)$$

$$\text{hydrogen: } \frac{m'}{m} = 0.99945$$

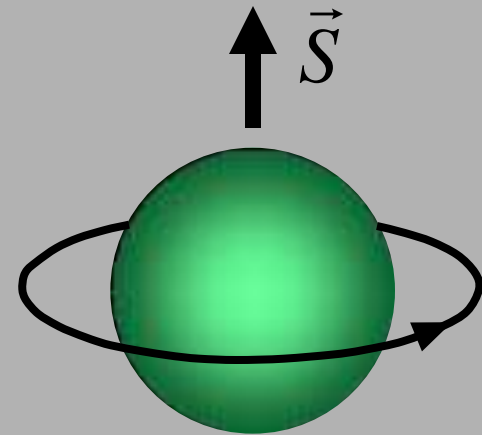
# EXCITATION AND IONIZATION POTENTIAL

## Excitation and Ionization Potential

- An electron revolving in a stationary orbit of an atom absorbs some energy the electron may jump over to an orbit of higher energy. This process is called excitation and the atom is said to be in the excited state. The energy absorbed to move from one orbit to the other is called **excitation potential**.
- If the energy supplied is large enough to remove an electron from the atom, then the atom is said to be ionized. The minimum energy needed to ionize an atom is called **ionization energy**. Here the removed electron will have zero energy. Therefore the Ionization potential of a hydrogen atom in the ground state is 13.6 eV.

# Intrinsic Spin

In 1925, grad students, Samuel Goudsmit and George Uhlenbeck, in Holland proposed that **the electron must have an intrinsic angular momentum** and therefore a magnetic moment.



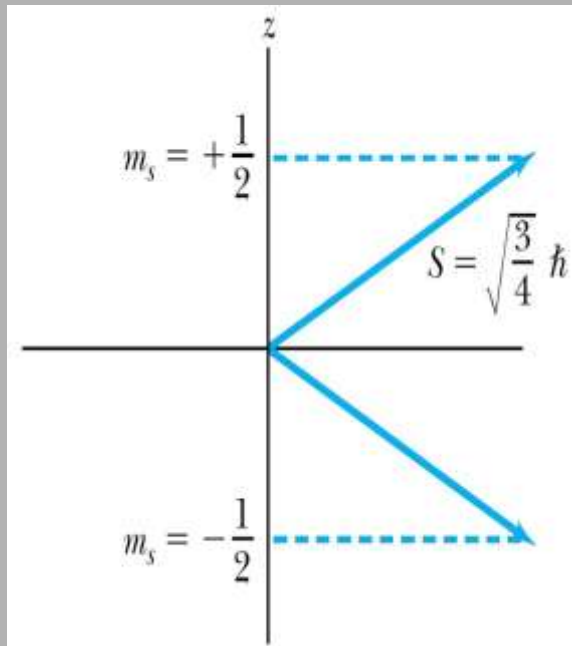
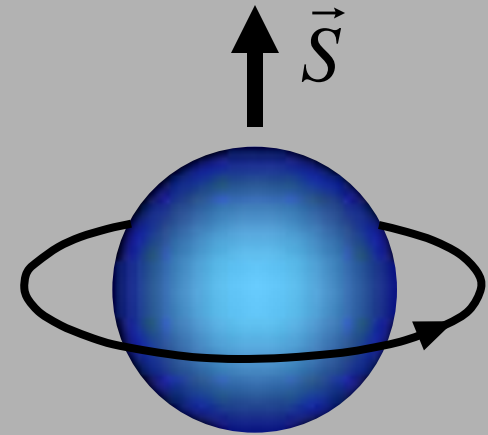
This seems reasonable, but Paul Ehrenfest showed that, if so, the surface of the spinning electron would be moving faster than the speed of light!

In order to explain experimental data, Goudsmit and Uhlenbeck proposed that **the electron must have an intrinsic spin quantum number  $s = \frac{1}{2}$ .**

# Intrinsic Spin

The spinning electron reacts similarly to the orbiting electron in a magnetic field.

The **magnetic spin quantum number**  $m_s$  has only two values,  $m_s = \pm 1/2$ .



And  $S_z = m_s \hbar$ .

The electron's spin is either “up” ( $m_s = +1/2$ ) or “down” ( $m_s = -1/2$ ) and can **never** be spinning with its magnetic moment  $\mu_S$  exactly along the  $z$  axis.

$$|\vec{S}| = \sqrt{s(s+1)} \hbar = \sqrt{3/4} \hbar$$

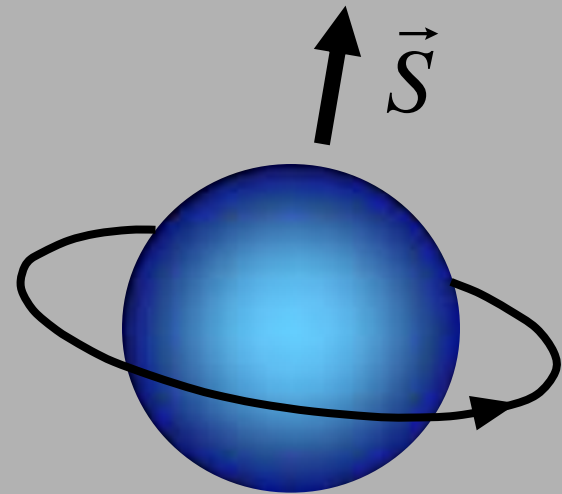
## What about $S_x$ and $S_y$ ?

Quantum mechanics says that, no matter how hard we try, we can't also measure them!

If we did, we'd measure  $\frac{1}{2} \hbar$ , just as we'd find for  $S_z$ .

But then this measurement would perturb  $S_z$ , which would then become unknown!

The total spin is  $|\vec{S}| = \sqrt{s(s+1)} \hbar = \sqrt{3/4} \hbar = \sqrt{(\frac{1}{2})^2 + (\frac{1}{2})^2 + (\frac{1}{2})^2} \hbar$ , so it'd be tempting to conclude that every component of the electron's spin is either "up" ( $+\frac{1}{2} \hbar$ ) or "down" ( $m_s = -\frac{1}{2} \hbar$ ). But this is not the case! Instead, they're undetermined. We'll see next that the uncertainty in each unmeasured component is equal to their maximum possible magnitude ( $\frac{1}{2} \hbar$ )!

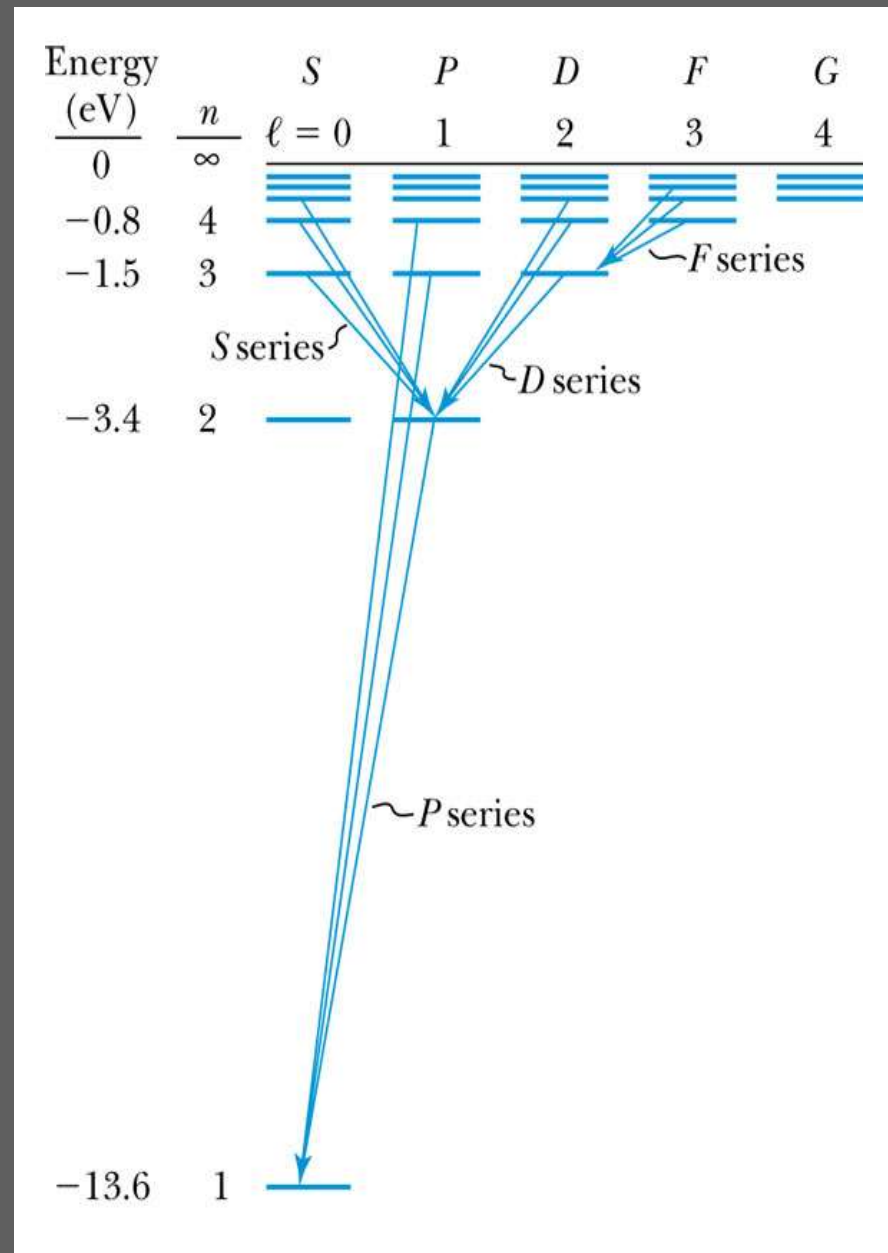


# Energy Levels and Electron Probabilities

For hydrogen, the energy level depends on the principal quantum number  $n$ .

An electron can make a transition from a state of any  $n$  value to any other.

But what about  $\ell$  and  $m_\ell$  quantum numbers?



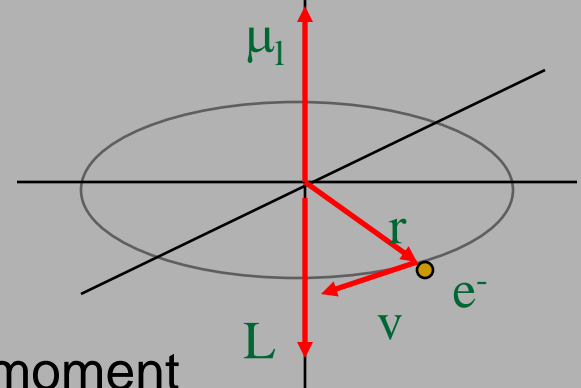


# Orbital magnetic dipole moments

Consider electron moving with velocity ( $v$ ) in a circular Bohr orbit of radius  $r$ . Produces a current

$$i = -\frac{e}{T} = -\frac{e\omega}{2\pi}$$

where  $T$  is the orbital period of the electron.



Current loop produces a magnetic field, with a moment

$$\mu_l = iA = -\frac{e\omega}{2\pi} \pi r^2 = -\frac{1}{2} e\omega r^2 \quad (1)$$

Specifies strength of magnetic dipole.

Magnitude of orbital angular momentum is  $L = mvr = m\omega r^2$ .

Combining with Eqn. 1  $\Rightarrow$

$$\mu_l = -\frac{e}{2m} L \quad (2)$$

An electron in the first Bohr orbit with  $L = \hbar$  has a magnetic moment defined as

$$\mu_B = \frac{e}{2m} \hbar$$

Bohr Magneton

# Orbital magnetic dipole moments

Magnetic moment can also be written in terms of the Bohr magneton:

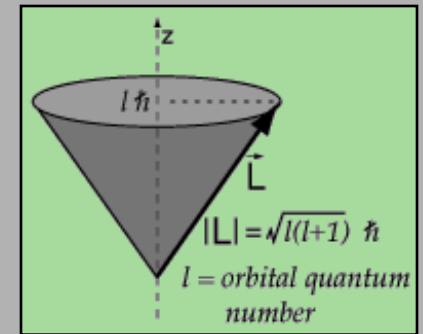
$$\mu_l = \frac{g_l \mu_B}{\hbar} L$$

where  $g_l$  is the *orbital g-factor* or *Landé g-factor*. Gives ratio of magnetic moment to angular momentum (in units of  $\hbar$ ).

In vector form, Eqn 2 can be written

$$\hat{\mu}_l = -\frac{g_l \mu_B}{\hbar} \hat{L}$$

As 
$$L = \sqrt{l(l+1)}\hbar \Rightarrow \mu_l = \frac{g_l \mu_B}{\hbar} \sqrt{l(l+1)}\hbar = g_l \mu_B \sqrt{l(l+1)}$$



The components of the angular momentum in the z-direction are

$$L_z = m_l \hbar \quad \text{where } m_l = -l, -l+1, \dots, 0, \dots, +l-1, +l.$$

The magnetic moment associated with the z-component is correspondingly

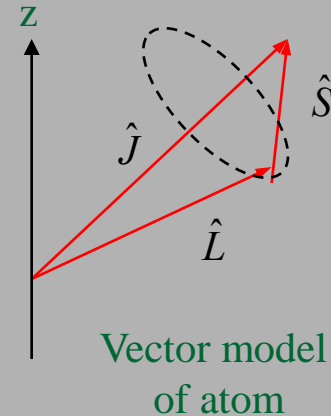
$$\mu_{l_z} = -\frac{g_l \mu_B}{\hbar} L_z = -\frac{g_l \mu_B}{\hbar} m_l \hbar = -g_l \mu_B m_l$$

# Total angular momentum

Orbital and spin angular momenta couple together via the spin-orbit interaction.

Internal magnetic field produces torque which results in precession of  $\hat{L}$  and  $\hat{S}$  about their sum, the *total angular momentum*:

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



Called *L-S coupling* or *Russell-Saunders coupling*.

Maintains fixed magnitude and z-components, specified by two quantum numbers  $j$  and  $m_j$ :

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

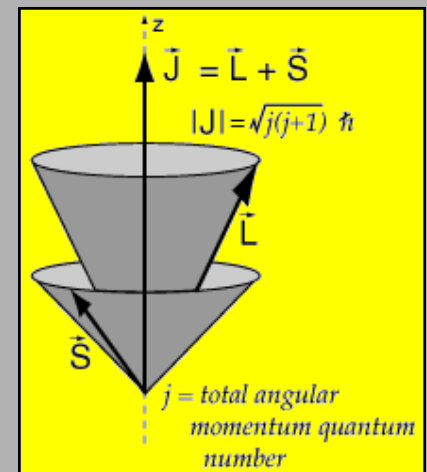
$$J_z = m_j\hbar$$

where  $m_j = -j, -j + 1, \dots, +j - 1, +j$ .

But what are the values of  $j$ ? Must use vector inequality

$$|\hat{L} + \hat{S}| \geq ||\hat{L}| - |\hat{S}||$$

$$\Rightarrow |\hat{J}| \geq ||\hat{L}| - |\hat{S}||$$



# Total angular momentum

From the previous page, we can therefore write

$$\sqrt{j(j+1)}\hbar \geq |\sqrt{l(l+1)}\hbar - \sqrt{s(s+1)}\hbar|$$

Since,  $s = 1/2$ , there are generally two members of series that satisfy this inequality:  $j = l + 1/2, l - 1/2$

For  $l = 0 \Rightarrow j = 1/2$

Some examples vector addition rules

$$J = L + S, L = 3, S = 1$$

$$L + S = 4, |L - S| = 2, \text{ therefore } J = 4, 3, 2.$$

$$L = l_1 + l_2, l_1 = 2, l_2 = 0$$

$$l_1 + l_2 = 2, |l_1 - l_2| = 2, \text{ therefore } L = 2$$

$$J = j_1 + j_2, j_1 = 5/2, j_2 = 3/2$$

$$j_1 + j_2 = 4, |j_1 - j_2| = 1, \text{ therefore } J = 4, 3, 2, 1$$

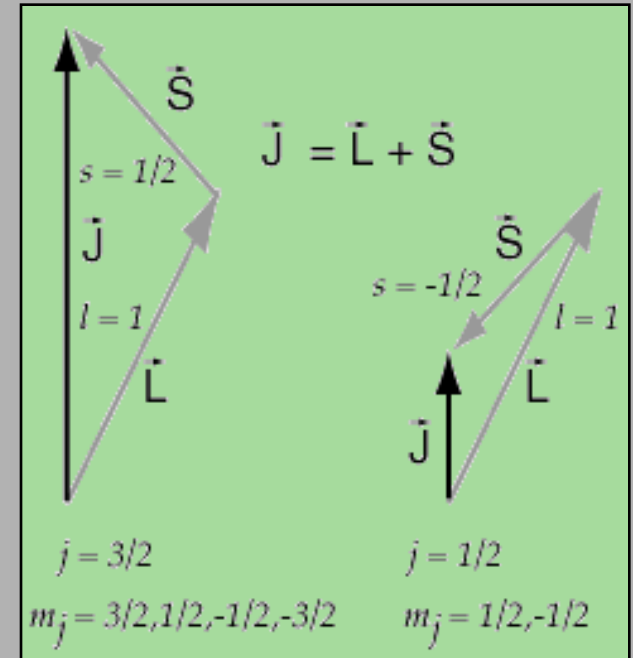
# Total angular momentum

For multi-electron atoms where the spin-orbit coupling is weak, it can be presumed that the orbital angular momenta of the individual electrons add to form a resultant orbital angular momentum  $L$ .

This kind of coupling is called *L-S coupling* or *Russell-Saunders coupling*.

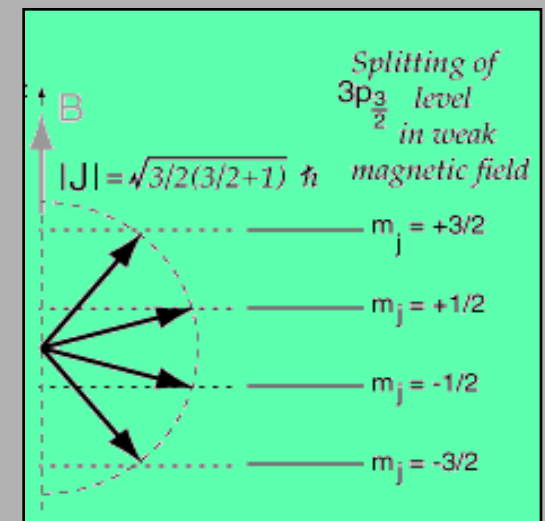
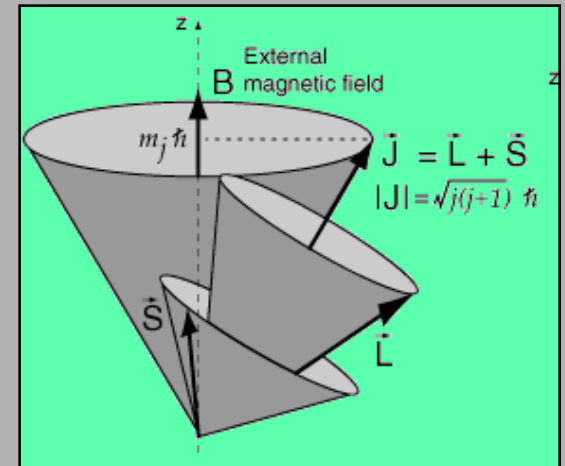
Found to give good agreement with observed spectral details for many light atoms.

For heavier atoms, another coupling scheme called *j-j coupling* provides better agreement with experiment.



# Total angular momentum in a magnetic field

- Total angular momentum can be visualised as precessing about any externally applied magnetic field.
- Magnetic energy contribution is proportional  $J_z$ .
- $J_z$  is quantized in values one unit apart, so for the upper level of the sodium doublet with  $j=3/2$ , the vector model gives the splitting in bottom figure.
- This treatment of the angular momentum is appropriate for weak external magnetic fields where the coupling between the spin and orbital angular momenta can be presumed to be stronger than the coupling to the external field.



# The Stern-Gerlach experiment

This experiment confirmed the quantization of electron spin into two orientations.

Potential energy of electron spin magnetic moment in magnetic field in z-direction is

$$\Delta E = -\hat{\mu}_s \cdot \hat{B} = -\mu_{s_z} B$$

$$= g_s \mu_B m_s B$$

The resultant force is

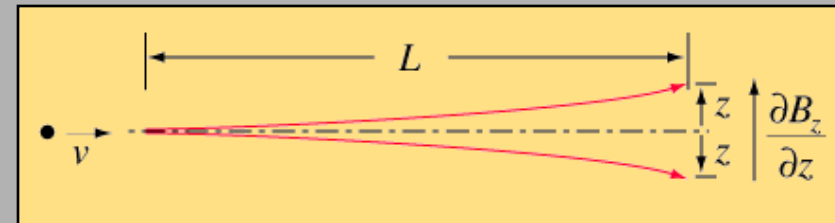
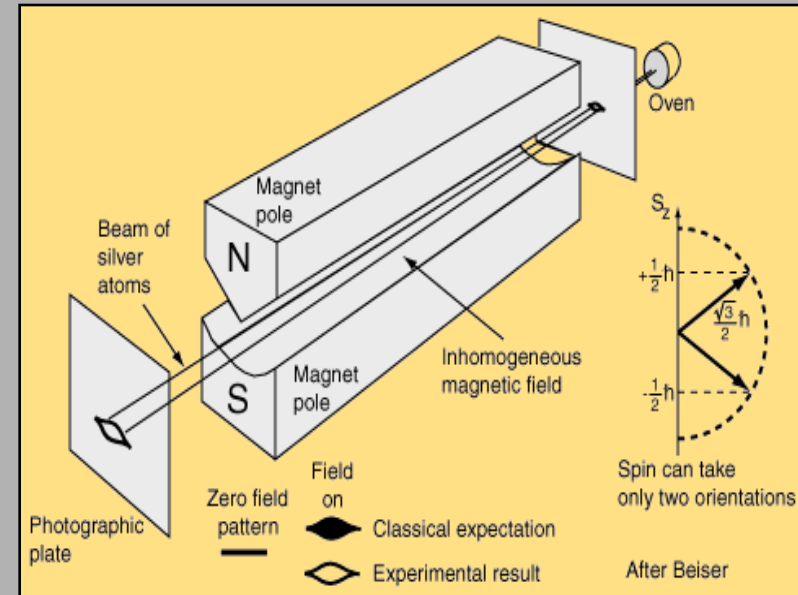
$$F_z = -\frac{d(\Delta E)}{dz} = -\mu_B g_s m_s \frac{dB_z}{dz}$$

As  $g_s m_s = \pm 1$ ,

$$F_z = \pm \mu_B \frac{dB_z}{dz}$$

The deflection distance is then,

$$z = 1/2 at^2 = 1/2 \frac{F}{m} \left[ \frac{L}{v} \right]^2 = \pm \frac{\mu_B L^2}{4KE} \frac{dB_z}{dz}$$



# The Stern-Gerlach experiment

Conclusion of Stern-Gerlach experiment:

With field on, classically expect random distribution at target. In fact find two bands as beam is split in two.

There is *directional quantisation*, parallel or antiparallel to  $B$ .

*Atomic magnetic moment* has  $\mu_z = \pm\mu_B$ .

Find same deflection for all atoms which have an s electron in the outermost orbital => all angular momenta and magnetic moments of all inner electrons cancel. Therefore only measure properties of outer s electron.

The s electron has orbital angular momentum  $l = 0$  => only observe spin.



# Spin-orbit interaction

Fine-structure in atomic spectra cannot be explained by Coulomb interaction between nucleus and electron.

Instead, must consider *magnetic interaction* between *orbital magnetic moment* and the *intrinsic spin magnetic moment*.

Called *spin-orbit interaction*.

Weak in one-electron atoms, but strong in multi-electron atoms where total orbital magnetic moment is large.

Coupling of spin and orbital AM yields a *total angular momentum*,  $\hat{j}$  .

# Spin-orbit interaction

Consider reference frame of electron: nucleus moves about electron. Electron therefore in current loop which produces magnetic field. Charged nucleus moving with  $v$  produces a current:

$$\hat{j} = -Ze\hat{v}$$

According to Ampere's Law, this produces a magnetic field, which at electron is

$$\hat{B} = \frac{\mu_0}{4\pi} \frac{\hat{j} \times \hat{r}}{r^3} = \frac{-Ze\mu_0}{4\pi} \frac{\hat{v} \times \hat{r}}{r^3}$$

Using Coulomb's Law:

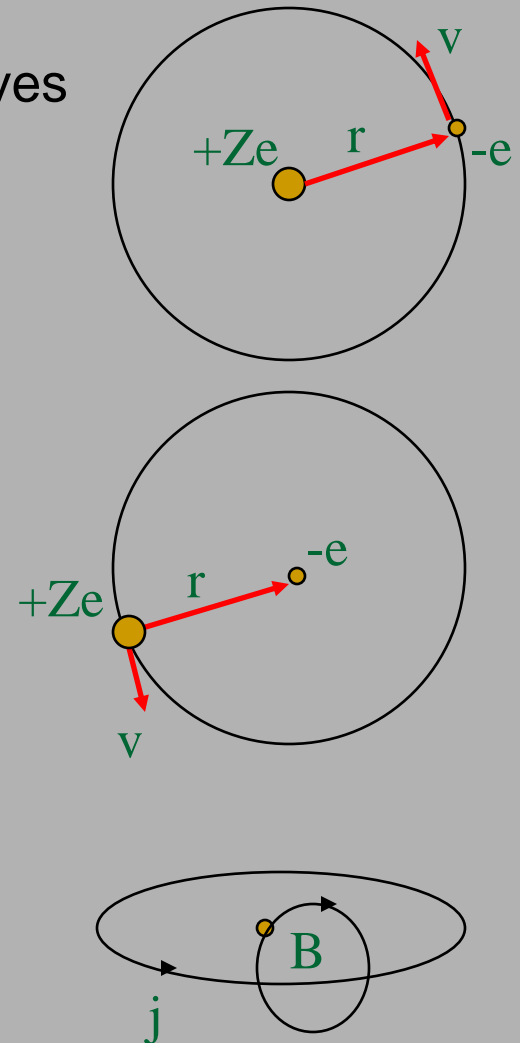
$$\hat{E} = \frac{Ze}{4\pi\epsilon_0} \frac{\hat{r}}{r^3}$$

$$\Rightarrow \hat{B} = -\frac{1}{c^2} \hat{v} \times \hat{E}$$

where

$$c = 1/\sqrt{\epsilon_0\mu_0}$$

This is the magnetic field experienced by electron through  $E$  exerted on it by nucleus.



# Spin-orbit interaction

We know that the orientation potential energy of magnetic dipole moment is

$$\Delta E = -\hat{\mu}_s \cdot \hat{B}$$

but as

$$\hat{\mu}_s = -\frac{g_s \mu_B}{\hbar} \hat{S} \Rightarrow \Delta E = \frac{g_s \mu_B}{\hbar} \hat{S} \cdot \hat{B}$$

Transforming back to reference frame with nucleus, must include the factor of 2 due to *Thomas precession* (Appendix O of Eisberg & Resnick):

$$\Delta E_{so} = \frac{1}{2} \frac{g_s \mu_B}{\hbar} \hat{S} \cdot \hat{B} \quad (6)$$

This is the *spin-orbit interaction energy*.

More convenient to express in terms of  $S$  and  $L$ . As force on electron is

$$\hat{F} = -e\hat{E} = -\frac{dV(r)}{dr} \frac{\hat{r}}{r} \Rightarrow \hat{E} = \frac{1}{e} \frac{dV(r)}{dr} \frac{\hat{r}}{r}$$

can write Eqn. 5 as

$$\hat{B} = -\frac{1}{ec^2} \frac{1}{r} \frac{dV(r)}{dr} \hat{v} \times \hat{r}$$

# Spin-orbit interaction

As  $\hat{L} = \hat{r} \times m\hat{v} = -m\hat{v} \times \hat{r} \Rightarrow \hat{B} = \frac{1}{emc^2} \frac{1}{r} \frac{dV(r)}{dr} \hat{L}$

Substituting the last expression for  $B$  into Eqn. 6 gives:  $\Delta E_{so} = \frac{g_s \mu_B}{2emc^2 \hbar} \frac{1}{r} \frac{dV(r)}{dr} \hat{S} \cdot \hat{L}$

Evaluating  $g_s$  and  $\mu_B$ , we obtain:

$$\Delta E_{so} = \frac{1}{2m^2 c^2} \frac{1}{r} \frac{dV(r)}{dr} \hat{S} \cdot \hat{L}$$

General form

For hydrogenic atoms,

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

Substituting into equation for  $\Delta E$ :

$$\Delta E_{so} = \frac{1}{2m^2 c^2} \frac{1}{r} \frac{Ze^2}{4\pi\epsilon_0 r^2} \hat{S} \cdot \hat{L}$$

Hydrogenic form

$$= \frac{e^2}{4\pi\epsilon_0 \hbar c} \frac{Z\hbar}{2m^2 cr^3} \hat{S} \cdot \hat{L} \quad (7)$$

$$\Delta E_{so} = \alpha \frac{Z\hbar}{2m^2 cr^3} \hat{S} \cdot \hat{L}$$

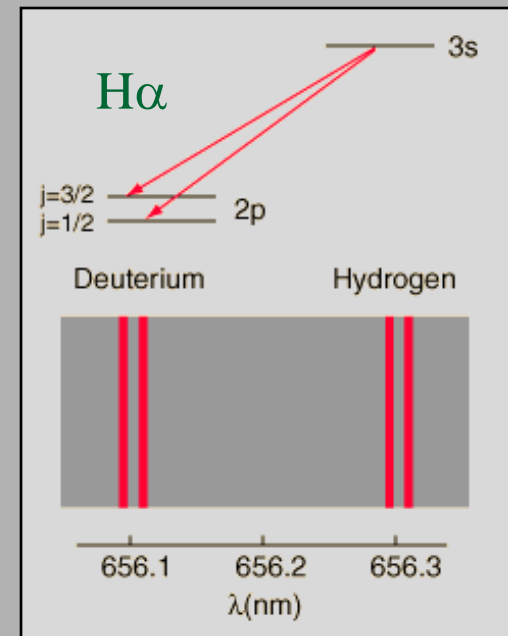
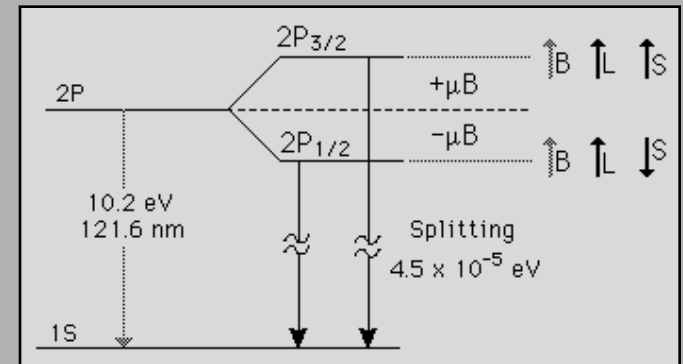
Expression for *spin-orbit interaction in terms of L and S*. Note,  $\alpha = e^2 / 4\pi\epsilon_0 \hbar c$  is the fine structure constant.

# Hydrogen fine structure

Spectral lines of H found to be composed of closely spaced *doublets*. Splitting is due to interactions between electron spin  $S$  and the orbital angular momentum  $L \Rightarrow$  *spin-orbit coupling*.

$H\alpha$  line is single line according to the Bohr or Schrödinger theory. Occurs at 656.47 nm for H and 656.29 nm for D (isotope shift,  $\Delta\lambda \sim 0.2$  nm).

Spin-orbit coupling produces fine-structure splitting of  $\sim 0.016$  nm. Corresponds to an internal magnetic field on the electron of about 0.4 Tesla.



# ZEEMAN EFFECT

Atoms in magnetic fields:

Normal Zeeman effect

Anomalous Zeeman effect

# Zeeman Effect

First reported by Zeeman in 1896. Interpreted by Lorentz.

Interaction between atoms and field can be classified into two regimes:

- ❖ Weak fields: *Zeeman effect*, either *normal* or *anomalous*.
- ❖ Strong fields: *Paschen-Back effect*.

Normal Zeeman effect agrees with the classical theory of Lorentz. Anomalous effect depends on electron spin, and is purely quantum mechanical.

# Normal Zeeman effect

Observed in atoms with no spin.

- Total spin of an  $N$ -electron atom is  $\hat{S} = \sum_{i=1}^N \hat{S}_i$
- Filled shells have no net spin, so only consider valence electrons. Since electrons have spin  $1/2$ , not possible to obtain  $S = 0$  from atoms with odd number of valence electrons.

Even number of electrons can produce  $S = 0$  state (e.g., for two valence electrons,  $S = 0$  or  $1$ ).

All ground states of Group II (divalent atoms) have  $ns^2$  configurations => always have  $S = 0$  as two electrons align with their spins antiparallel.

Magnetic moment of an atom with *no spin* will be due entirely to *orbital* motion:

$$\hat{\mu} = -\frac{\mu_B}{\hbar} \hat{L}$$



# Normal Zeeman effect

- Interaction energy between magnetic moment and a uniform magnetic field is:

$$\Delta E = -\hat{\mu} \cdot \hat{B}$$

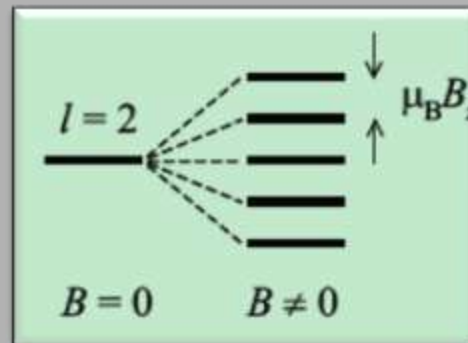
$$\hat{B} = \begin{pmatrix} 0 \\ 0 \\ B_z \end{pmatrix}$$

- Assume  $B$  is only in the z-direction:

- The interaction energy of the atom is therefore,

$$\Delta E = -\mu_z B_z = \mu_B B_z m_l$$

- where  $m_l$  is the orbital magnetic quantum number. This equation implies that  $B$  splits the degeneracy of the  $m_l$  states evenly.



# Normal Zeeman effect transitions

But what transitions occur? Must consider selection rules for  $m_l$ :  $\Delta m_l = 0, \pm 1$ .

Consider transitions between two Zeeman-split atomic levels. Allowed transition frequencies are therefore,

$$h\nu = h\nu_0 + \mu_B B_z$$

$$h\nu = h\nu_0$$

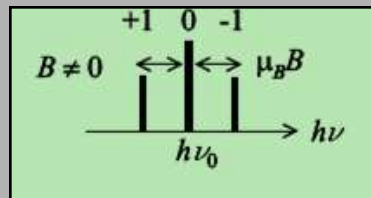
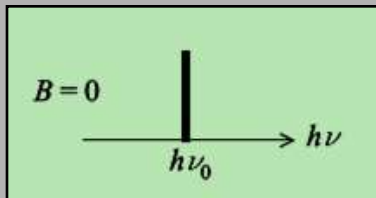
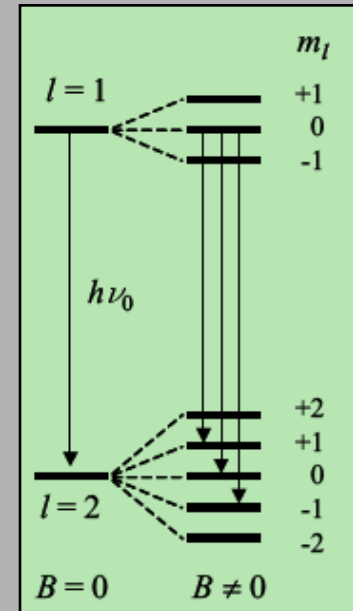
$$h\nu = h\nu_0 - \mu_B B_z$$

$$\Delta m_l = -1$$

$$\Delta m_l = 0$$

$$\Delta m_l = +1$$

- Emitted photons also have a polarization, depending on which transition they result from.



# Normal Zeeman effect transitions

*Longitudinal Zeeman effect:* Observing along magnetic field, photons must propagate in z-direction.

Light waves are transverse, and so only x and y polarizations are possible.

The z-component ( $\Delta m_l = 0$ ) is therefore absent and only observe  $\Delta m_l = \pm 1$ .

Termed  $\sigma$ -components and are circularly polarized.

*Transverse Zeeman effect:* When observed at right angles to the field, all three lines are present.

$\Delta m_l = 0$  are linearly polarized || to the field.

$\Delta m_l = \pm 1$  transitions are linearly polarized at right angles to field.

# Normal Zeeman effect transitions

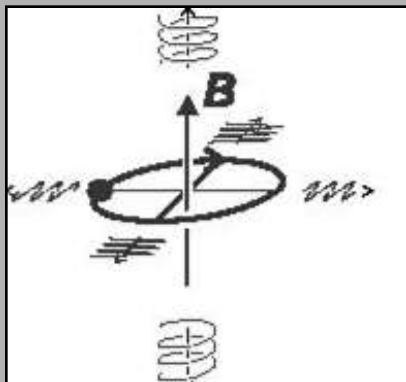
Last two columns of table below refer to the polarizations observed in the longitudinal and transverse directions.

The direction of circular polarization in the longitudinal observations is defined relative to  $B$

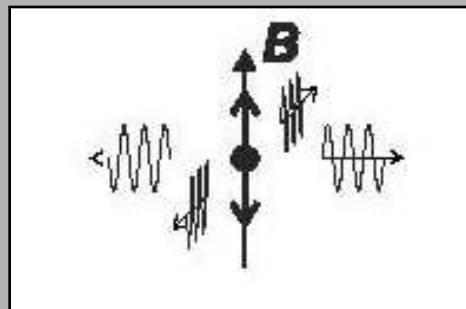
Interpretation proposed by Lorentz (1896)

$\Delta m_l$	Energy	Polarization	
		Longitudinal observation	Transverse observation
+1	$h\nu_0 - \mu_B B$	$\sigma^+$	$\mathcal{E} \perp B$
0	$h\nu_0$	not observed	$\mathcal{E} \parallel B$
-1	$h\nu_0 + \mu_B B$	$\sigma^-$	$\mathcal{E} \perp B$

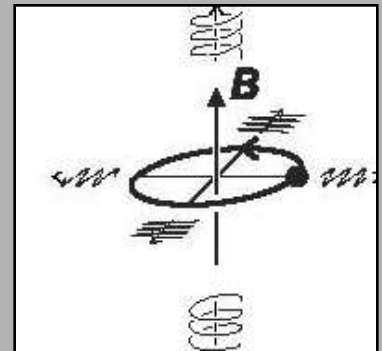
$\sigma^-$   
( $\Delta m_l = -1$ )



$\pi$   
( $\Delta m_l = 0$ )



$\sigma^+$   
( $\Delta m_l = +1$ )



# Anomalous Zeeman effect

Discovered by Thomas Preston in Dublin in 1897.

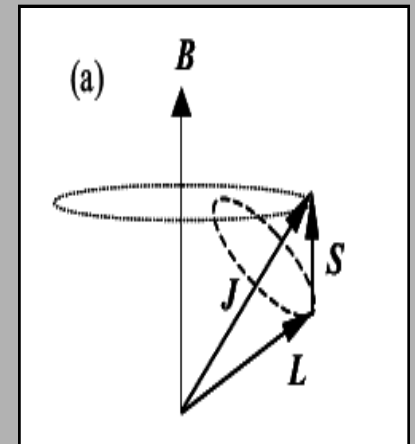
Occurs in atoms with non-zero spin => atoms with odd number of electrons.

In  $LS$ -coupling, the spin-orbit interaction couples the spin and orbital angular momenta to give a total angular momentum according to

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

In an applied  $B$ -field,  $J$  precesses about  $B$  at the Larmor frequency.

$L$  and  $S$  precess more rapidly about  $J$  due to spin-orbit interaction. Spin-orbit effect therefore stronger.



# Anomalous Zeeman effect

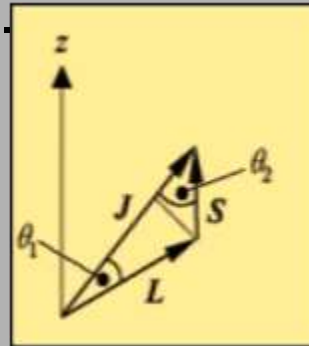
Interaction energy of atom is equal to sum of interactions of spin and orbital magnetic moments with  $B$ -field:

$$\begin{aligned}\Delta E &= -\mu_z B_z \\ &= -(\mu_z^{orbital} + \mu_z^{spin}) B_z \\ &= \left\langle \hat{L}_z + g_s \hat{S}_z \right\rangle \frac{\mu_B}{\hbar} B_z\end{aligned}$$

where  $g_s = 2$ , and the  $\langle \dots \rangle$  is the expectation value. The normal Zeeman effect is obtained by setting  $\hat{S}_z = 0$  and  $\hat{L}_z = m_l \hbar$ .

In the case of precessing atomic magnetic in figure on last slide, neither  $S_z$  nor  $L_z$  are constant. Only  $\hat{J}_z = m_j \hbar$  is well defined. Must therefore project  $L$  and  $S$  onto  $J$  and project onto  $z$ -axis =>

$$\hat{\mu} = - \left\langle \left| \hat{L} \right| \cos \theta_1 \frac{\hat{J}}{|\hat{J}|} + 2 \left| \hat{S} \right| \cos \theta_2 \frac{\hat{J}}{|\hat{J}|} \right\rangle \frac{\mu_B}{\hbar}$$



# Anomalous Zeeman effect

The angles  $\theta_1$  and  $\theta_2$  can be calculated from the scalar products of the respective vectors:

$$\begin{aligned}\hat{L} \cdot \hat{J} &= |L| |J| \cos\theta_1 \\ \hat{S} \cdot \hat{J} &= |S| |J| \cos\theta_2\end{aligned}$$

which implies that

$$\hat{\mu} = - \left\langle \frac{\hat{L} \cdot \hat{J}}{|\hat{J}|^2} + 2 \frac{\hat{S} \cdot \hat{J}}{|\hat{J}|^2} \right\rangle \frac{\mu_B}{\hbar} \hat{J} \quad (1)$$

Now, using  $\hat{S} = \hat{J} - \hat{L}$  implies that  $\hat{S} \cdot \hat{S} = (\hat{J} - \hat{L}) \cdot (\hat{J} - \hat{L}) = \hat{J} \cdot \hat{J} + \hat{L} \cdot \hat{L} - 2\hat{L} \cdot \hat{J}$

therefore  $\hat{L} \cdot \hat{J} = (\hat{J} \cdot \hat{J} + \hat{L} \cdot \hat{L} - \hat{S} \cdot \hat{S})/2$

so that

$$\begin{aligned}\left\langle \frac{\hat{L} \cdot \hat{J}}{|\hat{J}|^2} \right\rangle &= \frac{[j(j+1) + l(l+1) - s(s+1)]\hbar^2/2}{j(j+1)\hbar^2} \\ &= \frac{[j(j+1) + l(l+1) - s(s+1)]}{2j(j+1)}\end{aligned}$$

Similarly,  $\hat{S} \cdot \hat{J} = (\hat{J} \cdot \hat{J} + \hat{S} \cdot \hat{S} - \hat{L} \cdot \hat{L})/2$  and  $\left\langle \frac{\hat{S} \cdot \hat{J}}{|\hat{J}|^2} \right\rangle = \frac{[j(j+1) + s(s+1) - l(l+1)]}{2j(j+1)}$

# Anomalous Zeeman effect

We can therefore write Eqn. 1 as

$$\hat{\mu} = - \left( \frac{[j(j+1) + l(l+1) - s(s+1)]}{2j(j+1)} - 2 \frac{[j(j+1) + s(s+1) - l(l+1)]}{2j(j+1)} \right) \frac{\mu_B}{\hbar} \hat{j}$$

This can be written in the form

$$\hat{\mu} = -g_j \frac{\mu_B}{\hbar} \hat{j}$$

where  $g_j$  is the *Lande g-factor* given by

$$g_j = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

This implies that  $\mu_z = -g_j \mu_B m_j$

and hence the interaction energy with the  $B$ -field is

$$\Delta E = -\mu_z B_z = g_j \mu_B B_z m_j$$

Classical theory predicts that  $g_j = 1$ . Departure from this due to spin in quantum picture.



# Anomalous Zeeman effect spectra

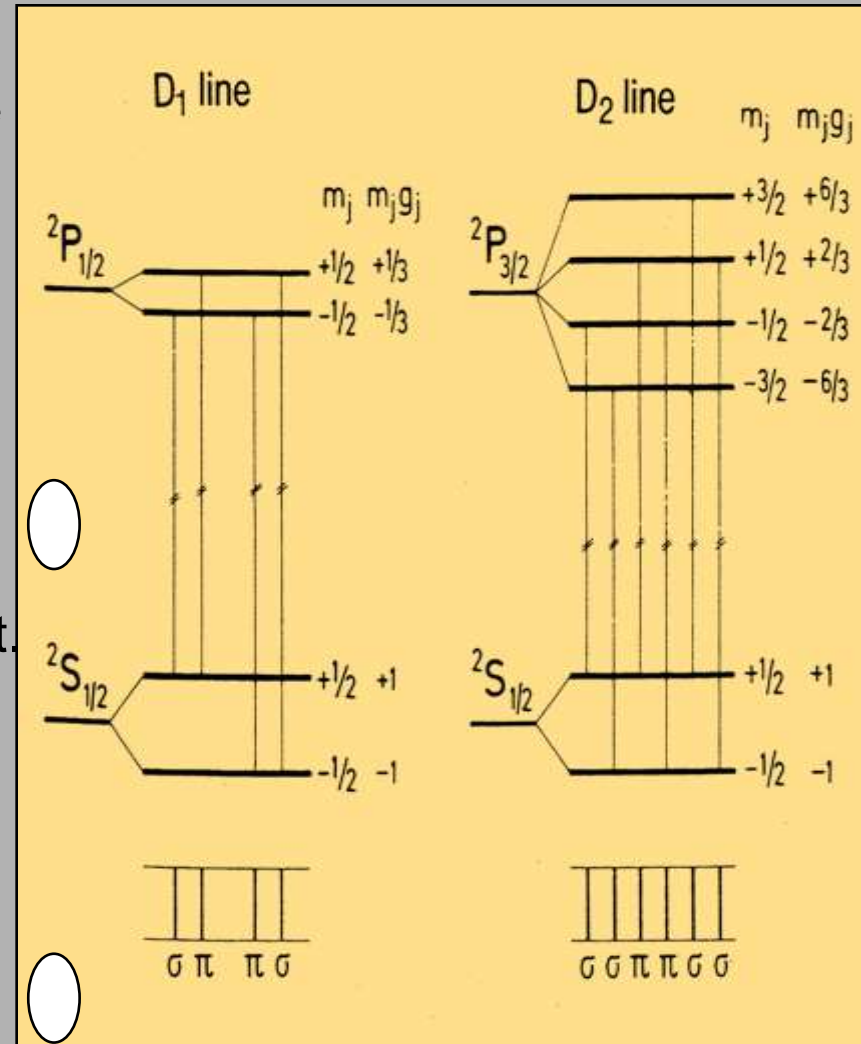
Spectra can be understood by applying the selection rules for  $J$  and  $m_j$ :

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

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

Polarizations of the transitions follow the same patterns as for normal Zeeman effect.

For example, consider the Na D-lines at right produced by  $3p \rightarrow 3s$  transition.

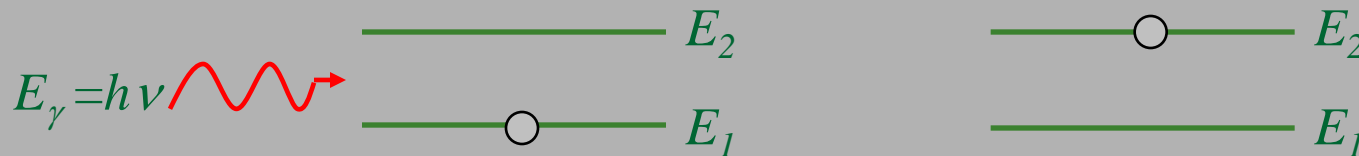


# Emission/Absorption of Radiation by Atoms

Emission/absorption lines are due to *radiative transitions*:

1. **Radiative (or Stimulated) absorption:**

Photon with energy ( $E_\gamma = h\nu = E_2 - E_1$ ) excites electron from lower *energy level*.



Can only occur if  $E_\gamma = h\nu = E_2 - E_1$

2. **Radiative recombination/emission:**

Electron makes transition to lower energy level and emits photon with energy

$$h\nu' = E_2 - E_1.$$

# Emission/Absorption of Radiation by Atoms

Radiative recombination can be either:

**Spontaneous emission:** Electron minimizes its total energy by emitting photon and making transition from  $E_2$  to  $E_1$ .



Emitted photon has energy  $E_\gamma' = h\nu' = E_2 - E_1$

**Stimulated emission:** If photon is strongly coupled with electron, cause electron to decay to lower energy level, releasing a photon of the same energy.



Can only occur if  $E_\gamma = h\nu = E_2 - E_1$  Also,  $h\nu' = h\nu$

# Selection Rules

We can use the wave functions to calculate transition probabilities for the electron to change from one state to another.

The probability is proportional to the mag square of the dipole moment:

$$\langle \vec{d} \rangle = \int \Psi_f^* e\vec{r} \Psi_i$$

where  $\Psi_i$  and  $\Psi_f$  are the initial and final states of the transition.

## Allowed transitions:

Electrons absorbing or emitting photons can change states when  $\Delta\ell = \pm 1$  and  $\Delta m_\ell = 0, \pm 1$ .

## Forbidden transitions:

Other transitions are possible but occur with much smaller probabilities.

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

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

$$\Delta m_\ell = 0, \pm 1$$

# Pauli Exclusion Principle

- ⑩ According to the quantum theory, two electrons in an atom can never be in the same quantum state at the same time.
- ⑩ This rule is known as the **Pauli exclusion principle** after Wolfgang Pauli, the physicist who discovered it.
- ⑩ Once all the quantum states in the first level are occupied by electrons, the next electron has to go into a higher energy level.

# Pauli principle

The total wave function must be antisymmetric under the interchange of any pair of identical fermions and symmetrical under the interchange of any pair of identical bosons.

Fermions:  $\psi(\mathbf{x}_1, \mathbf{x}_1) = \varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_1) - \varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_1) = 0$

**→ No two fermions can occupy the same state.**

- ⑩ There are symmetric and antisymmetric spatial wavefunctions which go with the anti and sym spin functions. Note a,b are the spatial quantum numbers n,l,m but not spin

$$\psi_{space}(sym) = \frac{1}{\sqrt{2}} (\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1))$$

$$\psi_{space}(asym) = \frac{1}{\sqrt{2}} (\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1))$$

- ⑩ when the two electrons are close to each other, the antisymmetric state is suppressed (goes to 0 if exactly the same point). Likewise the symmetric state is enhanced
- ⑩ → “Exchange Force” S=1 spin state has the electrons (on average) further apart (as antisymmetric space). So smaller repulsive potential and so lower energy
- ⑩ note if a=b, same space state, must have S=1 (“prove” Pauli exclusion)