The Hydrogen Atom

Thornton and Rex, Ch. 7

Applying Schrodinger's Eqn to the Hydrogen Atom

The potential: $V(r) = \frac{-1}{4\pi\varepsilon_0}\frac{e^2}{r}$

Use spherical polar coordinates
(with $\psi(x,y,z) \Rightarrow \psi(r,\theta,\phi)$):

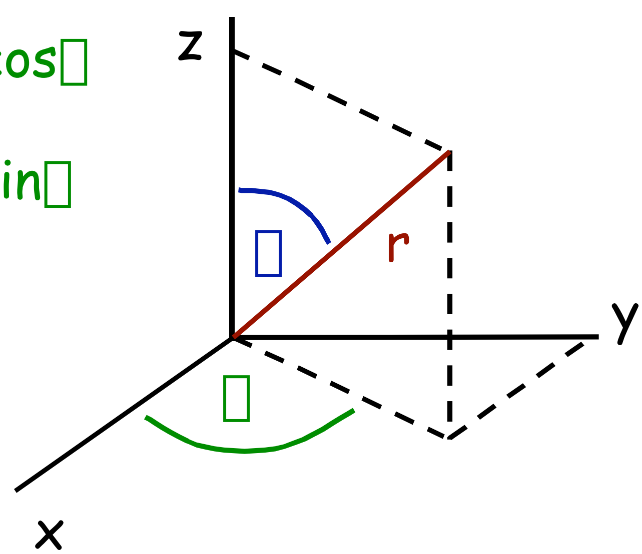
$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial \psi}{\partial \theta}\right)$$

$$+ \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2}(E-V)\,\psi = 0$$

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

$y = r \sin\theta \sin\phi$

$z = r \cos\theta$



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

$\theta = \cos^{-1}(z/r)$
Polar Angle

$\phi = \tan^{-1}(y/x)$
Azimuthal Angle

$\psi(r,\theta,\phi)$ is separable:

$\Rightarrow \quad \psi(r,\theta,\phi) = R(r)\, f(\theta)\, g(\phi)$

Substitute this into S Eqn and apply appropriate boundary conditions to R, f, g.

$\Rightarrow$ 3 separate equations and 3 quantum numbers. (For more, see section 7.2.)

$$\frac{d^2 g}{d\phi^2} = -m_\ell^2\, g$$

Azimuthal Eqn.

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2m}{\hbar^2}\left(E - V - \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right)R = 0$$

Radial Eqn.

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

Angular Eqn.

m_ℓ and ℓ are quantum numbers.

The Radial Equation

The Radial Equation is
the Associated Laguerre Equation.

We will find the ground-state solution.
Require $m_\ell = 0$, $\ell = 0$.

$$\Rightarrow \quad \frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2m}{\hbar^2}(E-V)R = 0$$

Substitute $V = -e^2/(4\pi\varepsilon_0 r)$ and
insert a trial solution:

$$R = A\, e^{-r/a_0}$$

This works if

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m e^2} \qquad \text{(Bohr Radius)}$$

and $E = -\hbar^2/(2ma_0^2) = -E_0 = -13.6\ \text{eV}$

Higher order solutions can be found in terms of associated Laguerre functions.

They are labeled by a quantum number n
(called the principal quantum number).

Energies are

$$E = - E_0 / n^2$$

(just like the Bohr prediction.)

Angular and Azimuthal Equations

The azimuthal equation is just a SHO equation with solution $g = A\, e^{im\phi}$.

Single-valuedness requires $g(\phi) = g(\phi + 2\pi)$.

$\Rightarrow$ m_ℓ is an integer.

The angular equation is the Associated Legendre Equation.

It is customary to combine the θ and ϕ solutions together as Spherical Harmonics $Y(\theta,\phi)$

The quantum numbers satisfy

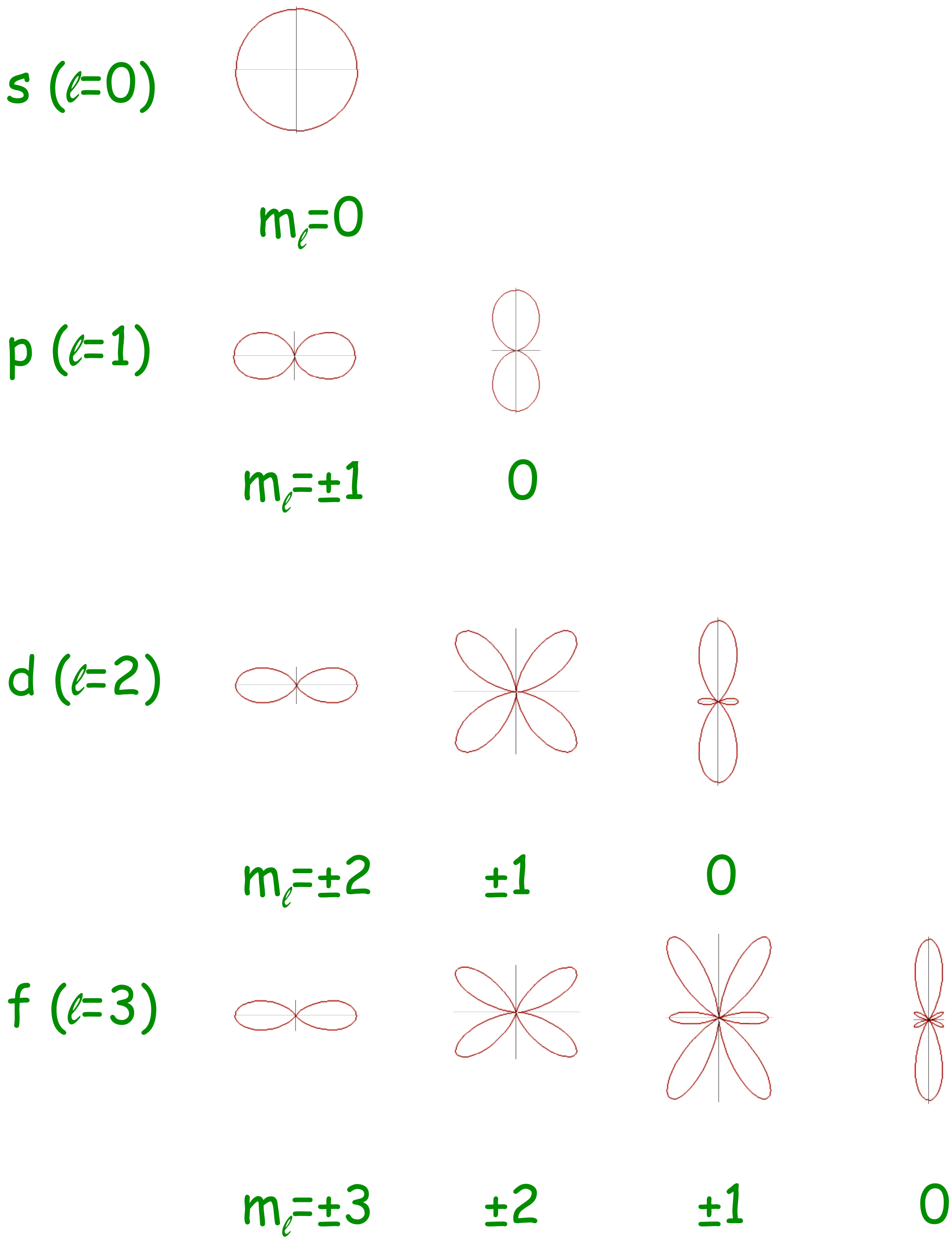
$$\ell = 0, 1, 2, 3, \ldots$$

and

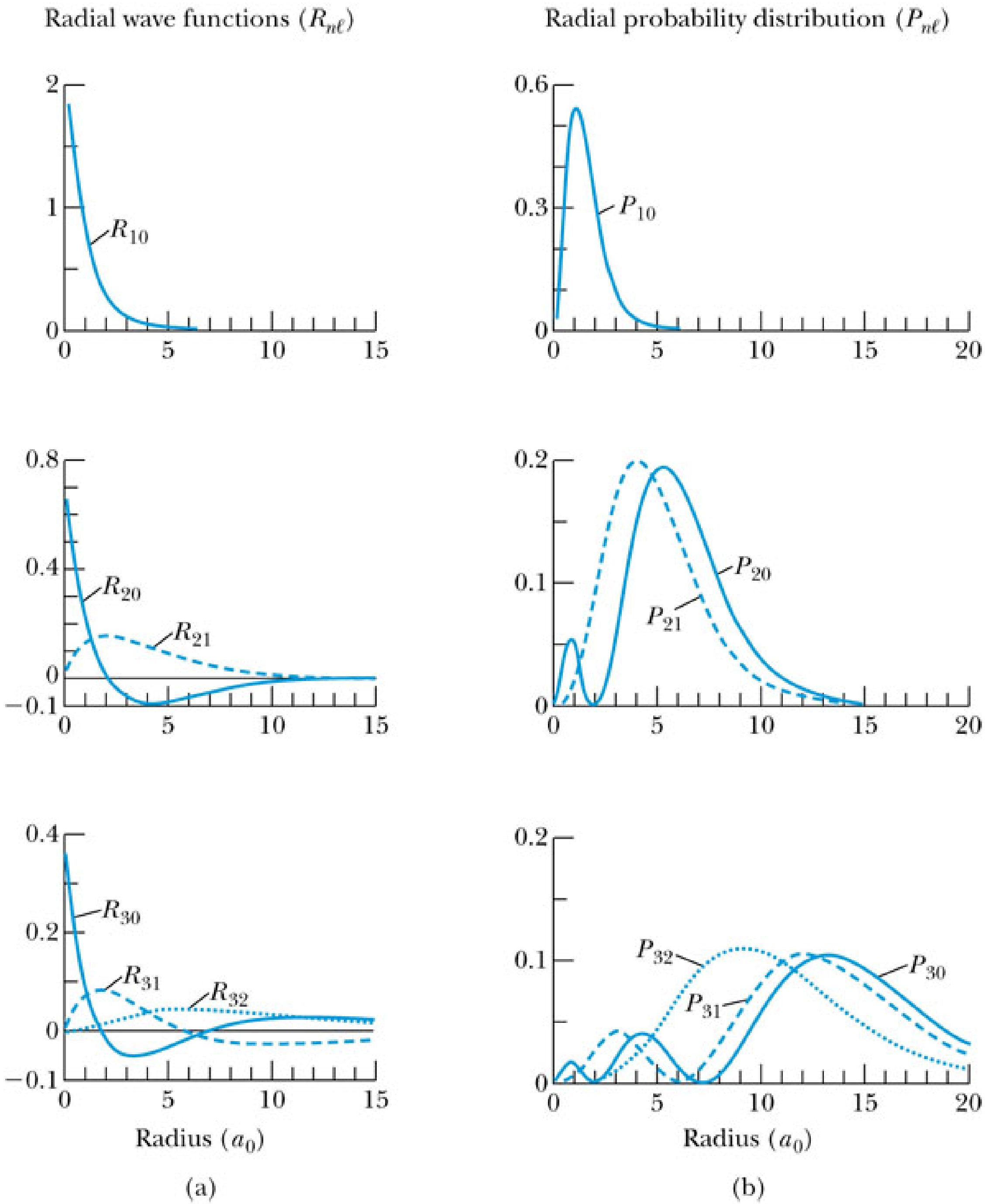
$$m_\ell = -\ell, -\ell+1, -\ell+2, \ldots, 0, \ldots, \ell-1, \ell$$

(They also satisfy $\ell < n$.)

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

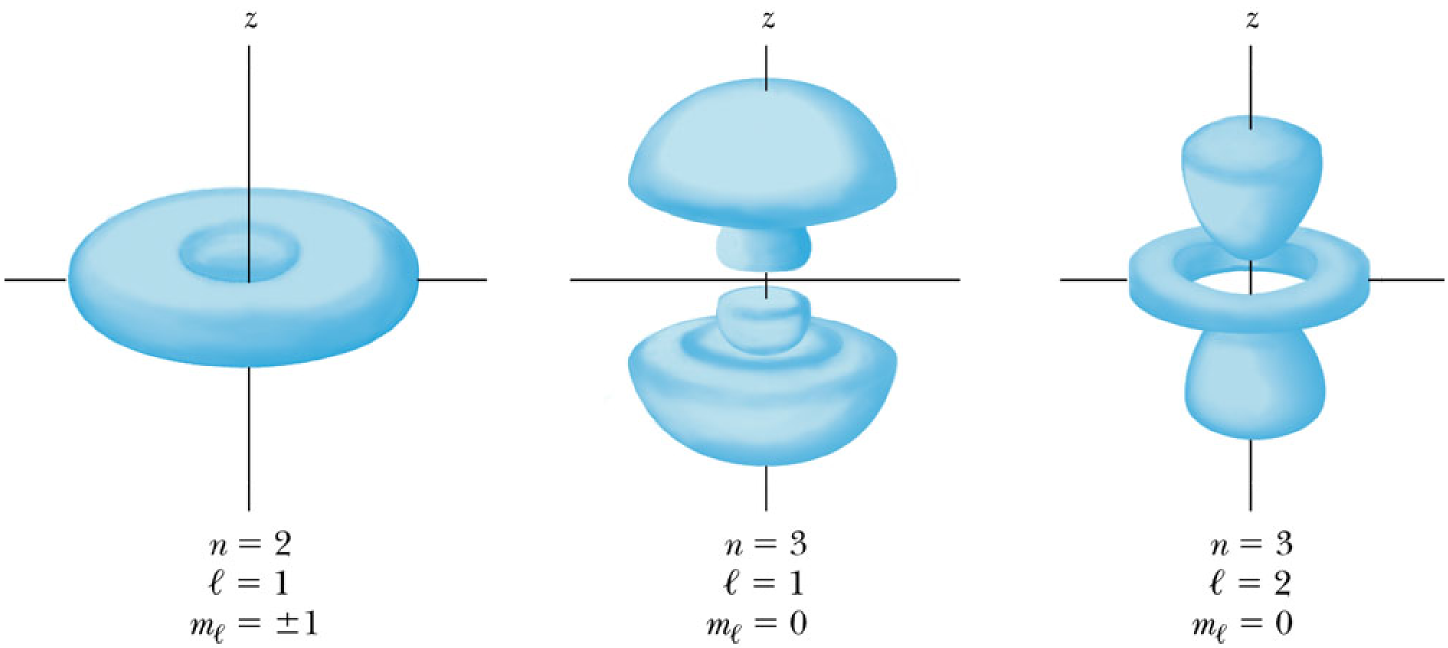


$R_{n\ell}$ and $P(r) = r^2 |R^2|$



Larger n peaks at larger r

P(x,y,z) from $r^2|R^2Y^*Y|$



No φ (x-y plane) dependence, only θ (angle from z axis)

in these basis functions since φ cancels in $|Y^*Y|$

Atomic Quantum Numbers

n Principal Quantum Number

ℓ Orbital Angular Momentum Quantum Number

m_ℓ Magnetic Quantum Number

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

$\ell = 0, 1, 2, 3, \ldots$

$m_\ell = -\ell, -\ell+1, -\ell+2, \ldots, 0, \ldots, \ell-1, \ell$

In summary:

$n > 0$

$\ell < n$

$|m_\ell| \leq \ell$

Angular Momentum

Angular momentum of electron in the atom:

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

(Note that this disagrees with Bohr's original guess of $L = n\hbar$.)

For a given n, the energy is $E_n = -E_0/n^2$ independent of ℓ.
The different ℓ states are degenerate.

Historical Notation:

$\ell =$	0	1	2	3	4	5
	↑	↑	↑	↑	↑	↑
	s	p	d	f	g	h

States are usually labeled by the n number and the ℓ letter.

For example: $n=3$, $\ell=1$ ⟶ 3p state.

Magnetic Quantum Number

ℓ determines the total angular momentum:

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

m_ℓ gives the z component of L:

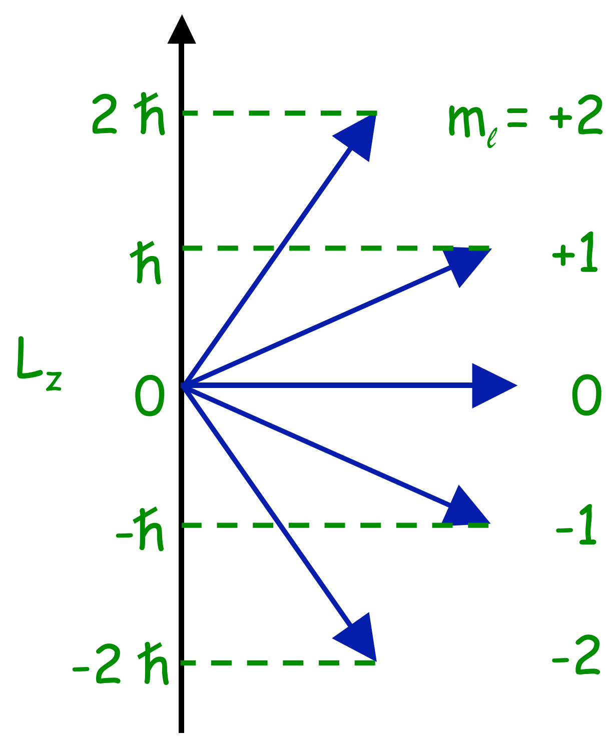
$$L_z = m_\ell \hbar$$

Direction of $\vec{L}$ can never lie on z axis:

$m_\ell < \sqrt{\ell(\ell+1)}$ always.

An example
for $\ell = 2$

□ $L = \sqrt{6}\ \hbar$

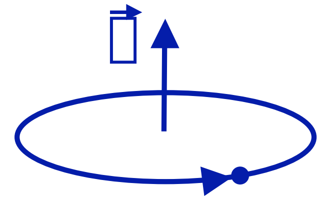


The choice of direction for the z axis is completely arbitrary.

L_x and L_y are undetermined, except for

$$L_x^2 + L_y^2 = L^2 - L_z^2$$

Magnetic Effects



An electron orbiting around a nucleus has magnetic moment $\vec{\mu}$:

$$\vec{\mu} = IA\,\hat{n} = \frac{-e}{(2\pi r/v)}(\pi r^2)\,\hat{n} = \frac{-erv}{2}\,\hat{n} = \frac{-e}{2m}\vec{L}$$

The component in the z direction is:

$$\mu_z = \frac{-e}{2m}L_z = \frac{-e}{2m}m_\ell \hbar = -m_\ell \mu_B$$

where $\mu_B = e\hbar/2m$
$= 9.274\times10^{-24}\,\mathrm{J/T}$
$= 5.788\times10^{-5}\,\mathrm{eV/T}$
is the Bohr magneton.

In an external magnetic field, $\vec{B}$, the magnetic dipole feels a torque:

$$\vec{\tau} = \vec{\mu} \times \vec{B}$$

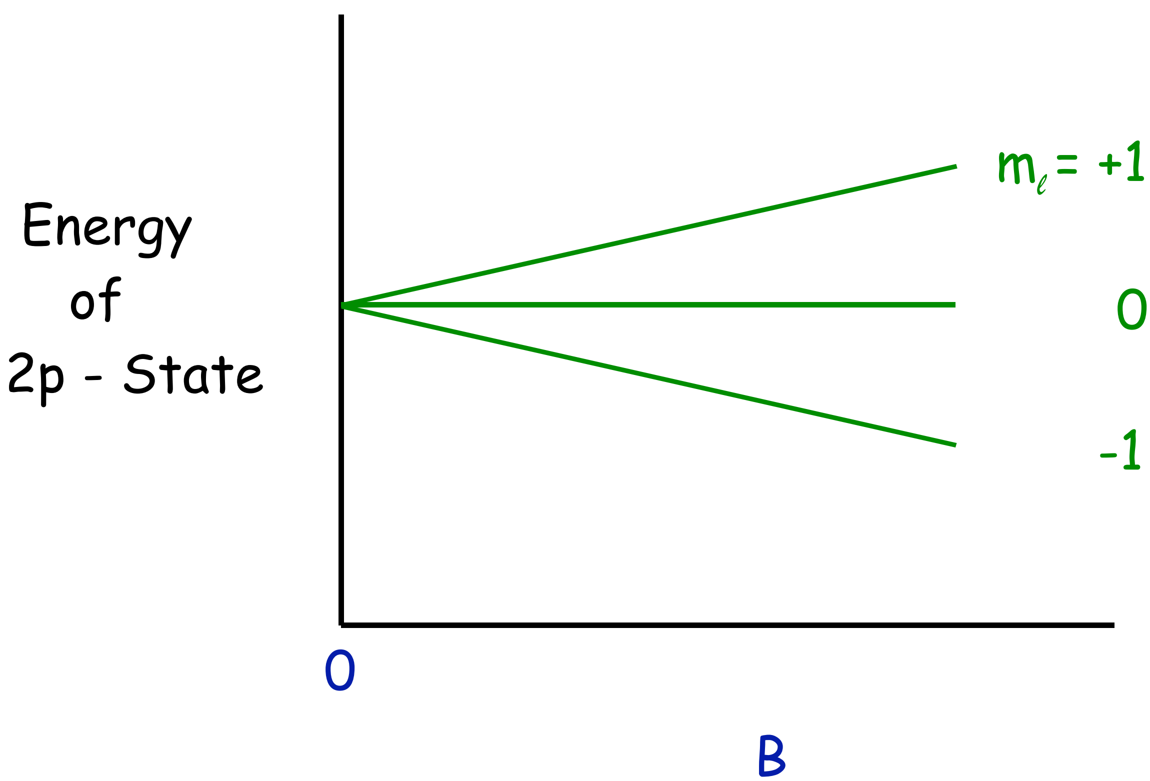
and has a potential energy: $V_B = -\vec{\mu}\cdot\vec{B}$

If $\vec{B}$ is in the z direction then

$$V_B = -\mu_z B = +m_\ell \mu_B B$$

The energies for different m_ℓ, which were degenerate for $B=0$, are now separated into $2\ell+1$ different levels.

This is called the Normal Zeeman Effect.



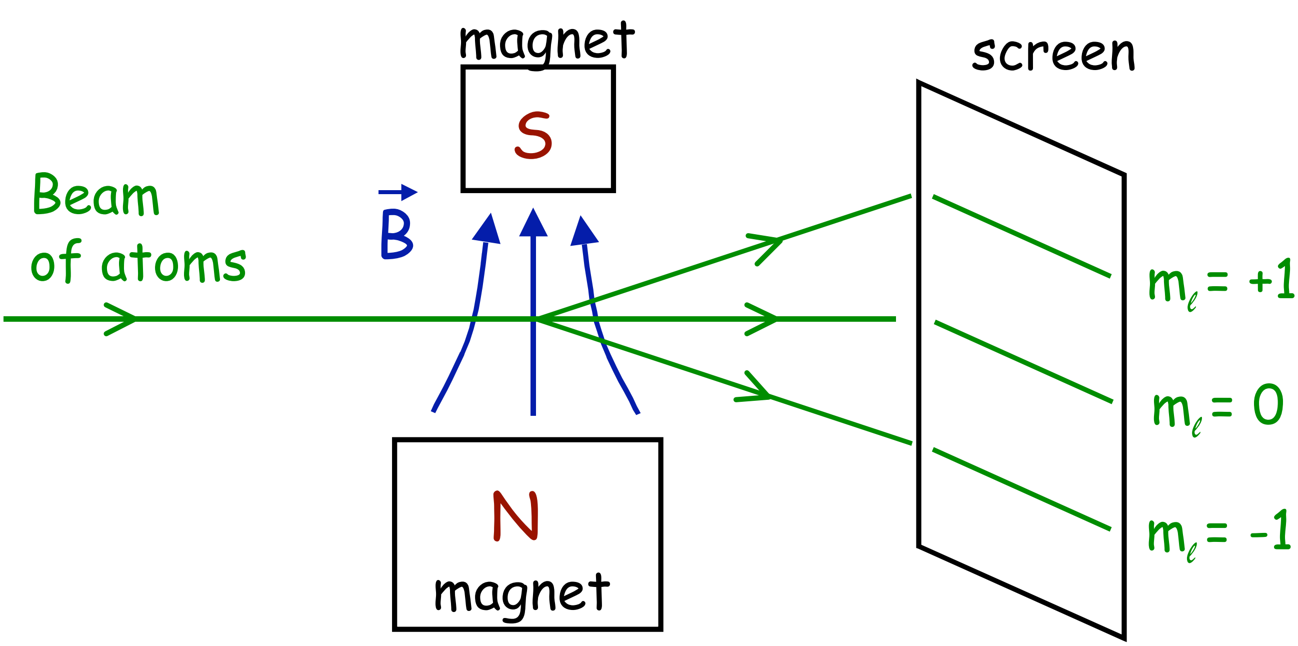
The Stern-Gerlach Experiment

In the presence of an inhomogeneous magnetic field, there will be a net force on the atoms, depending on m_ℓ :

$$F_z = -\frac{d\,V_B}{d\,z} = m_\ell \mu_B \frac{d\,B}{d\,z}$$

i.e.	In the +z direction	for $+m_\ell$
	No force	for $m_\ell=0$
	In the -z direction	for $-m_\ell$

Thus, one could split the atoms according to the quantum number m_ℓ :



Electron Spin

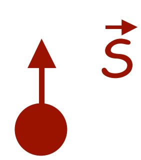
1922 - Stern and Gerlach did their experiment. The atoms split into two beams.

But the number of m_ℓ values is always odd: $(2\ell + 1)$!

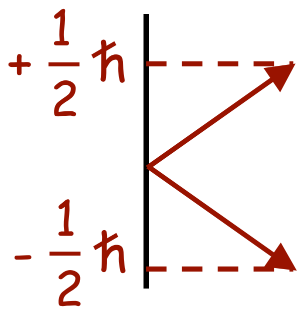
1925 - Goudsmit and Uhlenbeck proposed that the electron had an intrinsic spin and an intrinsic magnetic moment.

In analogy with orbital angular momentum they proposed a magnetic spin quantum number:

$$m_s = \pm 1/2$$



The electron's spin can either be oriented "up" or "down":



The total spin quantum number is s = 1/2:

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

$$\vec{\mu}_S = \frac{-e}{m}\vec{S} = -\,[\,2\,]\,\frac{\mu_B}{\hbar}\,\vec{S}$$

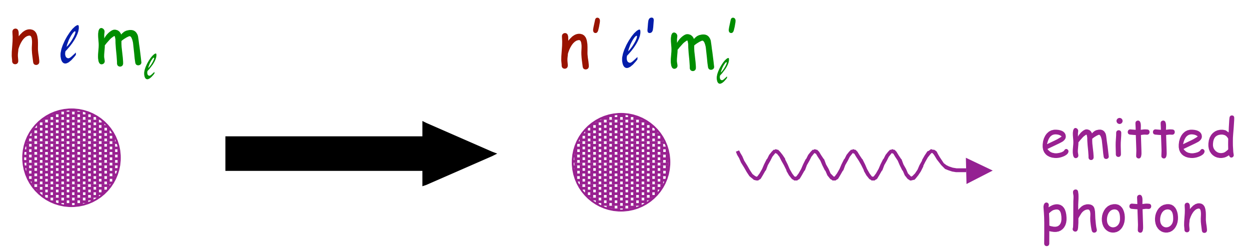
Compare with:

$$\vec{\mu}_L = \frac{-e}{2m}\vec{L} = -\,[\,1\,]\,\frac{\mu_B}{\hbar}\,\vec{L}$$

[*] are called gyromagnetic ratios:

$$g_s = 2 \qquad\qquad g_\ell = 1$$

Selection Rules



Allowed transitions:

- lifetimes $\tau \sim 10^{-9}$ sec

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

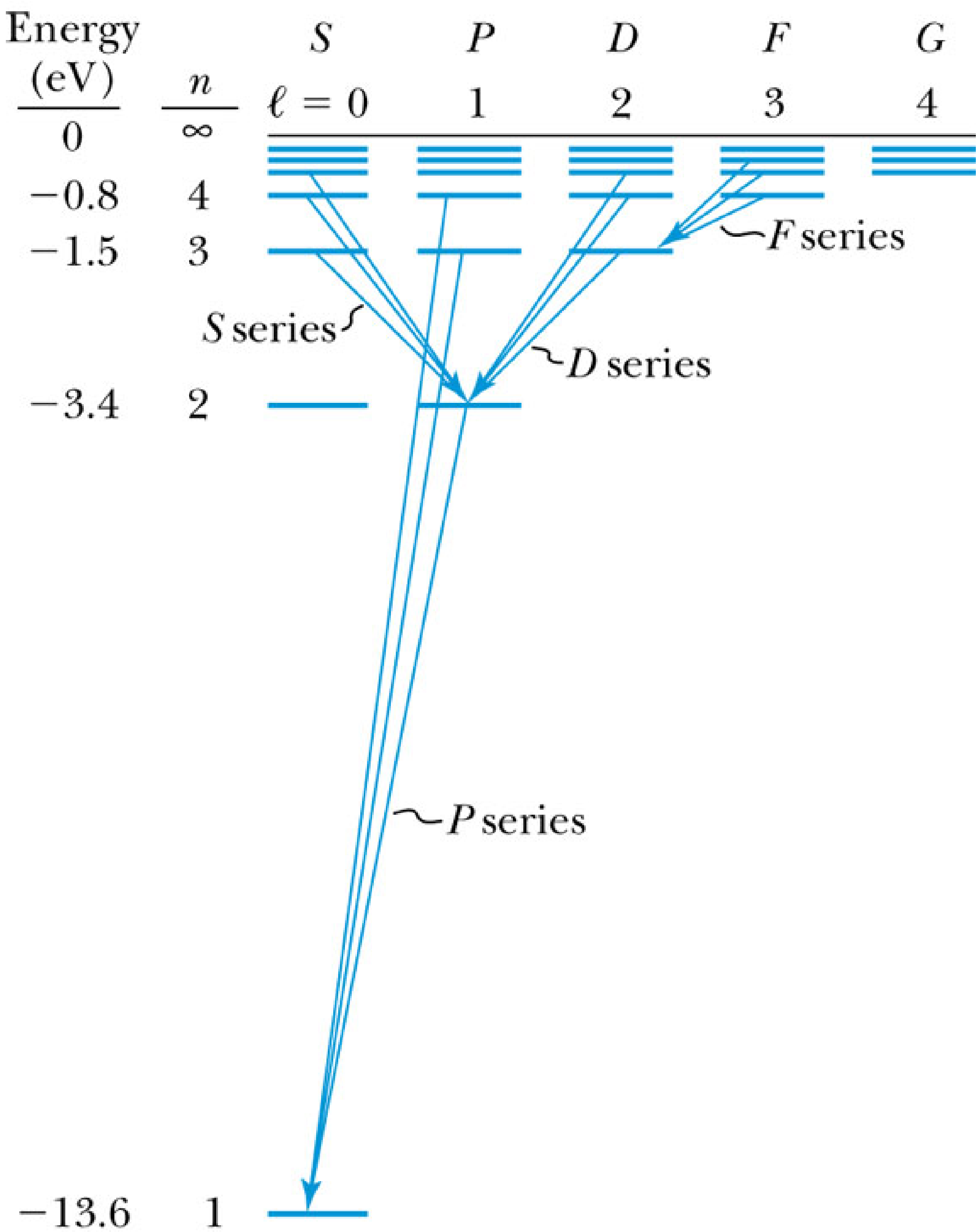
Forbidden transitions:

- lifetimes much longer

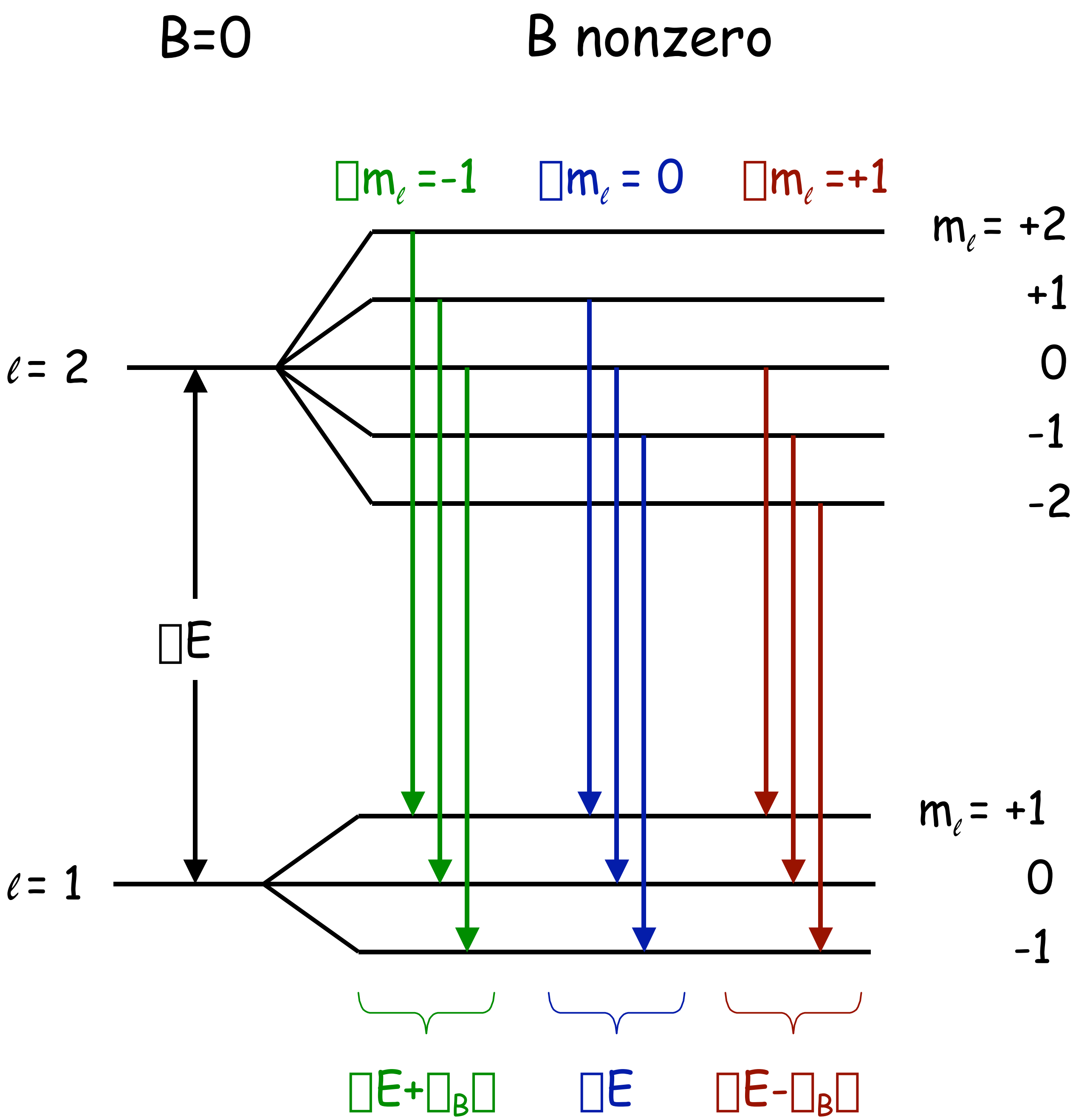
Ex. 2s $\rightarrow$ 1s, $\tau \sim 1/7$ sec

With no External B, E depends on n only

Allowed transitions must change the l quantum number



Selection Rules and Normal Zeeman Effect



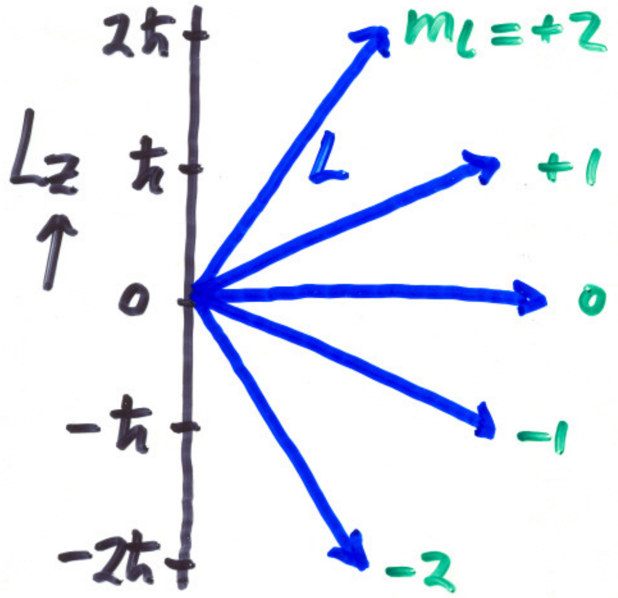
B field always splits spectral lines into 3 for normal Zeeman effect.

7.14 FOR A 3d STATE DRAW ALL THE POSSIBLE ORIENTATIONS OF THE ANGULAR MOMENTUM VECTOR $\vec{L}$. WHAT IS $L_x^2 + L_y^2$ FOR THE $m_\ell = -1$ COMPONENT?

3d $\Rightarrow$ $\ell = 2$

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

POSSIBLE VALUES OF $m_\ell = -2 \quad -1 \quad 0 \quad +1 \quad +2$
WITH $L_z = m_\ell \hbar$



FOR $m_\ell = -1 \Rightarrow L_z = -\hbar$

$L^2 = L_x^2 + L_y^2 + L_z^2$

$\therefore 6\hbar^2 = L_x^2 + L_y^2 + \hbar^2$

$\therefore L_x^2 + L_y^2 = \boxed{5\hbar^2}$

7.25 A HYDROGEN ATOM IN A 5f STATE IS IN A MAGNETIC FIELD OF 3T. WHAT IS THE ENERGY IN THE ABSENCE OF THE MAG. FIELD? HOW MANY STATES ARE THERE, AND WHAT ARE THEIR ENERGIES IN THE MAG. FIELD?

$n = 5 \qquad l = 3 \qquad m_l = 0, \pm 1, \pm 2, \pm 3$

$$E_5 = \frac{-13.6}{25} = -0.544 \text{ eV}$$

$$V_B = m_l B \mu_B = m_l \cdot 3 \cdot 5.79E{-5} \text{ eV/T}$$

$\Rightarrow$ $= 0$ FOR $m_l = 0$

$= \pm 1.74E{-4}$ eV FOR $m_l = \pm 1$

$= \pm 3.47E{-4}$ eV FOR $m_l = \pm 2$

$= \pm 5.21E{-4}$ eV FOR $m_l = \pm 3$