Quantum Numbers
(and their meaning)

Solution of the Schrödinger equation for the Hydrogen atom

$$\psi_{n\ell m_\ell}(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m_\ell}(\theta,\phi)$$

- The three quantum numbers:
  - n Principal quantum number
  - ℓ Orbital angular momentum quantum number
  - m_ℓ Magnetic quantum number
- The boundary conditions:
  - $n = 1, 2, 3, 4, . . .$ Integer
  - $\ell = 0, 1, 2, 3, . . . , n - 1$ Integer
  - $m_\ell = -\ell, -\ell + 1, . . . , 0, 1, . . . , \ell - 1, \ell$ Integer
- The restrictions for quantum numbers:
  - $n > 0$
  - $\ell < n$
  - $|m_\ell| \leq \ell$

Principal Quantum Number n

- In the hydrogen atom, this is the number of the Bohr orbit (n=1,2,3… no upper limit)
- Associated with the solution of R(r)
- Quantized energy: $E_n = \frac{-\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2 \frac{1}{n^2} = -\frac{E_0}{n^2}$
- (-) sign: proton-electron system bound

Orbital (Quantum Momentum) quantum number ℓ

- Associated with the solutions of R(r) and f(θ)
  - Boundary Conditions: ℓ = 0,1,…, n-1

- Classical Orbital Momentum: $\vec{L} = \vec{r} \times \vec{p}$

- Quantum Orbital Momentum: $L = \sqrt{\ell(\ell+1)}\hbar$

- ℓ = 0 state → L = 0

This disagrees with Bohr's semiclassical "planetary" model of electrons orbiting a nucleus $L = n\hbar$.

More on quantum number ℓ

- Energy is independent of the quantum number ℓ, we say the energy level is degenerate with respect to ℓ. Note: only true for the Hydrogen atom.

- States:
  - ℓ = 0 1 2 3 4 5 …
  - Letter s p d f g h …

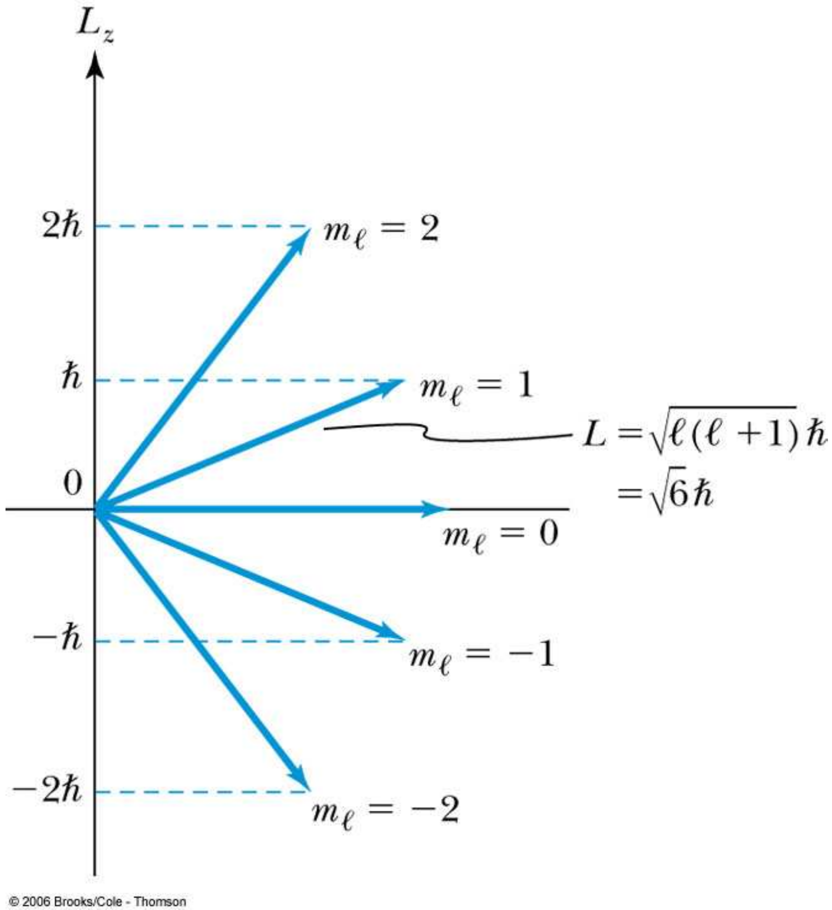
ℓ =	0	1	2	3	4	5	…
Letter	s (sharp)	p (principal)	d (diffuse)	f (fundamental)	g	h	…

- Atomic states are referred to by their n and ℓ.
- A state with $n = 2$ and $\ell = 1$ is called a $2p$ state.
- The boundary conditions require $n > \ell$.

The Magnetic quantum number m_ℓ

- The angle ϕ is a measure of the rotation about the z axis.
- The solution for $g(\phi)$ specifies that m_ℓ is an integer and related to the z component of $\vec{L}$:

$$L_z = m_\ell \hbar$$



- The relationship of L, L_z, ℓ, and m_ℓ for $\ell = 2$.
- $L = \sqrt{\ell(\ell+1)}\hbar = \sqrt{6}\hbar$ is fixed because L_z is quantized.
- Only certain orientations of $\vec{L}$ are possible and this is called **space quantization**.

Note: One cannot know L exactly, this would violate the uncertainty principle.

Intrinsic Spin m_s

- Samuel Goudsmit and George Uhlenbeck in Holland proposed that *the electron must have an intrinsic angular momentum* and therefore a magnetic moment (1925)

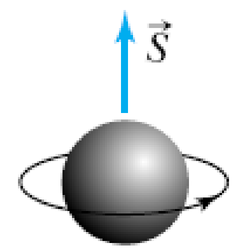
- Paul Ehrenfest showed that the surface of the spinning electron should be moving faster than the speed of light!

- In order to explain experimental data, Goudsmit and Uhlenbeck proposed that the electron must have an **intrinsic spin quantum number** $s = ½$. [Number of possible values: $2s+1 = 2 \rightarrow m_s=-½$ or $m_s=½$]

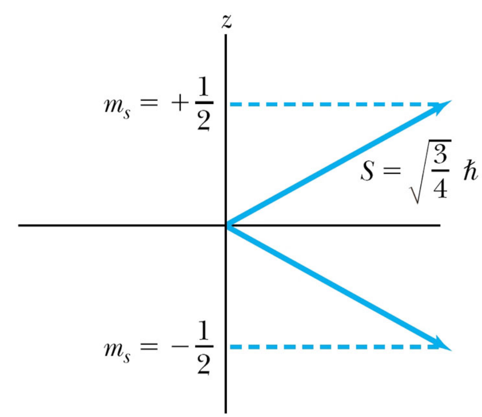
Intrinsic Spin m_s

- Does not appear from the solutions of the Schrödinger equation
- Appears when solving the problem in a relativistic way

- For the electron: $m_s = +½$ or $m_s = -½$



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



Understood ?

(a) If the principal quantum number n for a certain electronic state is equal to 3, what are the possible values of the orbital (angular momentum) quantum number ℓ?

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

(b) If the orbital quantum number ℓ for a certain electronic state is equal to 2, what are the possible values for the magnetic quantum number m_ℓ?

$$m_\ell = -\ell,-(\ell-1),\ldots,\ell-1,\ell \rightarrow m_\ell = -2,-1,0,1,2$$

(c) How many distinct electronic states are there with n=2?

(n,ℓ,m_ℓ,m_s):		
	(2,0,0,-½)	(2,0,0,½)
	(2,1,-1,-½)	(2,1,-1, ½)
	(2,1,0,-½)	(2,1,0, ½)
	(2,1,1,-½)	(2,1,1, ½)

Atomic Fine Structure

- Experimentally: By the 1920s, a fine structure in the spectra lines of Hydrogen and other atoms has been observed. Spectra lines appeared to be split in the presence of an external magnetic field.

INTERPRETATION:

- Energy is independent of the quantum number ℓ

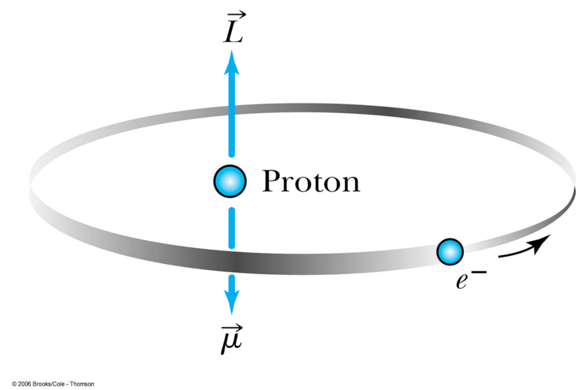
  → the energy level is degenerate with respect to ℓ

- Example: Considering n=2 and ℓ=1

  → m_ℓ = -1,0,1 e.g. 3 quantum states are degenerate at the same energy

  These 3 magnetic states would behave differently under a magnetic field resulting in the degeneracy being lifted !

Magnetic Moment



- Model:
  - electron circulating around the nucleus → Loop of current I = dq/dt = q/T
    - T, time it takes for the electron to make one rotation: T = 2πr/v
    - Introducing p = mv → T = 2πrm/p
  - Magnetic Moment induced: μ = IA = (qp/2πmr)(πr^2)
    - Simplification: μ = (q/2m)rp, introducing L=rp → μ = (q/2m)|$\vec{L}$|

Magnetic moment: $$\vec{\mu} = -\frac{e}{2m}\vec{L}$$

The (Normal) Zeeman Effect (I)

- Potential energy of the dipole created by the electron orbiting around the nucleus (under a magnetic field $\vec{B}$):

$$V_B = -\vec{\mu} \cdot \vec{B}$$

- One can only know one component of $\vec{L}$: ($L_z = m_\ell \hbar$)
- Along z, the magnetic moment becomes:

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

Bohr Magneton
$\mu_B = 9.274 \times 10^{-24}$ J/T

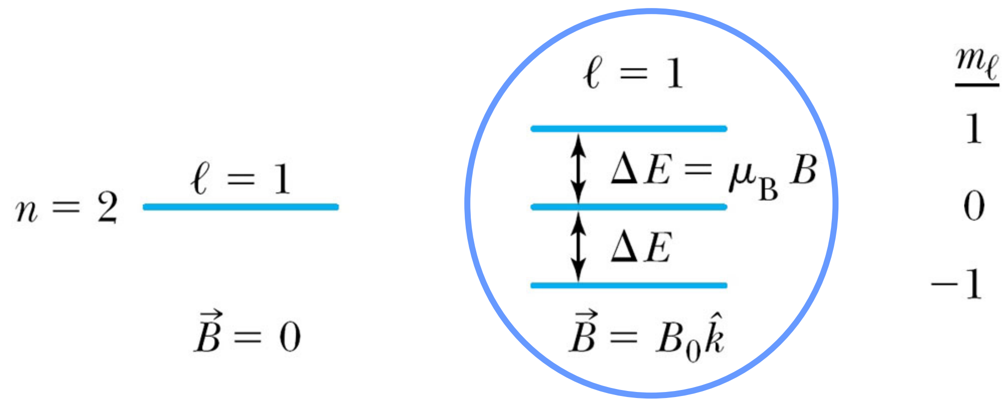
- Quantization: $V_B = -\mu_z B = +\mu_B m_\ell B$

The (Normal) Zeeman Effect (II)

- When a magnetic field is applied, the 2*p* level of atomic hydrogen is split into three different energy states with energy difference of $\Delta E = \mu_B B\, \Delta m_\ell$.

Potential energy of the dipole: $V_B = -\mu_z B = +\mu_B m_\ell B$

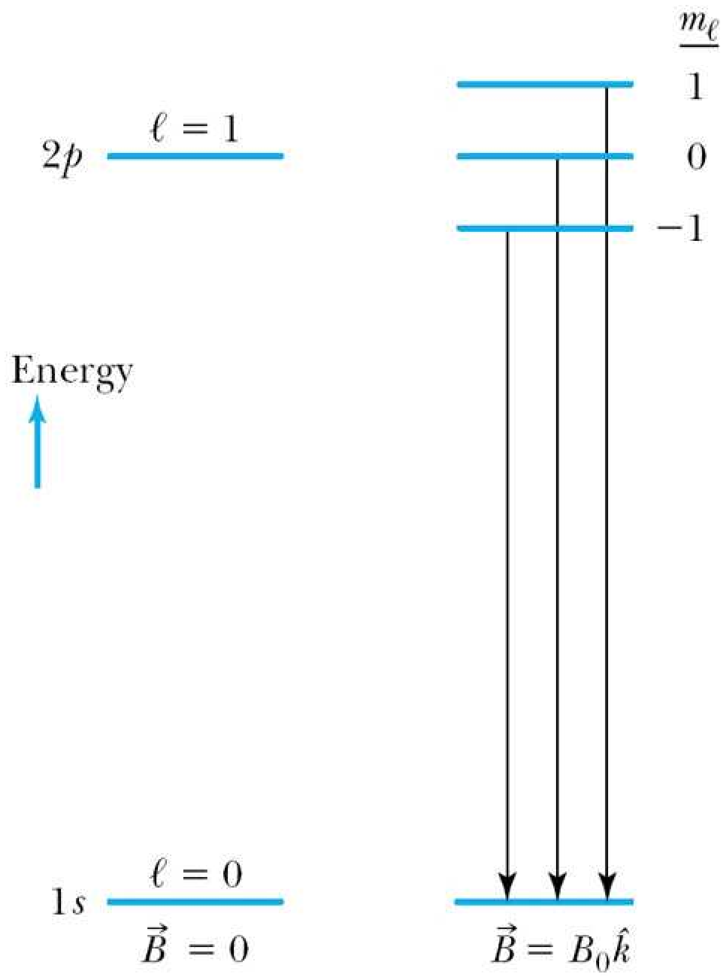
m_ℓ	Energy
1	$E_0 + \mu_B B$
0	E_0
−1	$E_0 - \mu_B B$



Fine Structure

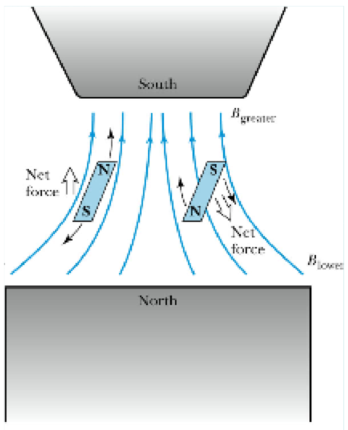
Fine Structure

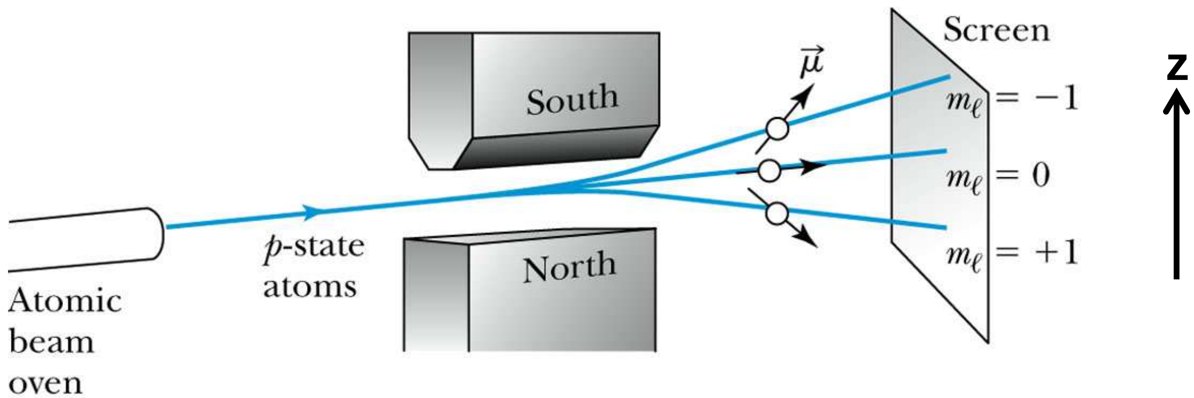
Transition 2p → 1s



Stern & Gerlach Experiment (1922)

- An atomic beam of particles in the $\ell = 1$ state pass through a magnetic field along the *z* direction.





$$V_B = -\mu_z B \qquad F_z = -(dV_B / dz) = \mu_z (dB / dz)$$

- The $m_\ell = +1$ state will be deflected down, the $m_\ell = -1$ state up, and the $m_\ell = 0$ state will be undeflected.
- If the space quantization were due to the magnetic quantum number m_ℓ, m_ℓ states is always odd $(2\ell + 1)$ and should produce odd number of lines → But it doesn't. Why?