PHYS 3313 – Section 001
Lecture #23

Tuesday, Apr. 16, 2014

Dr. Jaehoon Yu

- Schrodinger Equation for Hydrogen Atom
- Quantum Numbers
- Solutions to the Angular Equations
- Zeeman Effect
- Intrinsic Spin

Announcements

- Research paper deadline is Monday, Apr. 28
- Research presentation file deadline is Sunday, Apr. 27
- Reminder: Homework #5
  - CH6 end of chapter problems: 34, 39, 46, 62 and 65
  - Due Wednesday, Apr. 16
- Homework #6
  - CH7 end of chapter problems: 7, 8, 9, 12, 17 and 29
  - Due on Wednesday, Apr. 23, in class
- Quiz number 4
  - At the beginning of the class Wednesday, Apr. 23
  - Covers up to what we finish Monday, Apr. 21

Reminder: Special project #5

- Show that the Schrodinger equation becomes Newton’s second law in the classical limit. (15 points)
- Deadline Monday, Apr. 21, 2014
- You MUST have your own answers!

Quantum Numbers

- The full solution of the radial equation requires an introduction of a quantum number, n, which is a non-zero positive integer.
- The three quantum numbers:
  - n Principal quantum number
  - ℓ Orbital angular momentum quantum number
  - m_ℓ Magnetic quantum number
- The boundary conditions put restrictions on these
  - $n = 1, 2, 3, 4, . . .$ (n>0) Integer
  - $\ell = 0, 1, 2, 3, . . . , n - 1$ ($\ell < n$) Integer
  - $m_\ell = -\ell, -\ell + 1, . . . , 0, 1, . . . , \ell - 1, \ell$ ($|m_\ell| \le \ell$) Integer
- The predicted energy level is $E_n = -\frac{E_0}{n^2}$

Ex 7.3: Quantum Numbers & Degeneracy

What are the possible quantum numbers for the state n=4 in atomic hydrogen? How many degenerate states are there?

n	ℓ	m_ℓ
4	0	0
4	1	-1, 0, +1
4	2	-2, -1, 0, +1, +2
4	3	-3, -2, -1, 0, +1, +2, +3

The energy of a atomic hydrogen state is determined only by the primary quantum number, thus, all these quantum states, 1+3+5+7 = 16, are in the same energy state.

Thus, there are 16 degenerate states for the state n=4.

Hydrogen Atom Radial Wave Functions

- The radial solution is specified by the values of *n* and *ℓ*
- First few radial wave functions $R_{n\ell}$

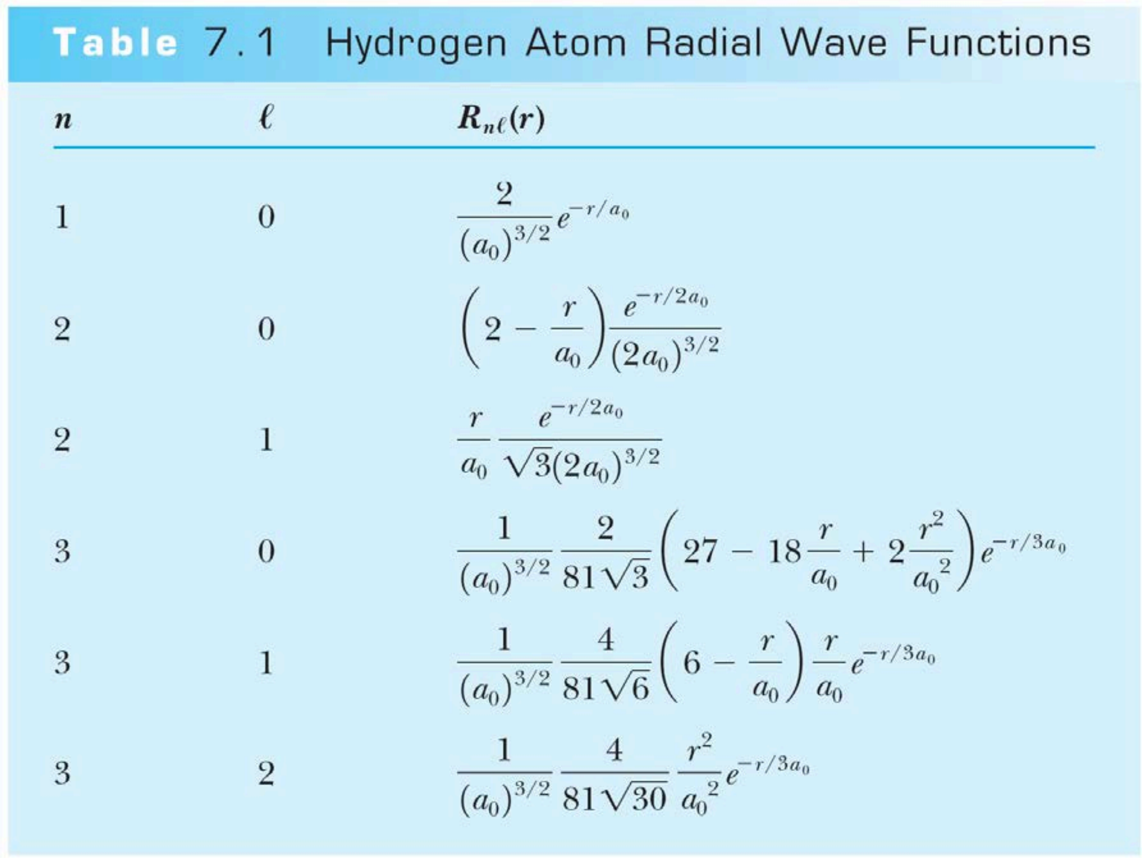


Table 7.1 Hydrogen Atom Radial Wave Functions

n	ℓ	$R_{n\ell}(r)$
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	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{30}} \frac{r^2}{a_0{}^2} e^{-r/3a_0}$

Solution of the Angular and Azimuthal Equations

- Solutions of the azimuthal eq. are $e^{im_l\phi}$ or $e^{-im_l\phi}$
- Solutions to the angular and azimuthal equations are linked because both have m_ℓ
- Group these solutions together into functions

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

---- spherical harmonics

Normalized Spherical Harmonics

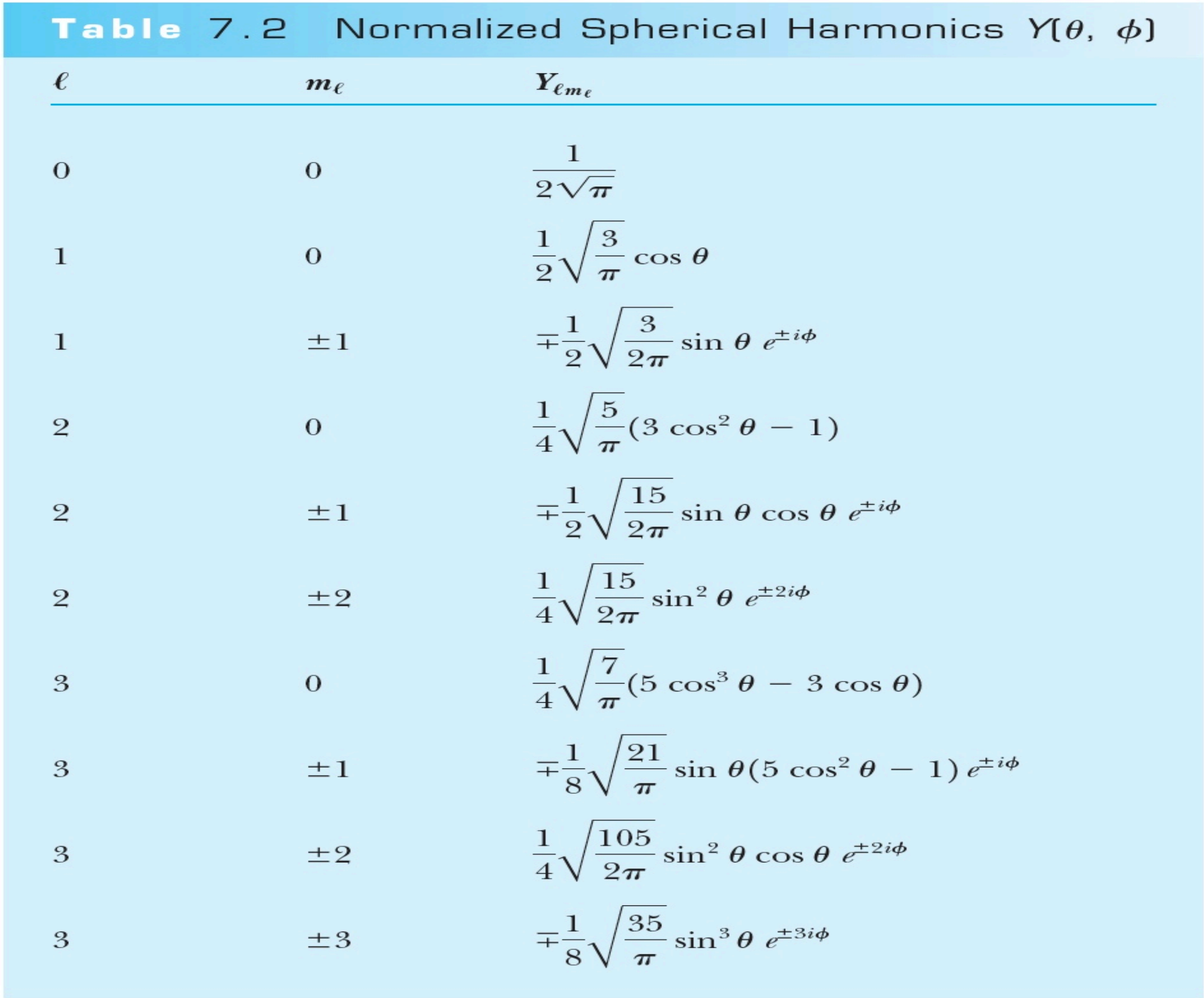


Table 7.2 Normalized Spherical Harmonics $Y(\theta, \phi)$

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

Ex 7.1: Spherical Harmonic Function

Show that the spherical harmonic function Y11(θ,ϕ) satisfies the angular Schrodinger equation.

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{df}{d\theta}\right)+\left[l(l+1)-\frac{m_l^2}{\sin^2\theta}\right]f=0$$

$$Y_{11}(\theta,\phi)=-\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{i\phi}=A\sin\theta$$

Inserting $l=1$ and $m_l=1$ into the angular Schrodinger equation, we obtain

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dY_{11}}{d\theta}\right)+\left[1(1+1)-\frac{1}{\sin^2\theta}\right]Y_{11}=\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dY_{11}}{d\theta}\right)+\left(2-\frac{1}{\sin^2\theta}\right)Y_{11}$$

$$=\frac{A}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\sin\theta}{d\theta}\right)+A\left(2-\frac{1}{\sin^2\theta}\right)\sin\theta=\frac{A}{\sin\theta}\frac{d}{d\theta}(\sin\theta\cos\theta)+A\left(2-\frac{1}{\sin^2\theta}\right)\sin\theta$$

$$=\frac{A}{\sin\theta}\frac{d}{d\theta}\left(\frac{1}{2}\sin 2\theta\right)+A\left(2-\frac{1}{\sin^2\theta}\right)\sin\theta=\frac{A}{\sin\theta}\cos 2\theta+A\left(2-\frac{1}{\sin^2\theta}\right)\sin\theta$$

$$=\frac{A}{\sin\theta}\left(1-2\sin^2\theta\right)+A\left(2-\frac{1}{\sin^2\theta}\right)\sin\theta=\frac{A}{\sin\theta}-2A\sin\theta+A\left(2-\frac{1}{\sin^2\theta}\right)\sin\theta=0$$

Solution of the Angular and Azimuthal Equations

- The radial wave function *R* and the spherical harmonics *Y* determine the probability density for the various quantum states.
- Thus the total wave function $\Psi(r,\theta,\phi)$ depends on *n*, ℓ, and m_ℓ. The wave function can be written as

$$\psi_{nlm_l}(r,\theta,\phi) = R_{nl}(r)\,Y_{lm_l}(\theta,\phi)$$

Orbital Angular Momentum Quantum Number ℓ

- It is associated with the $R(r)$ and $f(\theta)$ parts of the wave function.
- Classically, the orbital angular momentum $\vec{L} = \vec{r} \times \vec{p}$ with $L = mv_{\text{orbital}}r$.
- ℓ is related to the magnitude of L by $L = \sqrt{l(l+1)}\hbar$
- In an ℓ = 0 state, $L = \sqrt{0(1)}\hbar = 0$.

It disagrees with Bohr's semi-classical "planetary" model of electrons orbiting a nucleus $L = n\hbar$.

Orbital Angular Momentum Quantum Number ℓ

- A certain energy level is **degenerate** with respect to ℓ when the energy is independent of ℓ.
- Use letter names for the various ℓ values

– ℓ =	0	1	2	3	4	5 . . .
– Letter =	*s*	*p*	*d*	*f*	*g*	*h* . . .

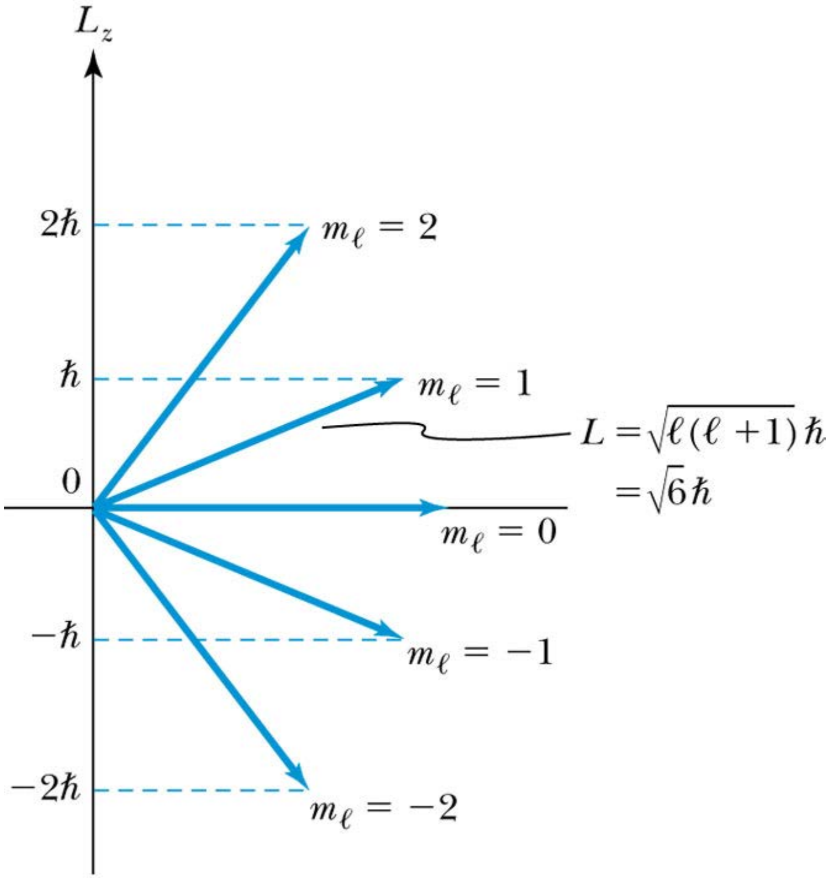
- Atomic states are referred by their n and ℓ
  - s=sharp, p=principal, d=diffuse, f =fundamental, then alphabetical
- A state with $n = 2$ and $\ell = 1$ is called the 2*p* state
  - Is 2d state possible?
- The boundary conditions require $n > \ell$

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 *L*.

$$L_z = m_l \hbar$$

- The relationship of *L*, L_z, ℓ, and m_ℓ for ℓ = 2.
- $L = \sqrt{l(l+1)}\hbar = \sqrt{6}\hbar$ is fixed.
- Because L_z is quantized, only certain orientations of $\vec{L}$ are possible and this is called **space quantization**.
- m_ℓ is called the magnetic moment since z axis is chosen customarily along the direction of magnetic field.



Magnetic Quantum Number m_ℓ

- Quantum mechanics allows $\vec{L}$ to be quantized along only one direction in space, and because of the relationship $L^2 = L_x^2 + L_y^2 + L_z^2$, once a second component is known, the third component will also be known. ➔ violation of uncertainty principle
  - One of the three components, such as L_z, can be known clearly but the other components will not be precisely known
- Now, since we know there is no preferred direction,

$$\langle L_x^2 \rangle = \langle L_y^2 \rangle = \langle L_z^2 \rangle$$

- We expect the average of the angular momentum components squared to be: $\langle L^2 \rangle = 3\langle L_z^2 \rangle = \dfrac{3}{2l+1}\sum_{m_l=-l}^{+l} m_l^2\hbar^2 = l(l+1)\hbar^2$

Magnetic Effects on Atomic Spectra—The Normal Zeeman Effect

- A Dutch physicist Pieter Zeeman showed as early as 1896 that the spectral lines emitted by atoms in a magnetic field split into multiple energy levels. It is called the Zeeman effect.

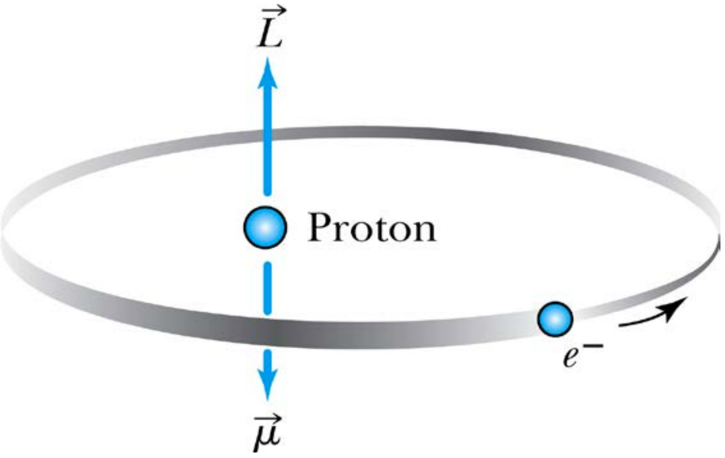
The Normal Zeeman effect:

- A spectral line of an atom is split into three lines.
- Consider the atom to behave like a small magnet.
- The current loop has a magnetic moment $\mu = IA$ and the period $T = 2\pi r / v$. If an electron can be considered as orbiting a circular current loop of $I = dq / dt$ around the nucleus, we obtain

$$\mu = IA = qA/T = \pi r^2(-e)/(2\pi r/v) = -erv/2 = -\frac{e}{2m}mrv = -\frac{e}{2m}L$$

- $\vec{\mu} = -\frac{e}{2m}\vec{L}$ where $L = mvr$ is the magnitude of the orbital angular momentum

The Normal Zeeman Effect



- If there is no magnetic field to align them, $\vec{\mu}$ points in random directions.
- The dipole has a potential energy

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

- The angular momentum is aligned with the magnetic moment, and the torque between $\vec{\mu}$ and $\vec{B}$ causes a precession of $\vec{\mu}$.

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

Where **$\mu_B = e\hbar / 2m$** is called the Bohr magneton.

- $\vec{\mu}$ cannot align exactly in the z direction and has only certain allowed quantized orientations.

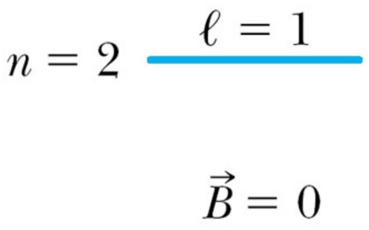
The Normal Zeeman Effect

- The potential energy is quantized due to the magnetic quantum number m_ℓ.

$$V_B = -\mu_z B = +\mu_B m_l B$$

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

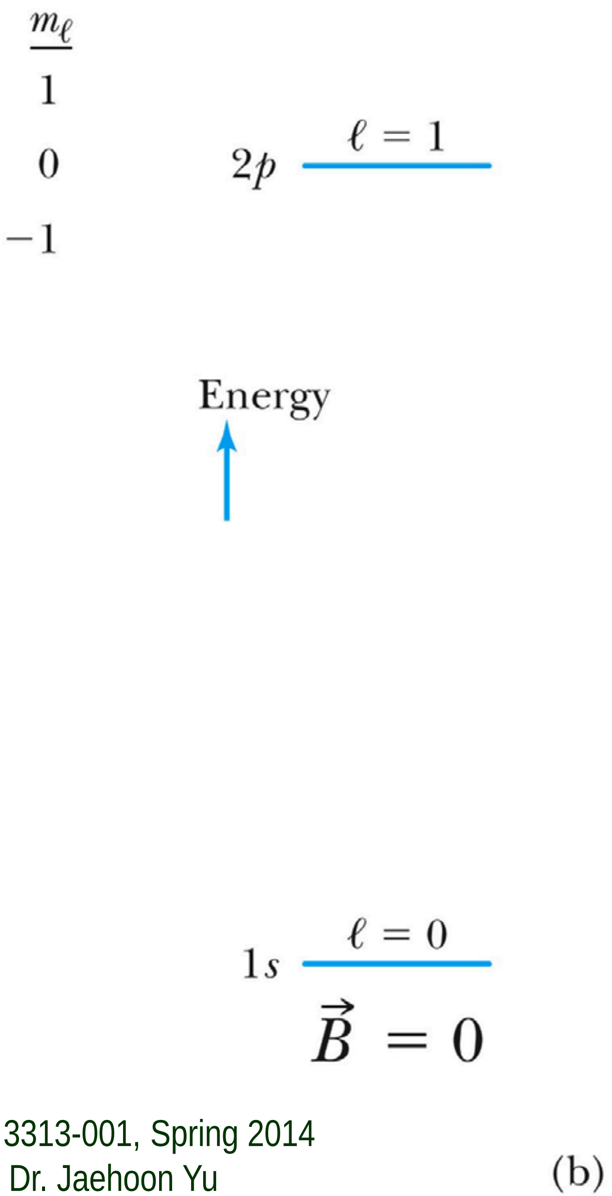
m_ℓ	**Energy**
1	$E_0 + \mu_B B$
0	E_0
−1	$E_0 - \mu_B B$



- So split is into a total of 2ℓ+1 energy states

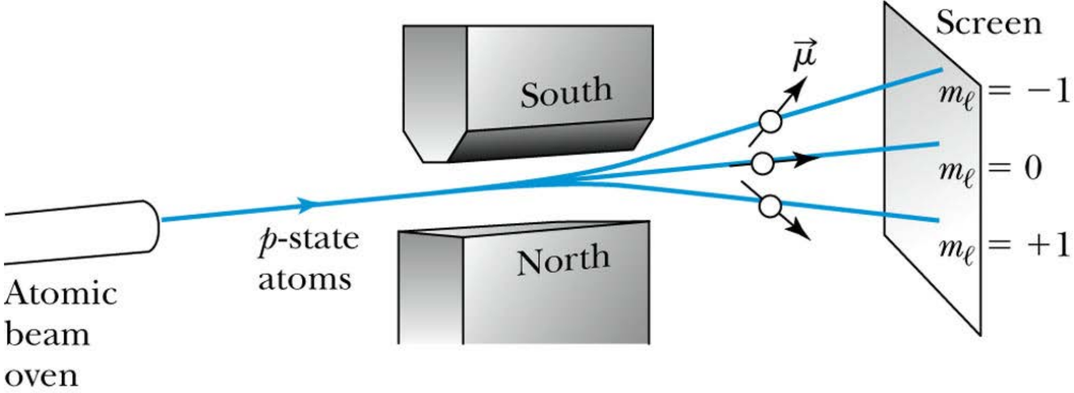
The Normal Zeeman Effect

- A transition from 1s to 2p
- A transition from 2p to 1s



The Normal Zeeman Effect

- An atomic beam of particles in the ℓ = 1 state pass through a magnetic field along the *z* direction. (Stern-Gerlach experiment)



- $V_B = -\mu_z B$
- $F_z = -\left(dV_B/dz\right) = \mu_z\left(dB/dz\right)$
- The m_ℓ = +1 state will be deflected down, the m_ℓ = −1 state up, and the m_ℓ = 0 state will be undeflected. ➔ saw only 2 with silver atoms
- If the space quantization were due to the magnetic quantum number m_ℓ, the number of m_ℓ states is always odd at (2ℓ + 1) and should have produced an odd number of lines.

Intrinsic Spin

- In 1920, to explain spectral line splitting of Stern-Gerlach experiment, Wolfgang Pauli proposed the forth quantum number assigned to electrons
- In 1925, Samuel Goudsmit and George Uhlenbeck in Holland proposed that *the electron must have an intrinsic angular momentum* and therefore a magnetic moment.
- Paul Ehrenfest showed that the surface of the spinning electron should be moving faster than the speed of light to obtain the needed angular momentum!!
- In order to explain experimental data, Goudsmit and Uhlenbeck proposed that the electron must have an **intrinsic spin quantum number** $s = 1/2$.