PHYS 3313 – Section 001
Lecture #18

Monday, Nov. 12, 2012
Dr. Jaehoon Yu

- Quantum Numbers
- Principal Quantum Number
- Orbital Angular Momentum Quantum Number
- Magnetic Quantum Number
- The Zeeman Effect
- Intrinsic Spin

Announcements

- Quiz #3 results
  - Class average: 17.7/50
    - Equivalent to 35.4/100
    - Previous averages: 27.4/100 and 67.3/100
- Homework #7
  - CH7 end of chapter problems: 7, 8, 9, 12, 17 and 29
  - Due on Monday, Nov. 19, in class
- Reading assignments
  - CH7.6 and the entire CH8
- Colloquium Wednesday
  - At 4pm, Wednesday, Nov. 14, in SH101
  - Dr. Masaya Takahashi of UT South Western Medical

Physics Department
The University of Texas at Arlington
COLLOQUIUM

MR Imaging at high magnetic field -A challenge to new biological information from science to clinical application-

Dr. Masaya Takahashi

University of Texas Southwestern Medical Center/
Advanced Imaging Research Center/Radiology,

4:00 pm Wednesday November 14, 2012 room 101 SH

Abstract:

Recent technical progress in noninvasive imaging techniques - notably magnetic resonance imaging (MRI) - in terms of improvement in achievable signal-to-noise ratio and spatial/temporal resolution, has been overcoming several fundamental difficulties. Subsequently, there is an increase in demand to have a better diagnostic tool with which to determine the mechanism, location and stage of the diseases. An important challenge is the development of more powerful, multi-variate methods for characterization of anatomical and functional changes, predicting individual outcome and responsiveness to particular therapies on the basis of clinical and laboratory characteristics. More investigators have been applying higher magnetic field strengths (3 Tesla or higher) in research and clinical settings. Higher magnetic field strength is expected to afford higher spatial resolution and/or a decrease in the length of total scan time due to its higher signal intensity. In the first half of this lecture, we will review the advance MRI and contrast agents that are state-of-the-art at high magnetic field strength in which we hope one can take a hint in their expertise. We have been dedicated to the development of new acquisition and processing methods by means of MRI during the past years, permitting quantitative characterization of the pathophysiological change. Amide proton transfer (APT) imaging is one of the chemical exchange saturation transfer (CEST) imaging methods that are the most practical molecular MR imaging. With this method the exchange between protons of free tissue water and the amide groups (-NH) of endogenous mobile proteins and peptides is imaged. In the second half of this lecture, we will illustrate the CEST/APT imaging and its contrast agent.

Refreshments will be served at 3:30p.m in the Physics Lounge

Principal Quantum Number *n*

- It results from the solution of *R*(*r*) in the separate Schrodinger Eq. because *R*(*r*) includes the potential energy *V*(*r*).

  The result for this quantized energy is

$$E_n = -\frac{\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2 \frac{1}{n^2} = -\frac{E_0}{n^2}$$

- The negative means the energy *E* indicates that the electron and proton are bound together.

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
  - $n = 1, 2, 3, 4, \ldots$ (n>0) Integer
  - $\ell = 0, 1, 2, 3, \ldots, n-1$ ($\ell < n$) Integer
  - $m_\ell = -\ell, -\ell+1, \ldots, 0, 1, \ldots, \ell-1, \ell$ ($|m_\ell| \le \ell$) 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

- The solutions for 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.

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

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

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

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 $L = mv_{orbital}r$.
- ℓ is related to 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* . . .

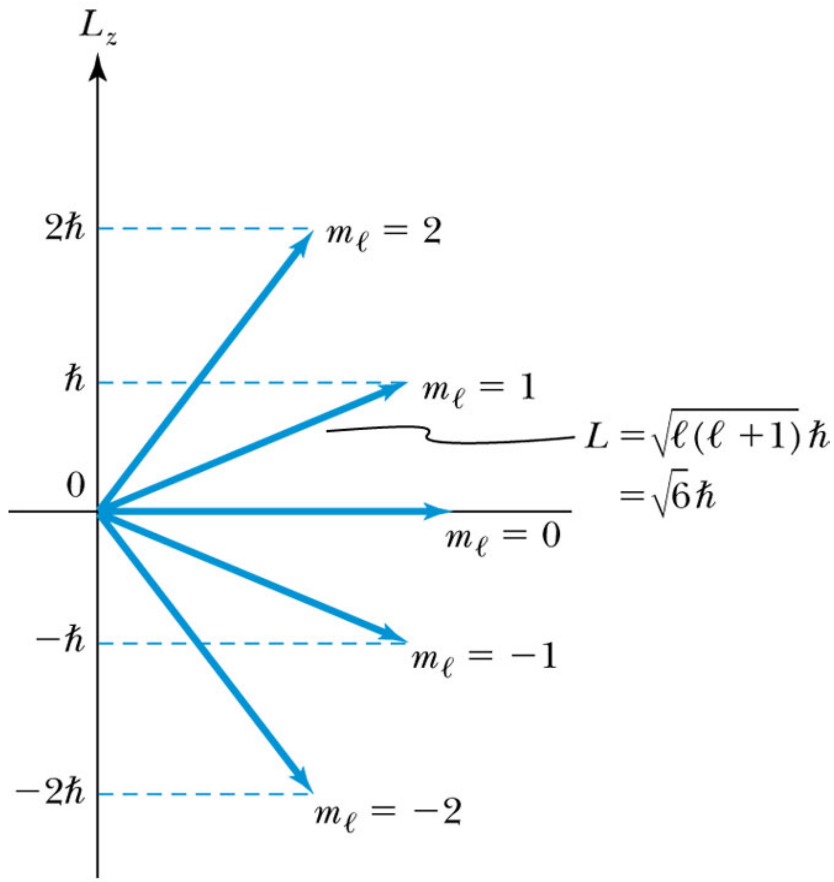
- Atomic states are referred to by their *n* and ℓ
- A state with $n = 2$ and $\ell = 1$ is called a 2*p* state
- The boundary conditions require $n > \ell$

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



Magnetic Quantum Number m_ℓ

- Quantum mechanics allows $\vec{L}$ to be quantized along only one direction in space. Because of the relation $L^2 = L_x^2 + L_y^2 + L_z^2$, once a second component is known, the third component will also be 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 .

$$\langle L^2 \rangle = 3\langle L_z^2 \rangle = \frac{3}{2l+1}\sum_{m_l=-l}^{+l} m_l^2\hbar^2 = l(l+1)\hbar^2$$

Magnetic Effects on Atomic Spectra—The Normal Zeeman Effect

- The Dutch physicist Pieter Zeeman showed the spectral lines emitted by atoms in a magnetic field split into multiple energy levels. It is called the **Zeeman effect**.

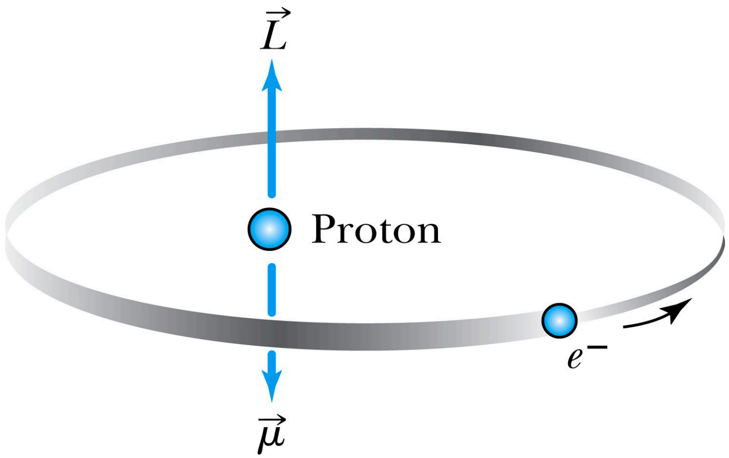
Normal Zeeman effect:

- 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



- Since 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 $\vec{\mu}$.

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

Where **μ_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.

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

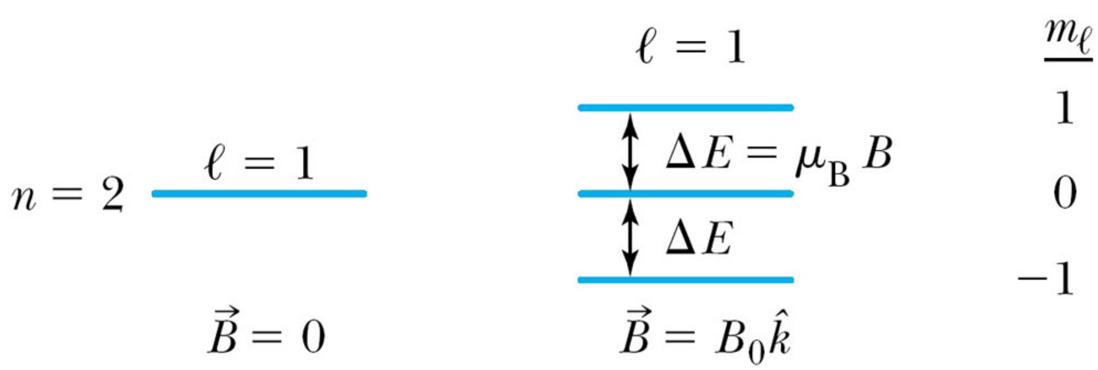
The Normal Zeeman Effect

- 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 $\Delta E = \mu_B B \, \Delta m_\ell$.

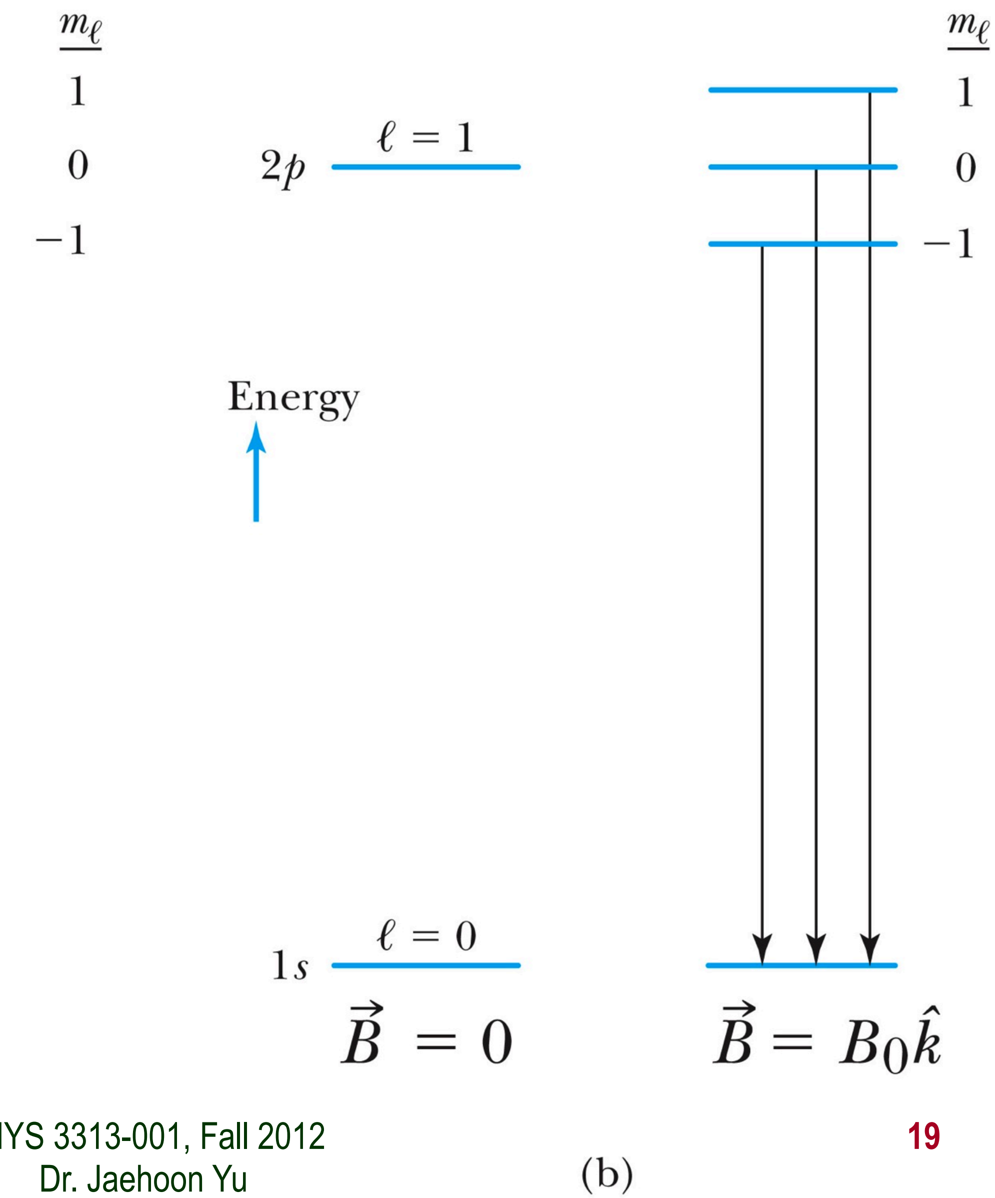
m_ℓ	**Energy**
1	$E_0 + \mu_B B$
0	E_0
−1	$E_0 - \mu_B B$



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

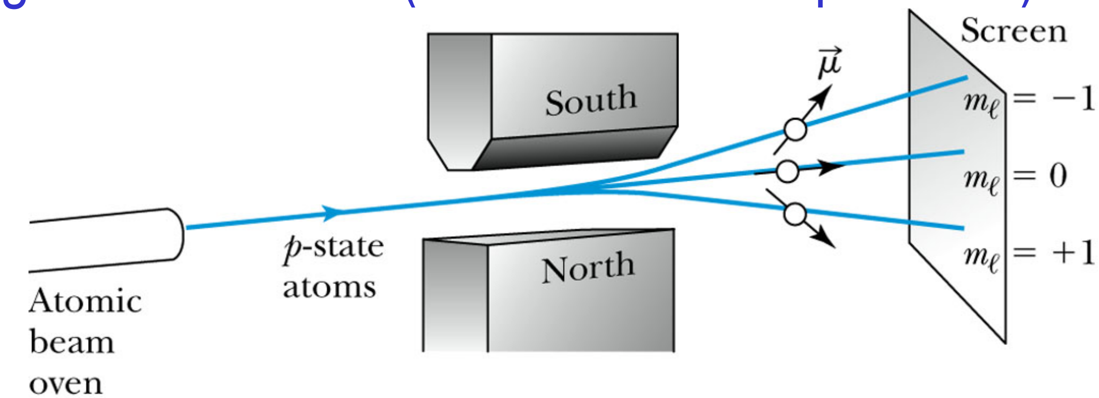
The Normal Zeeman Effect

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



The Normal Zeeman Effect

- An atomic beam of particles in the $\ell = 1$ 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 $m_\ell = +1$ 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 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** $s = 1/2$.

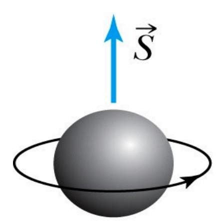
Intrinsic Spin

- The spinning electron reacts similarly to the orbiting electron in a magnetic field. (Dirac showed that this is ecessary due to special relativity..)
- We should try to find L, L_z, ℓ, and m_ℓ.
- The **magnetic spin quantum number** m_s has only two values, $m_s = \pm½$.

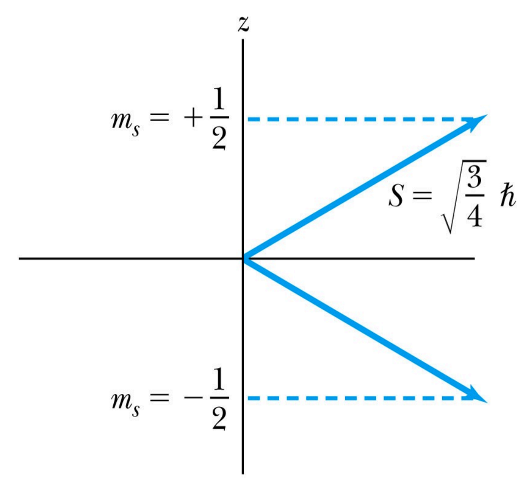
The electron's spin will be either "up" or "down" and can never be spinning with its magnetic moment μ_s exactly along the z axis.

For each state of the other quantum numbers, there are two spins values

The **intrinsic spin angular momentum** vector $\left|\vec{S}\right| = \sqrt{s(s+1)}\hbar = \sqrt{3/4}\hbar$



(a)



(b)

Intrinsic Spin

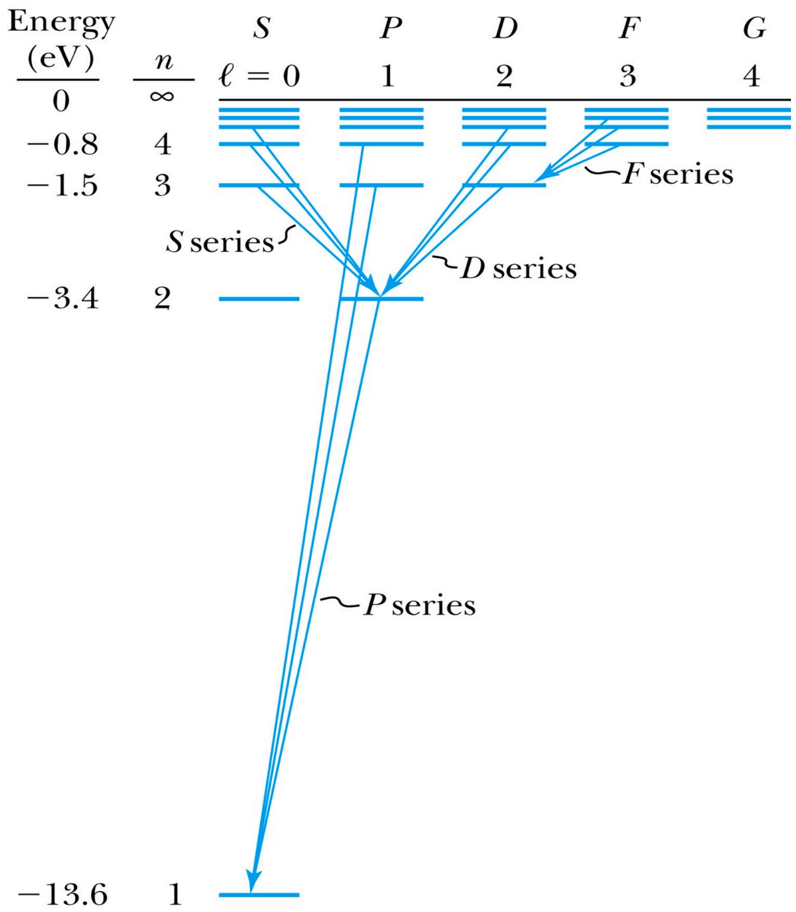
- The magnetic moment is $\vec{\mu}_s = -(e/m)\vec{S}$ or $-2\mu_B\vec{S}/\hbar$.
- The coefficient of $\vec{S}/\hbar$ is $-2\mu_B$ as with $\vec{L}$ is a consequence of theory of relativity.
- The **gyro-magnetic ratio** (ℓ or s).
- $g_\ell = 1$ and $g_s = 2$, then

$$\vec{\mu}_l = -\frac{g_l \mu_B \vec{L}}{\hbar} = -\frac{\mu_B \vec{L}}{\hbar} \quad \text{and} \quad \vec{\mu}_s = -\frac{g_l \mu_B \vec{L}}{\hbar} = -2\frac{\mu_B \vec{L}}{\hbar}$$

- The z component of $\vec{S}$ is $S_z = m_s\hbar = \pm\hbar/2$.
- In $\ell = 0$ state → no splitting due to $\vec{\mu}_l$.
  → there is space quantization due to the intrinsic spin $\vec{\mu}_s$.
- Apply m_ℓ and the potential energy becomes $V_B = -\vec{\mu}_s \cdot \vec{B} = +\frac{2}{m}\vec{S}\cdot\vec{B}$

Energy Levels and Electron Probabilities

- For hydrogen, the energy level depends on the principle quantum number *n*.



- In ground state an atom cannot emit radiation. It can absorb electromagnetic radiation, or gain energy through inelastic bombardment by particles.

Selection Rules

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

Allowed transitions: Electrons absorbing or emitting photons to change states when $\Delta\ell = \pm 1$.

Forbidden transitions: Other transitions possible but occur with much smaller probabilities when $\Delta\ell \neq \pm 1$.

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

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

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

Probability Distribution Functions

- We must use wave functions to calculate the probability distributions of the electrons.
- The "position" of the electron is spread over space and is not well defined.
- We may use the radial wave function $R(r)$ to calculate radial probability distributions of the electron.
- The probability of finding the electron in a differential volume element $d\tau$ is

$$dP = \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)d\tau$$

Probability Distribution Functions

- The differential volume element in spherical polar coordinates is

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

  Therefore,

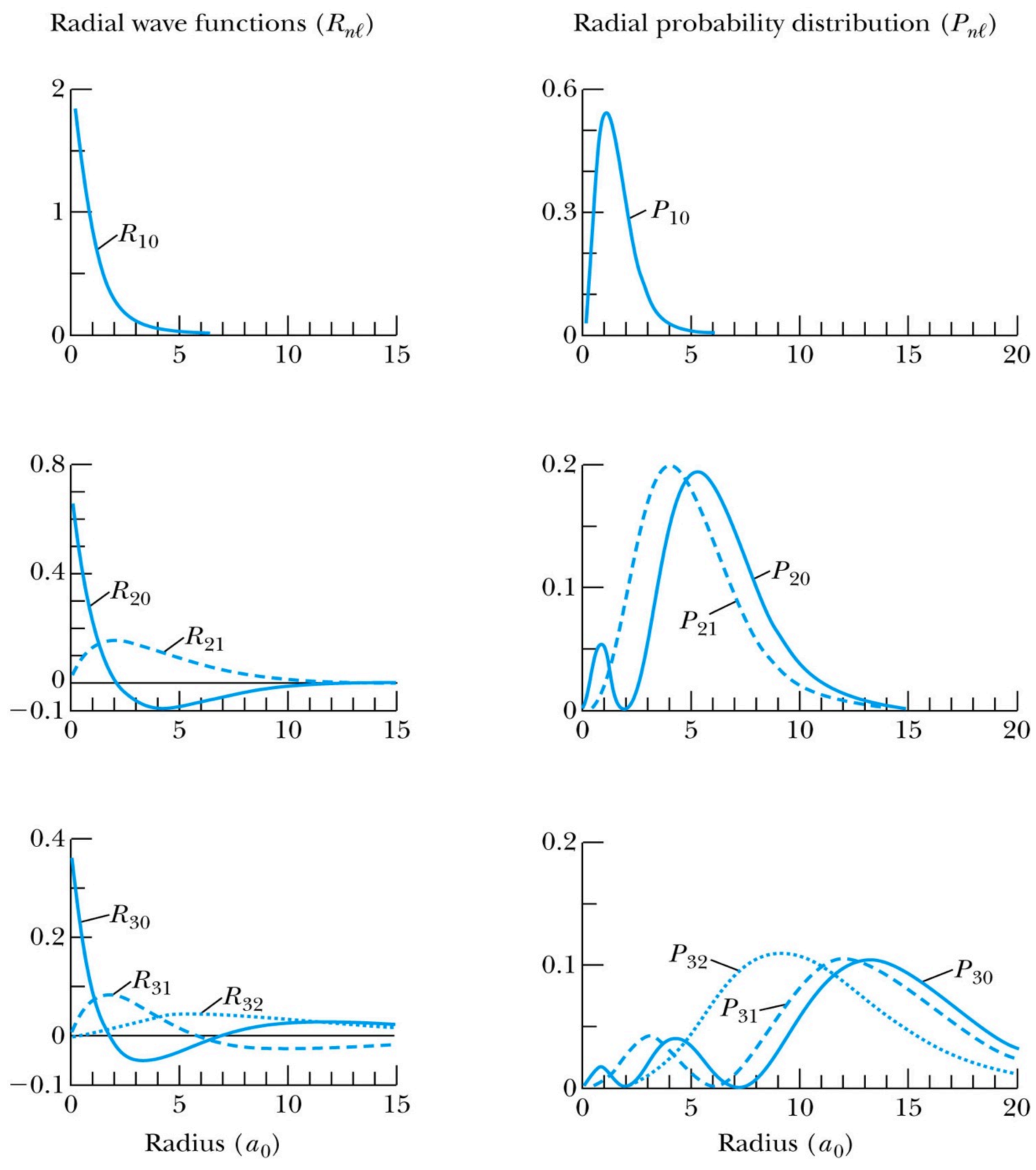
$$P(r)dr = r^2 R^*(r) R(r) dr \int_0^{\pi} |f(\theta)|^2 \sin\theta\, d\theta \int_0^{2\pi} g(\phi) d\phi$$

- We are only interested in the radial dependence.

$$P(r)dr = r^2 |R(r)|^2 dr$$

- The radial probability density is $P(r) = r^2|R(r)|^2$ and it depends only on n and l.

Probability Distribution Functions



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

Probability Distribution Functions

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