# PHYS 3313 – Section 001
# Lecture # 23

*Monday, April 27, 2015*

*Dr. Barry Spurlock*

- Hydrogen Atom Wave Functions
- Solution for Angular and Azimuthal Equations
- Angular Momentum Quantum Numbers
- Magnetic Quantum Numbers
- Zeeman Effects
- Equipartition Theorem
- Quantum Distributions

# Announcements

- Research paper deadline is Monday, May 4
- Research presentation deadline is 8pm, Sunday, May 3
- Reminder Homework #6
  - CH7 end of chapter problems: 7, 8, 9, 12, 17 and 29
  - Due on Wednesday, Apr. 29, in class
- Reading assignments
  - CH7.6 and the entire CH8
- Quiz number 5
  - At the beginning of the class Wednesday, Apr. 29
  - Covers up to what we finish Monday, Apr. 27
  - Bring Your Own Formula sheet
- Final comprehensive exam 11am – 1:30pm, Monday, May 11

# Hydrogen Atom Radial Wave Functions

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

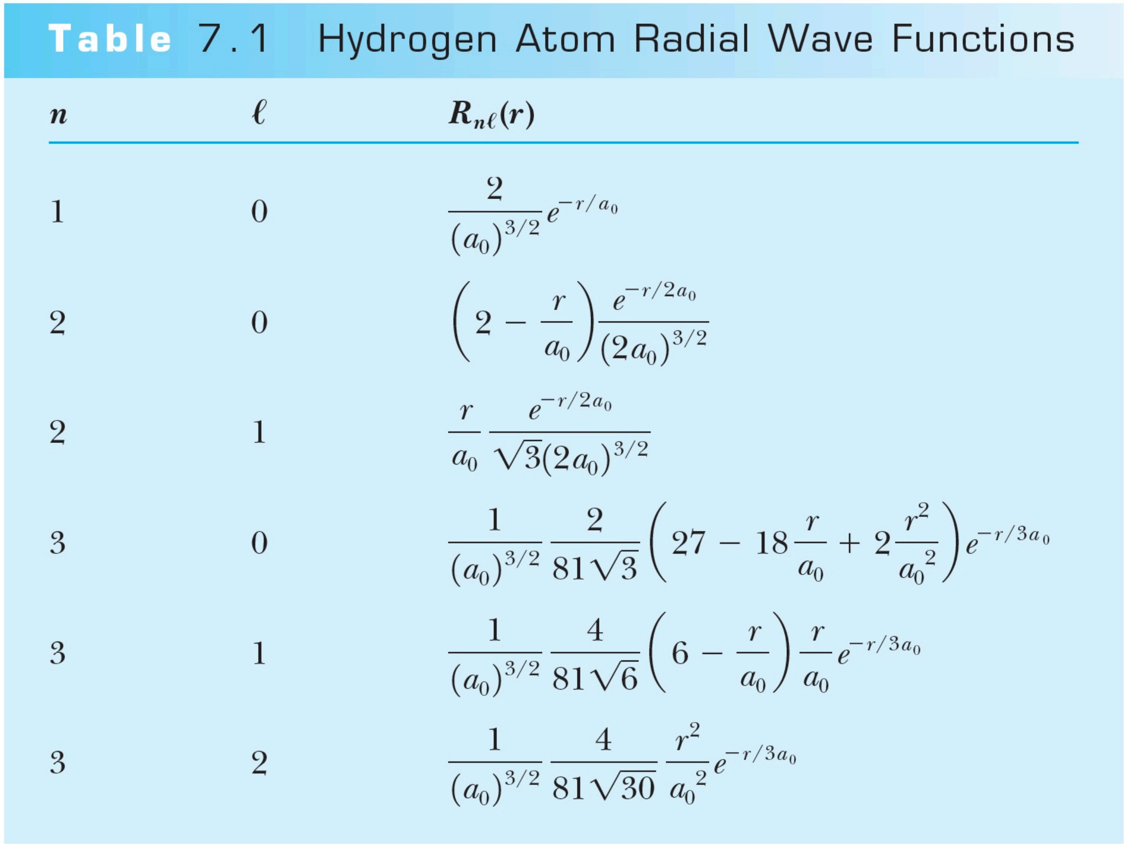


**Table 7.1** Hydrogen Atom Radial Wave Functions

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

# 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 $m_\ell$
- Group these solutions together into functions

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

**---- spherical harmonics**

# Normalized Spherical Harmonics

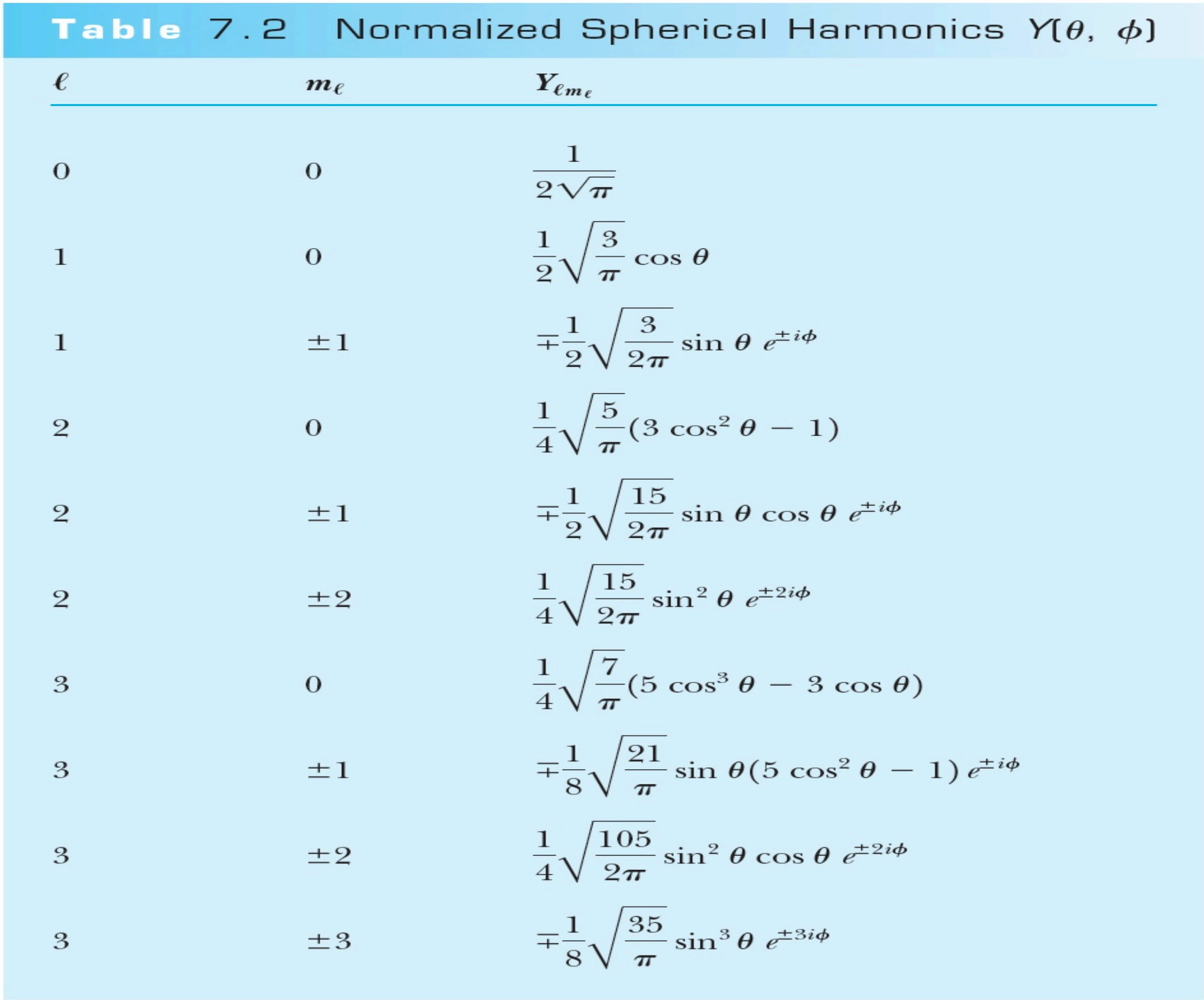


**Table 7.2** Normalized Spherical Harmonics $Y(\theta, \phi)$

| $\ell$ | $m_\ell$ | $Y_{\ell m_\ell}$ |
|---|---|---|
| 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 | $\pm 3$ | $\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{\pm 3i\phi}$ |

# 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 ψ(r,θ,ϕ) depends on *n*, ℓ, and $m_\ell$. 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*(*θ*) 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 $L = n\hbar$.

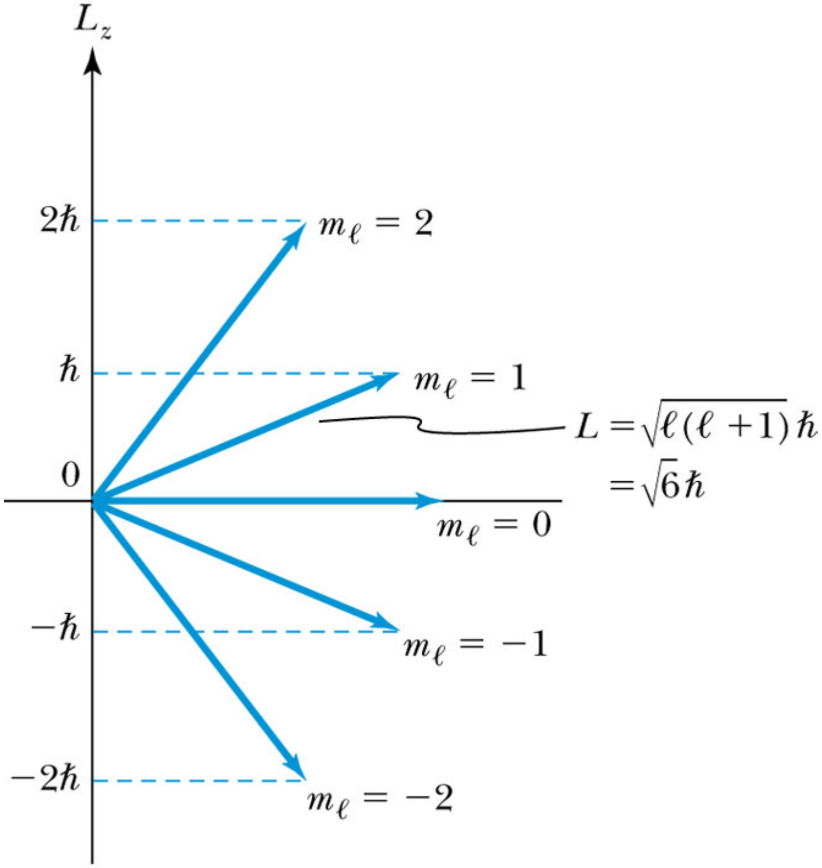
# Orbital Angular Momentum Quantum Number $\ell$

- Certain energy level is **degenerate** with respect to $\ell$ when the energy is independent of $\ell$.
- Use letter names for the various $\ell$ values
  - $\ell$ = 0 1 2 3 4 5 . . .
  - Letter = *s* *p* *d* *f* *g* *h* . . .
- Atomic states are referred by their *n* and $\ell$
  - **s**=**s**harp, **p**=**p**rincipal, **d**=**d**iffuse, **f** =**f**undamental, 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 $m_\ell$

- The angle $\phi$ is a measure of the rotation about the z axis.
- The solution for $g(\phi)$ specifies that $m_\ell$ is an integer and related to the $z$ component of $L$.

$$L_z = m_l \hbar$$



- The relationship of $L$, $L_z$, $\ell$, and $m_\ell$ 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**.
- $m_\ell$ is called the magnetic moment since z axis is chosen customarily along the direction of magnetic field.

# Magnetic Quantum Number $m_\ell$

- 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**.

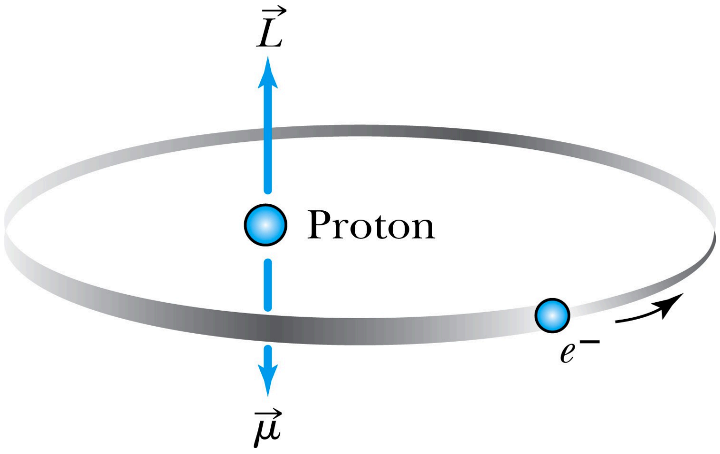
**The Normal Zeeman effect**:

- 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



- 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 $\vec{\mu}$ .

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

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.

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

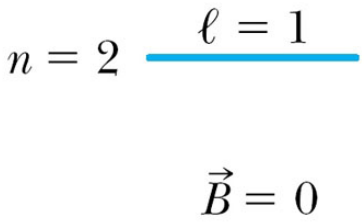
# The Normal Zeeman Effect

- The potential energy is quantized due to the magnetic quantum number $m_\ell$.

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

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

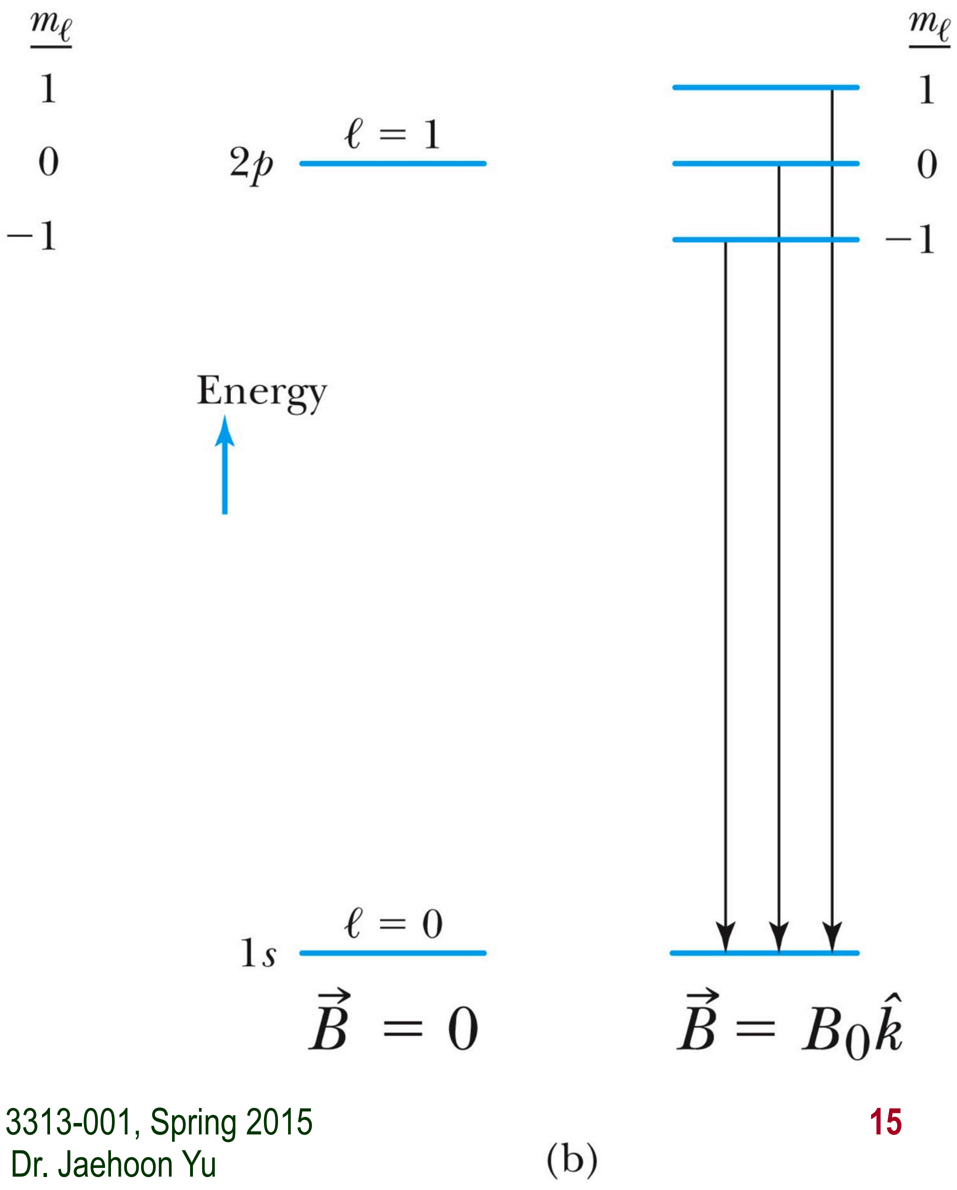
| $m_\ell$ | **Energy** |
|---|---|
| 1 | $E_0 + \mu_B B$ |
| 0 | $E_0$ |
| −1 | $E_0 - \mu_B B$ |



- So split is into a total of $2\ell+1$ energy states

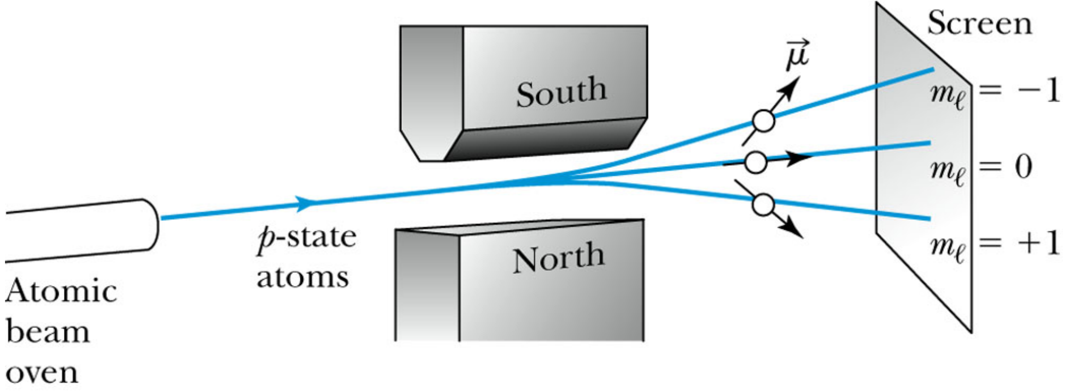
# The Normal Zeeman Effect

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



# 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 $m_\ell$ = +1 state will be deflected down, the $m_\ell$ = −1 state up, and the $m_\ell$ = 0 state will be undeflected. ➔ saw only 2 with silver atom
- If the space quantization were due to the magnetic quantum number $m_\ell$, the number of $m_\ell$ 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** $s = ½$.

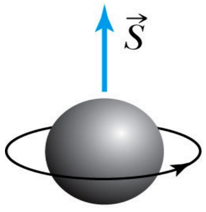
# Intrinsic Spin

- The spinning electron reacts similarly to the orbiting electron in a magnetic field. (Dirac showed that this is necessary due to special relativity..)
- We should try to find $L$, $L_z$, $\ell$, and $m_\ell$.
- The **magnetic spin quantum number** $m_s$ has only two values, $m_s = \pm 1/2$.

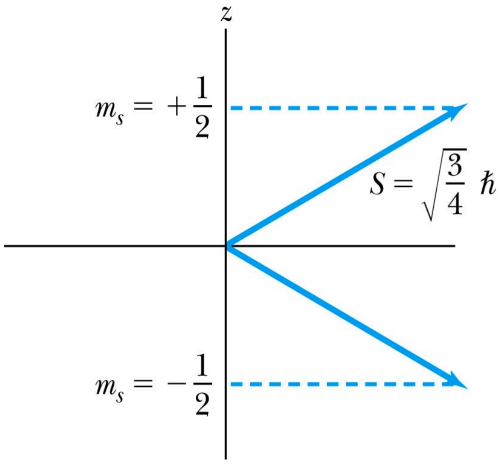
The electron's spin will be either "up" or "down" and can never be spinning with its magnetic moment $\mu_s$ exactly along the z axis.

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

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



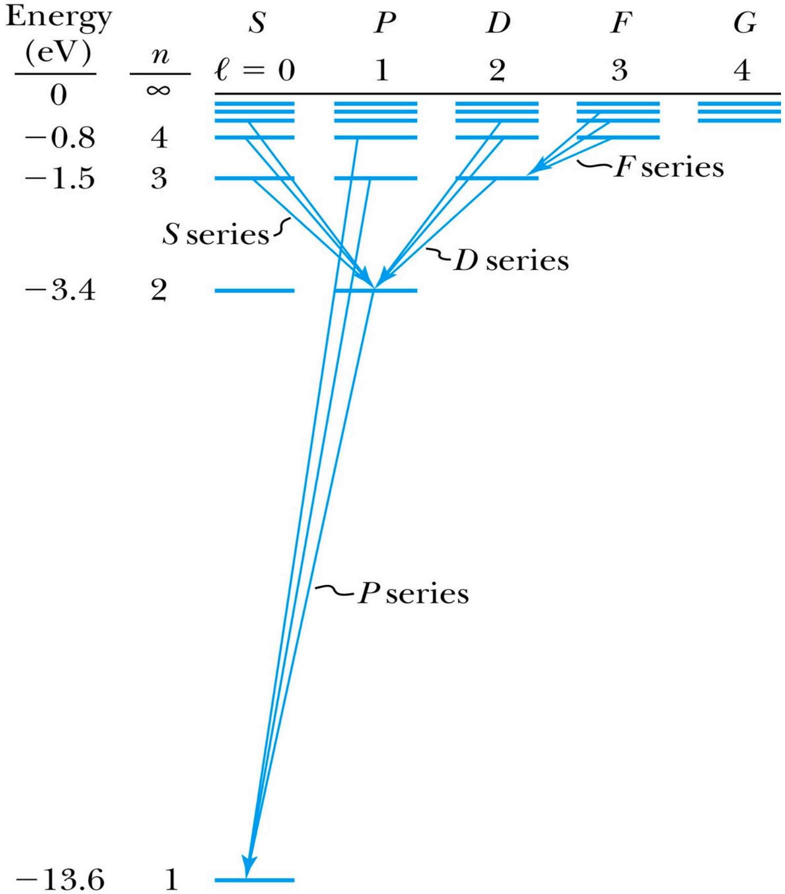
(a)



(b)

# 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 can change states when $\Delta\ell = \pm1$. (Evidence for the photon carrying one unit of angular momentum!)

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

$$\Delta\ell = \pm1$$

$$\Delta m_\ell = 0, \pm1$$

**Forbidden transitions**: Other transitions possible but occur with much smaller probabilities when $\Delta\ell \neq \pm1$.

# 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

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

# Equipartition Theorem

- The formula for average kinetic energy 3kT/2 works for monoatomic molecule what is it for diatomic molecule?
- Consider oxygen molecule as two oxygen atoms connected by a massless rod ➔ This will have both translational and rotational energy
- How much rotational energy is there and how is it related to temperature?
- **Equipartition Theorem**:
  - *In equilibrium a mean energy of ½ kT per molecule is associated with each independent quadratic term in the molecule's energy.*
  - Each independent phase space coordinate: ***degree of freedom***
  - Essentially the mean energy of a molecule is *½ kT *NDoF*

# Equipartition Theorem

- In a monoatomic ideal gas, each molecule has

$$K = \tfrac{1}{2} m v^2 = \tfrac{1}{2} m\left(v_x^2 + v_y^2 + v_z^2\right)$$

- There are three degrees of freedom.
- Mean kinetic energy is $3\left(\tfrac{1}{2} kT\right) = \tfrac{3}{2} kT$
- In a gas of *N* helium molecules, the total internal energy is

$$U = N\bar{E} = \tfrac{3}{2} NkT$$

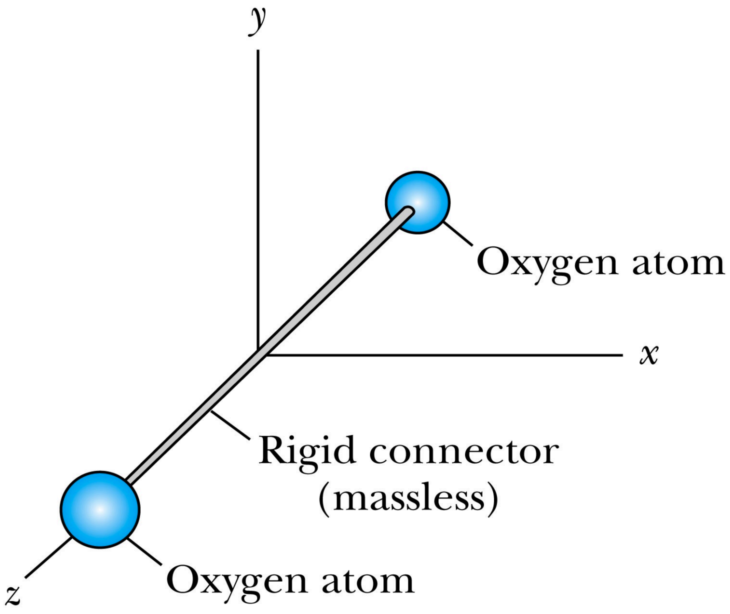
- The heat capacity at constant volume is $C_V = \dfrac{\partial U}{\partial T} = \tfrac{3}{2} Nk$
- For the heat capacity for 1 mole,

$$c_V = \tfrac{3}{2} N_A k = \tfrac{3}{2} R = 12.5\,\mathrm{J/K}$$

- using the ideal gas constant *R* = 8.31 J/K.

# The Rigid Rotator Model

- For diatomic gases, consider the rigid rotator model.



- The molecule has rotational E only when it rotates about *x* or *y* axis.
- The corresponding rotational energies are $\frac{1}{2}I_x\omega_x^2$ and $\frac{1}{2}I_y\omega_y^2$
- There are five degrees of freedom (three translational and two rotational)➔ resulting in mean energy of 5kT/2 per molecule according to equi-partition principle ($C_V$=5R/2)

# Table of Measured Gas Heat Capacities

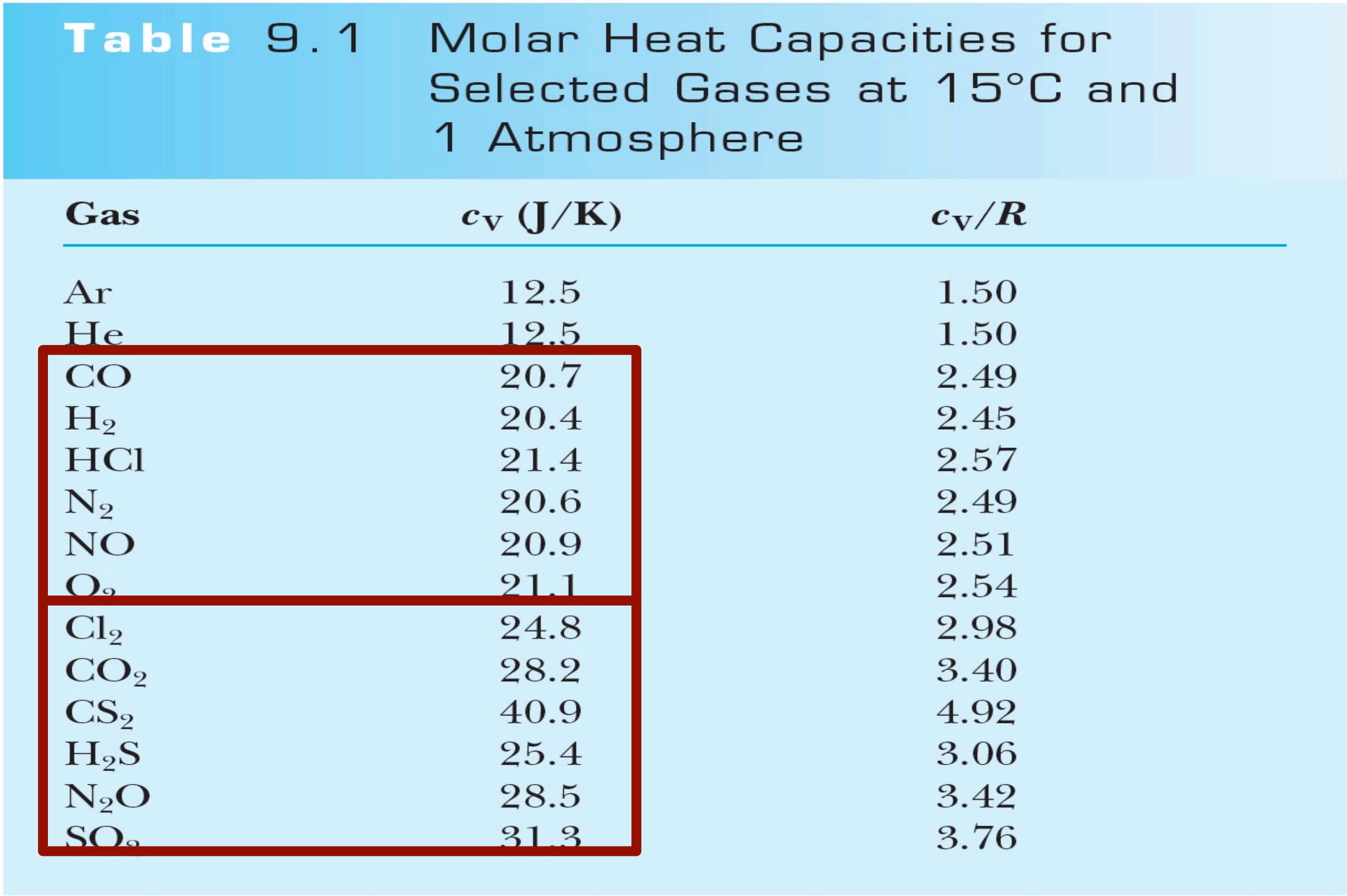


**Table 9.1** Molar Heat Capacities for Selected Gases at 15°C and 1 Atmosphere

| Gas | $c_V$ (J/K) | $c_V/R$ |
|---|---|---|
| Ar | 12.5 | 1.50 |
| He | 12.5 | 1.50 |
| CO | 20.7 | 2.49 |
| $H_2$ | 20.4 | 2.45 |
| HCl | 21.4 | 2.57 |
| $N_2$ | 20.6 | 2.49 |
| NO | 20.9 | 2.51 |
| $O_2$ | 21.1 | 2.54 |
| $Cl_2$ | 24.8 | 2.98 |
| $CO_2$ | 28.2 | 3.40 |
| $CS_2$ | 40.9 | 4.92 |
| $H_2S$ | 25.4 | 3.06 |
| $N_2O$ | 28.5 | 3.42 |
| $SO_2$ | 31.3 | 3.76 |