Chapter 7

Atomic Physics

Schrödinger Equation in 3D infinite square well

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+V\psi=E\psi$$

$$\psi(x,y,z)=\psi_1(x)\psi_2(y)\psi_3(z)$$

$$\psi(x,y,z)=Asin(k_1x)sin(k_2y)sin(k_3z)$$

$$k_i=\frac{n_i\pi}{L_i}$$

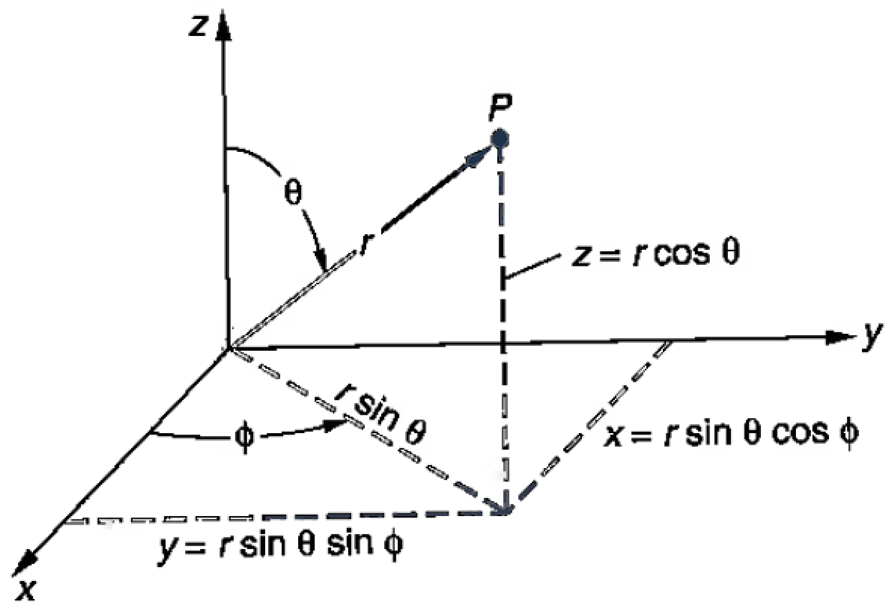
$$E_{n_1n_2n_3}=\frac{\hbar^2\pi^2}{2m}\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}+\frac{n_3^2}{L_3^2}\right)$$

Schrödinger Equation in 3D Spherical Coordinate

Electrons in hydrogen-like atom

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]+V\psi=E\psi$$

$$V(r)=-\frac{Zke^2}{r}$$



Range of variables

Cartesian

$x, y, z: -\infty \rightarrow +\infty$

Spherical

$r: 0 \rightarrow +\infty$

$\theta: 0 \rightarrow \pi$

$\phi: 0 \rightarrow 2\pi$

Schrödinger Equation in 3D Spherical Coordinate

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]-\frac{Zke^2}{r}\psi=E\psi$$

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

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}[E-V]=l(l+1)$$

$$\frac{1}{g}\frac{d^2g}{d\phi^2}=-m^2 \longrightarrow g_m(\phi)=e^{im\phi}$$

$$l(l+1)sin^2\theta+\frac{sin\theta}{f}\frac{d}{d\theta}\left(sin\theta\frac{df}{d\theta}\right)=m^2 \longrightarrow f_{lm}(\theta)=\frac{(sin\theta)^{|m|}}{2^l l!}\left[\frac{d}{d(cos\theta)}\right]^{l+|m|}(cos^2\theta-1)^l$$

Schrödinger Equation in 3D Spherical Coordinate

$$Y_{lm}(\theta, \phi) = f_{lm}(\theta) g(\phi) = e^{im\phi} \frac{(sin\theta)^{|m|}}{2^l l!} \left[\frac{d}{d(cos\theta)}\right]^{l+|m|} (cos^2\theta - 1)^l$$

$$\psi(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

See Table 7-1 for some of the $Y_{lm}(\theta, \phi)$ functions

Radial Function of Schrödinger Equation

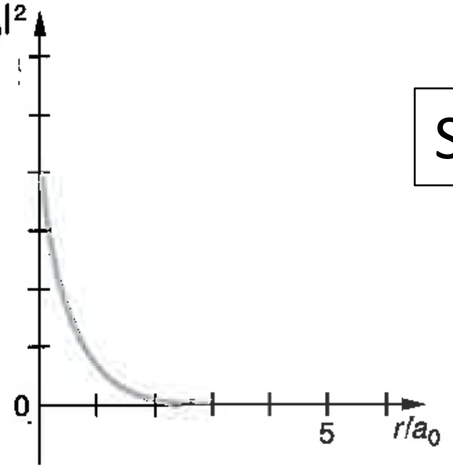
$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}[E-V]=l(l+1)$$

$$-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)+\left[-\frac{kZe^2}{r}+\frac{\hbar^2 l(l+1)}{2\mu r^2}\right]R(r)=ER(r)$$

$$E_n=-\left(\frac{kZe^2}{\hbar}\right)^2\frac{\mu}{2n^2}=-\frac{Z^2E_1}{n^2}$$

Radial Function of Schrödinger Equation

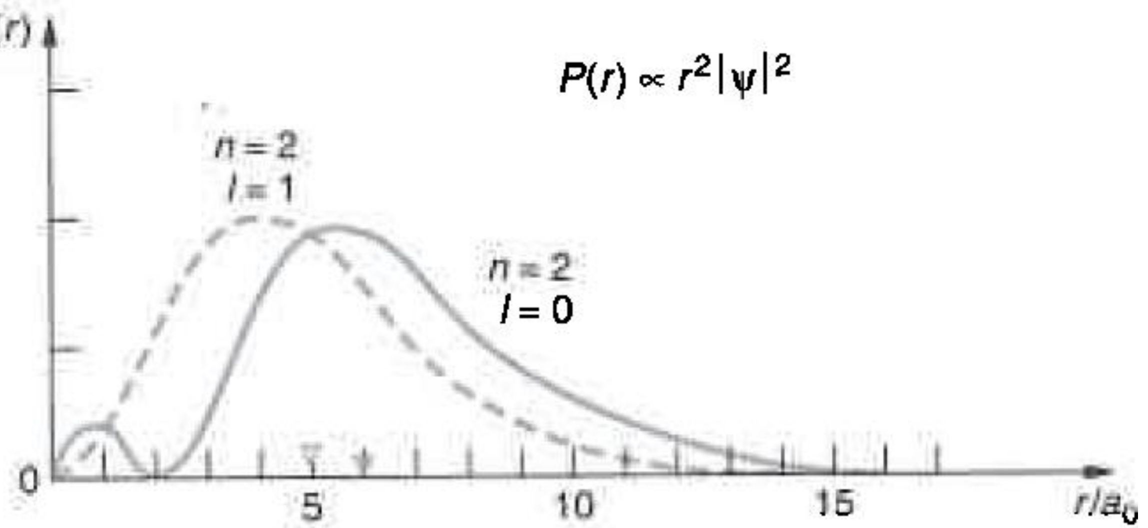
$$R_{10} = \frac{2}{\sqrt{a_0^3}} e^{-r/a_0}$$



See Table 7-2 for more $R_{nl}(r)$ functions

$$R_{20} = \frac{1}{\sqrt{2a_0^3}} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$

$$R_{21} = \frac{1}{2\sqrt{6a_0^3}} \frac{r}{a_0} e^{-r/2a_0}$$



Summary of the Quantum Numbers

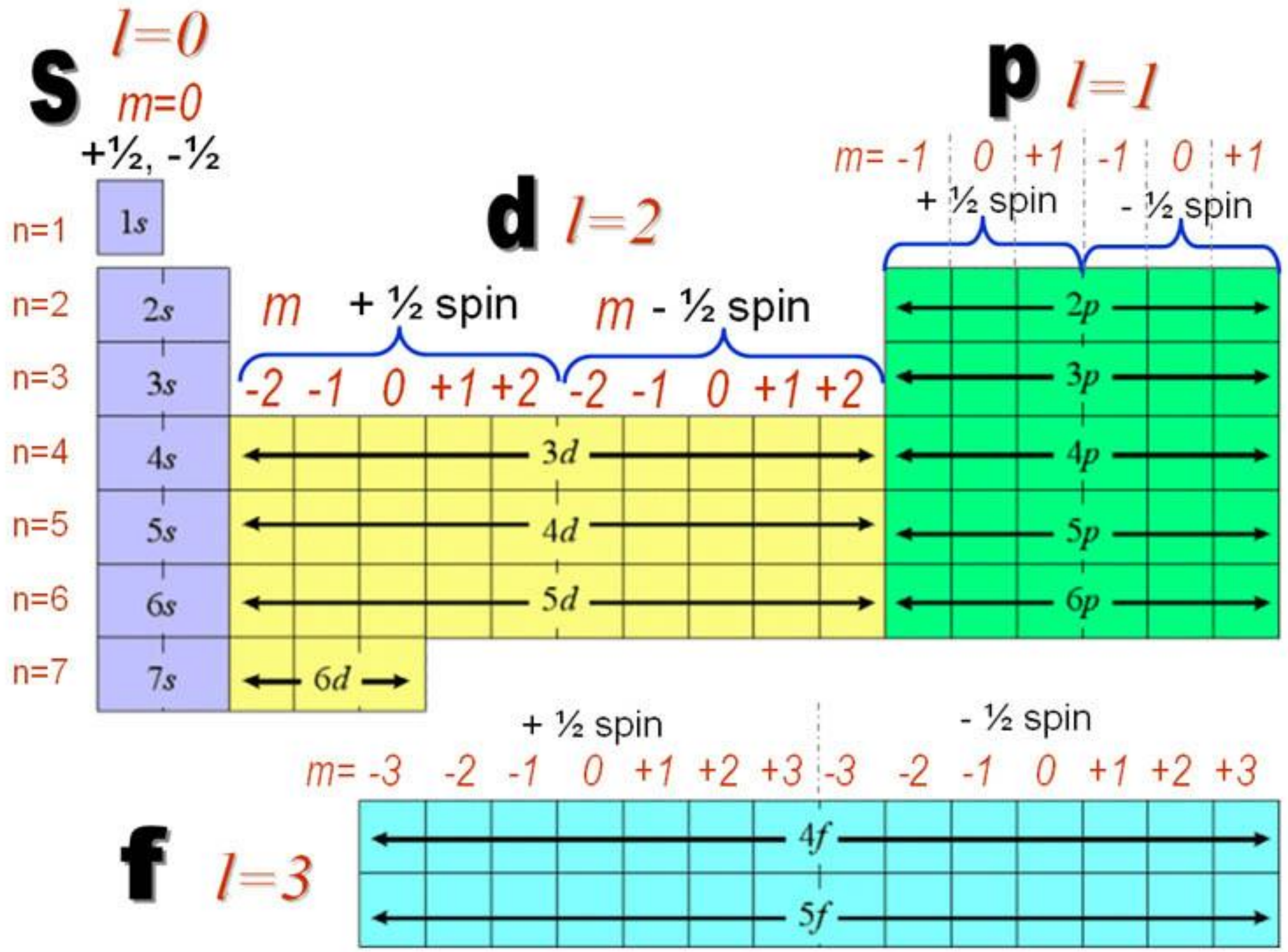
$$\psi(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

Principal quantum number: $n = 1,2,3,\ldots$

Angular momentum (orbital) quantum number: $l = 0,1,2,3,\ldots,(n-1)$

Magnetic quantum number: $m = -l,-l+1,\ldots,-2,-1,0,1,2,\ldots,l-1,l$

Periodic Table and Quantum Numbers



Angular Momentum

$$E = \frac{p_r^2}{2\mu} + \frac{L^2}{2\mu r^2} + V$$

$$(p_r^2)_{op} = -\hbar^2 \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)$$

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) - \frac{\hbar^2}{2\mu}\frac{1}{r^2}\left[\frac{1}{sin\theta}\frac{\partial}{\partial \theta}\left(sin\theta \frac{\partial \psi}{\partial \theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2 \psi}{\partial \phi^2}\right] - \frac{Zke^2}{r}\psi = E\psi$$

$$(L^2)_{op} = -\hbar^2 \left[\frac{1}{sin\theta}\frac{\partial}{\partial \theta}\left(sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right]$$

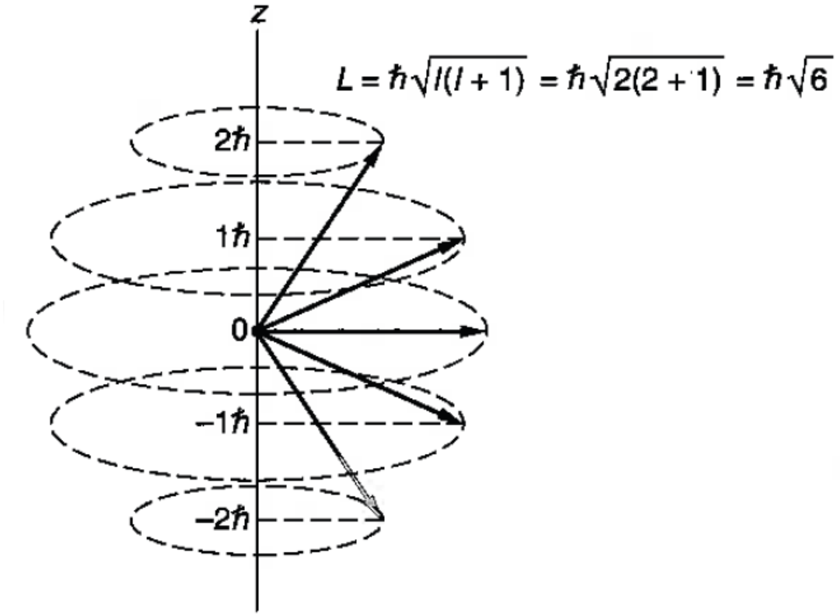
Angular Momentum

$$-\hbar^2\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y_{lm}(\theta,\phi)=l(l+1)\hbar^2Y_{lm}(\theta,\phi)$$

$$(L^2)_{op}Y_{lm}(\theta,\phi)=l(l+1)\hbar^2Y_{lm}(\theta,\phi)=L^2Y_{lm}(\theta,\phi)$$

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

$$L_z=m\hbar$$



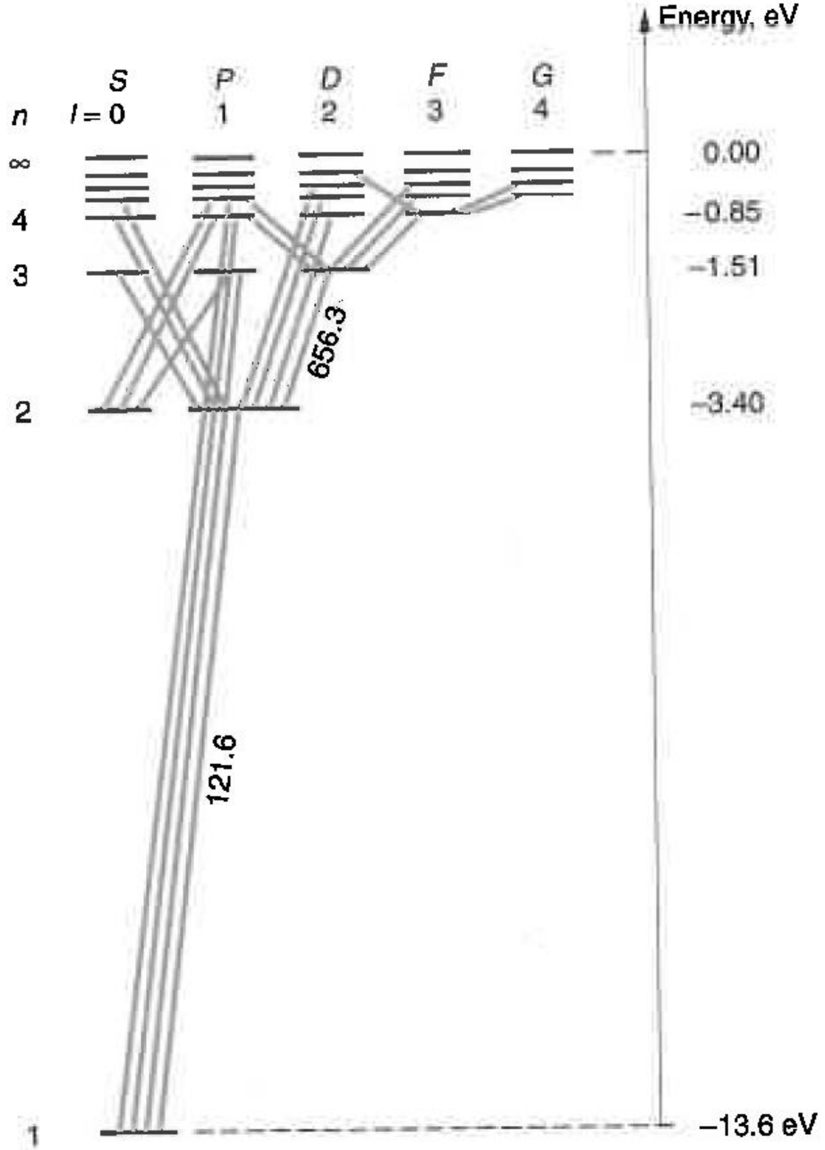
Example

- If a system has angular momentum characterized by the quantum number $l = 2$, what are the possible value of L_z, what is the magnitude L, and what is the smallest-possible angle between $\vec{L}$ and the z axis?

Spectroscopy transitions and selection rules

$\Delta m = 0 \; or \; \pm 1$

$\Delta l = \pm 1$



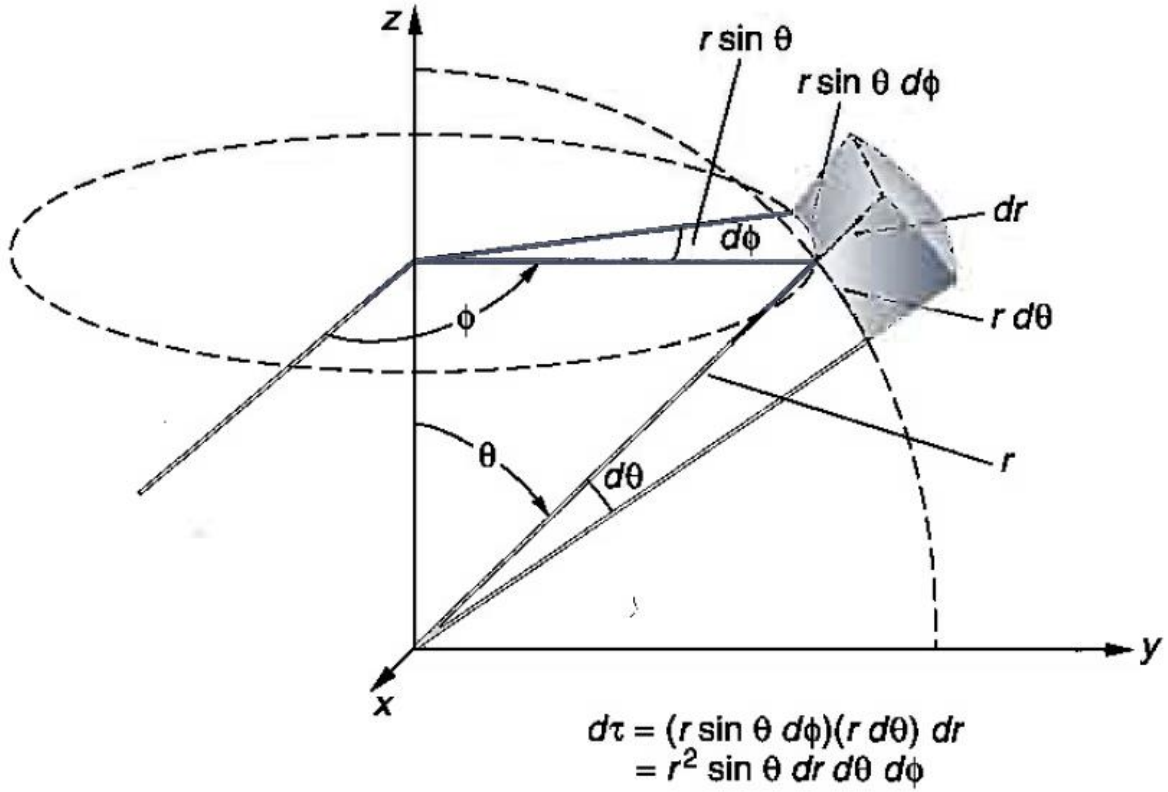
Hydrogen Atom Wave Functions

$$\psi_{nlm}(r,\theta,\phi) = C_{nlm}R_{nl}(r)Y_{lm}(\theta,\phi)$$

Determine the coefficient C_{nlm}

$$\int \psi^* \psi d\tau = 1$$

$$d\tau = (r sin\theta d\phi)(r d\theta)(dr)$$



Hydrogen Atom Wave Functions

Example – the ground state $\psi_{100}(r,\theta,\phi) = C_{100}R_{10}(r)Y_{00}(\theta,\phi)$

$$\int \psi^*\psi d\tau = 1 \quad \Rightarrow \quad C_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}$$

$$\int_0^\infty P(r)dr = 1 \quad \Rightarrow \quad P(r)dr = 4\pi r^2 C_{100}^2 e^{-2Zr/a_0} dr$$

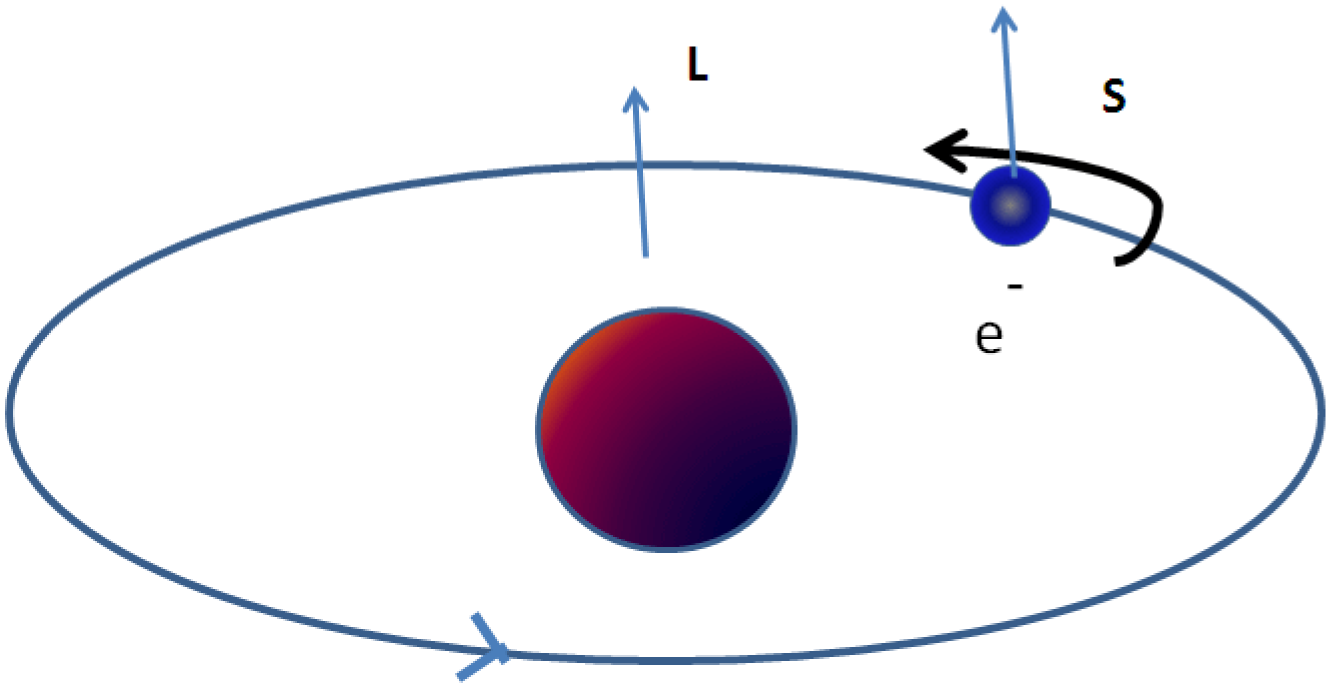
Example

- Find the Coefficient of the state (*nlm*) = (200) for hydrogen atom.
- Find the probability function of the state (*nlm*) = (200) for hydrogen atom. (I will do it. but if you finished the first example, try this one.)

Electron Spin

$$|\vec{S}| = S = \sqrt{s(s+1)}\hbar$$

$$m_s = \pm\frac{1}{2}\hbar \;\Rightarrow\; s = \frac{1}{2}$$



Complete Hydrogen Atom Wave Function

$$\psi_{100}(r,\theta,\phi) = C_{100}R_{10}(r)Y_{00}(\theta,\phi)$$

$$\psi = C_1\psi_{nlm_lm_{s1}} + C_2\psi_{nlm_lm_{s2}}$$

$$\psi = C_1\psi_{100+1/2} + C_2\psi_{100-1/2}$$

Pauli Exclusion Principle: Valid for particles with half integer spin (Fermions)

No more than one electron may occupy a given quantum state specified by a particular set of single-particle quantum numbers, *n, l,* m_l, m_s

Magnetic Moment

Define: Magnetic dipole moment

$$\vec{\mu} = I\vec{A}$$

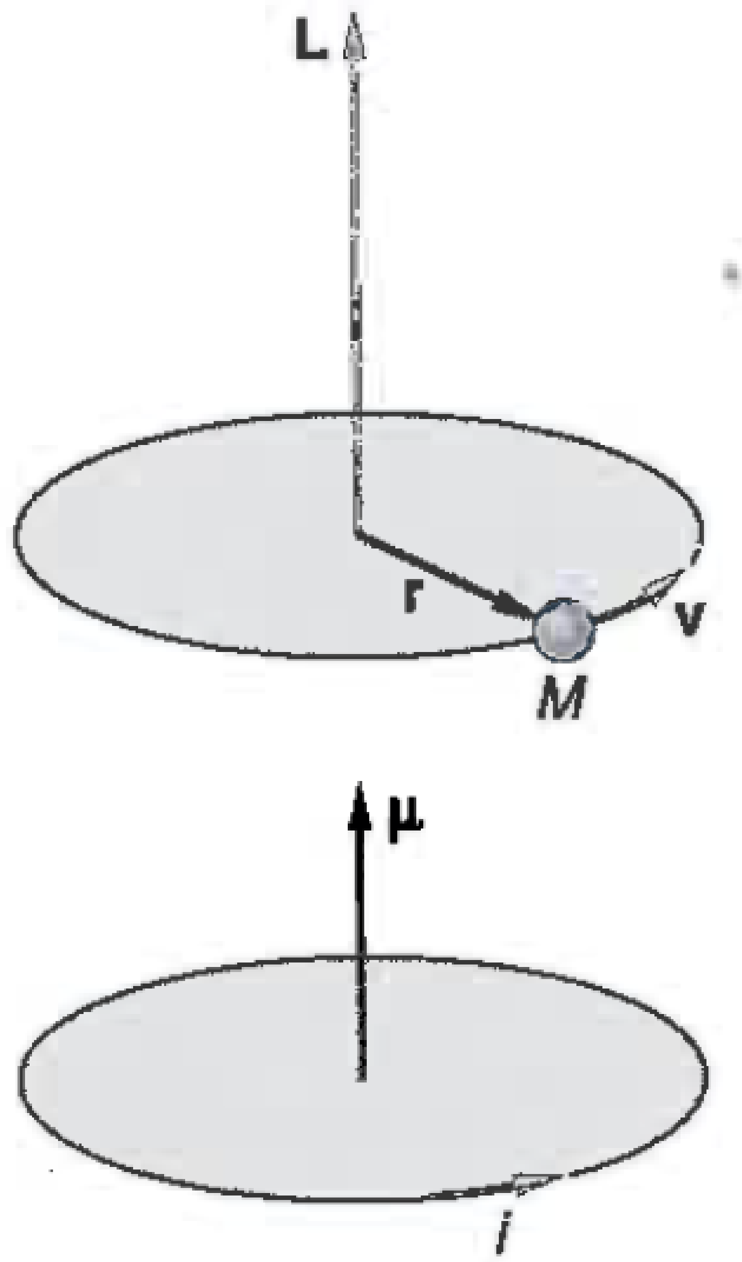
A loop of current is a magnetic dipole moment!!

Electrons in an atom

Orbital motion:

$$\vec{\mu} = \frac{q}{2m_e}\vec{L}$$

$$\vec{\mu} = -\frac{e}{2m_e}\vec{L}$$



Magnetic Moment of Electron Orbital

$$\mu_L = \frac{e}{2m_e} L = \frac{\mu_B}{\hbar} L = \frac{\mu_B}{\hbar}\sqrt{l(l+1)}\hbar = \sqrt{l(l+1)}\mu_B$$

Bohr magneton: $$\mu_B = \frac{e\hbar}{2m_e}$$

$$\mu_{Lz} = -\frac{e\hbar}{2m_e} m = -m\mu_B$$

In general:

$$\mu = \sqrt{l(l+1)} g\mu_B$$

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

$$\mu_z = -mg\mu_B$$

Gyromagnetic ratio (g-factor):

$$\mu_L = \sqrt{l(l+1)}\mu_B$$

g could be g_L or g_S

$$\mu_{Lz} = -\mu_B m$$

$$g_L = 1$$

Magnetic Moment of Electron Spin

$$\vec{\mu}_S = -\frac{g_S \mu_B}{\hbar} \vec{S}$$

$$\mu_S = \frac{g_S \mu_B}{\hbar} S = g_S \sqrt{s(s+1)} \mu_B = g_S \sqrt{\frac{3}{4}} \mu_B$$

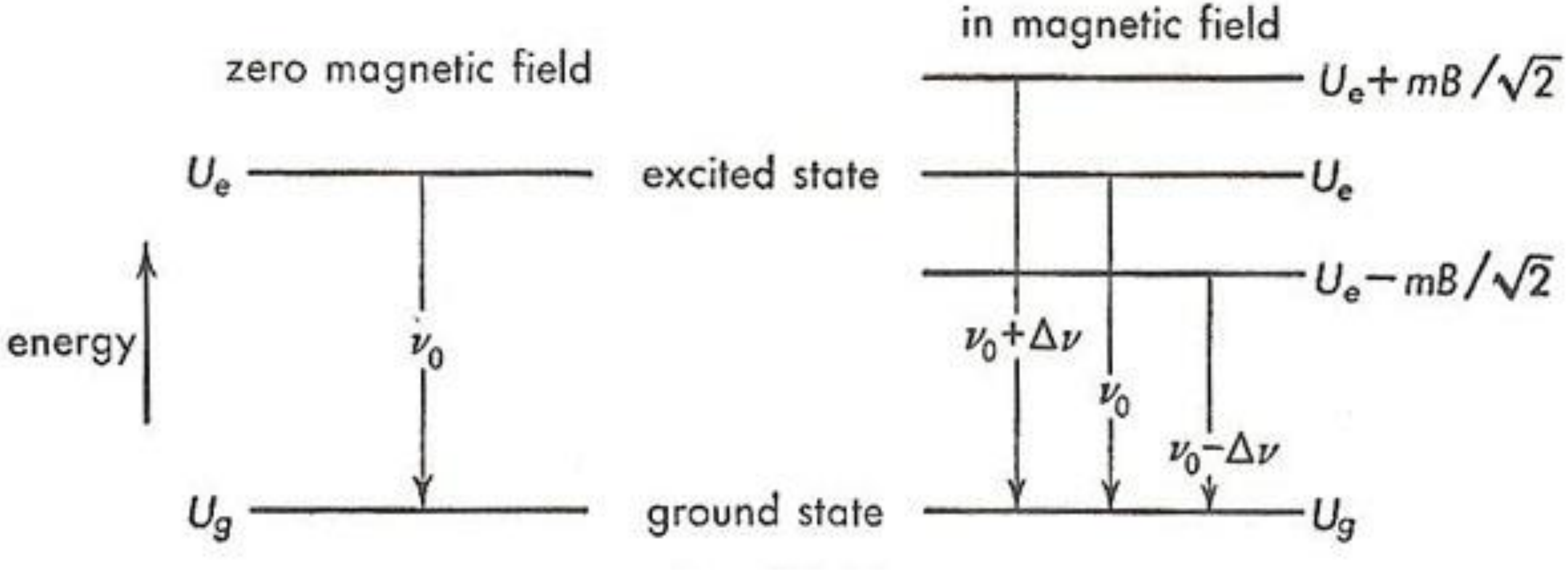
$$\mu_{Sz} = -g_S m_s \mu_B = \pm \frac{1}{2} g_S \mu_B$$

From Stern-Gerlach experiment:

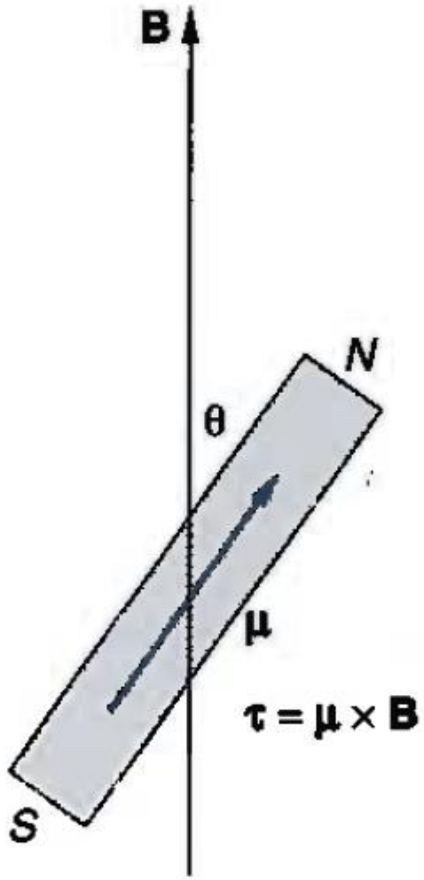
$$g_S = 2.002319$$

Magnetic Moment in Magnetic Field

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



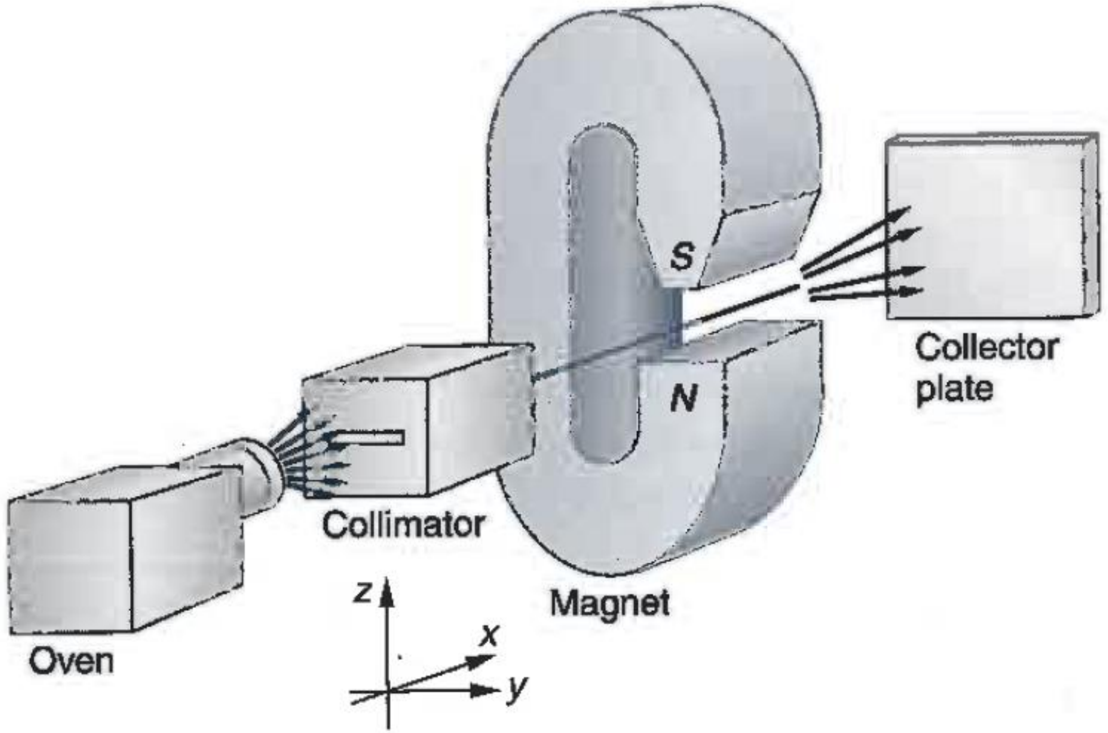
$$\vec{\tau} = \vec{\mu} \times \vec{B}$$



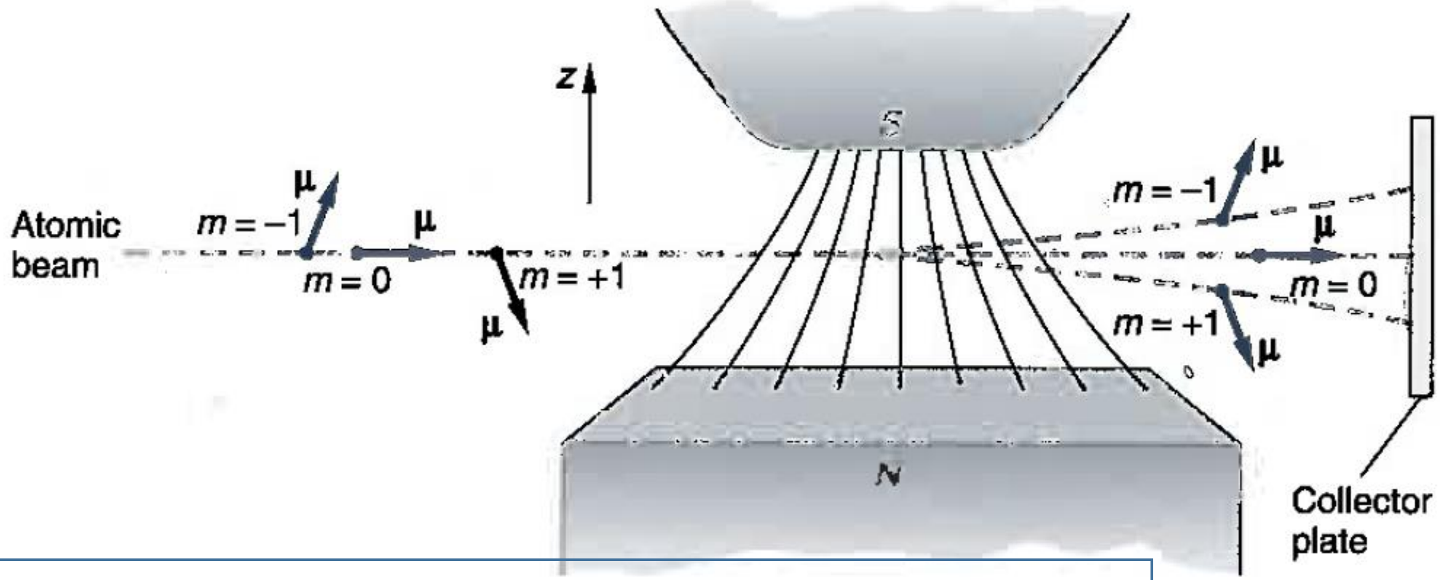
Stern-Gerlach Experiment

$$\vec{F} = -\nabla U_m = -\nabla\left(-\vec{\mu} \cdot \vec{B}\right)$$

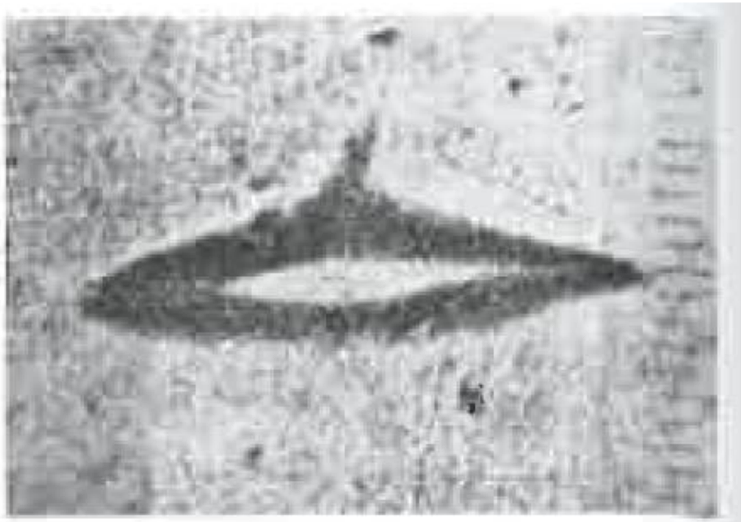
$$F_z = \mu_z(dB/dz) = -mg\mu_B(dB/dz)$$



Stern-Gerlach Experiment



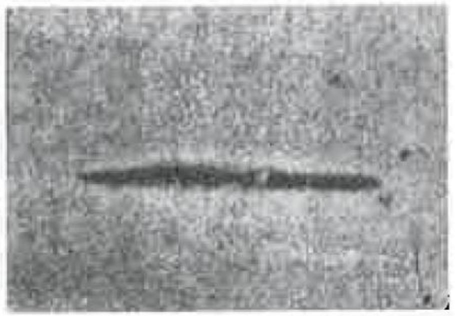
Reality for Silver (l = 0):



Electron Spin made it so!

Expected:

l = 1



l = 0

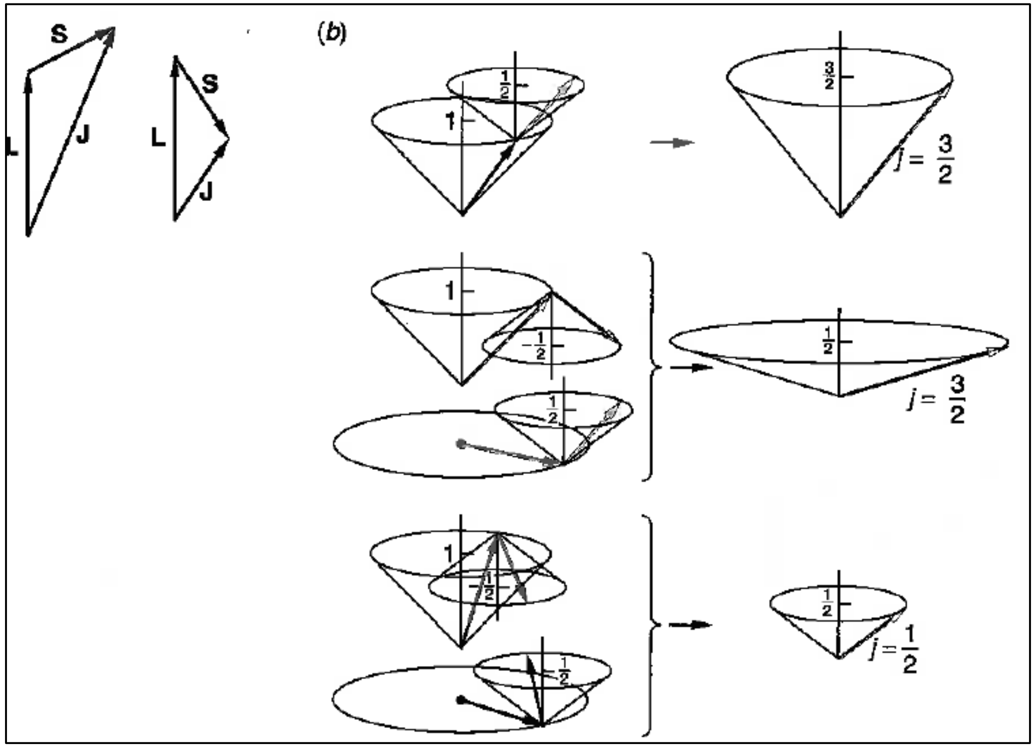
Total Angular Momentum

$$\vec{J} = \vec{L} + \vec{S}$$

$$|\vec{J}| = \sqrt{j(j+1)}\hbar$$

$j = l + s$ or $j = |l - s|$

$$J_z = m_j \hbar$$



Total angular momentum of two electrons with different L

$$\vec{J} = \vec{L}_1 + \vec{L}_2$$

$$j = l_1 + l_2, l_1 + l_2 - 1, \ldots, |l_1 - l_2|$$

Spectroscopic Notation

$$n^{2s+1}l_j$$

$1^2S_{1/2}$ (n=1; l=0; s=1/2; j=1/2)

$2^2S_{1/2}$ (n=2; l=0; s=1/2; j=1/2)

$2^2P_{1/2}$ (n=2; l=1; s=1/2; j=1/2)

$2^2P_{3/2}$ (n=2; l=1; s=1/2; j=3/2)

Spin-Orbit Coupling

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