Zeeman Effect

- Hydrogen Atom: 3D Spherical Coordinates
  - Ψ = (spherical harmonics)(radial) and probability density P
  - E, L^2, Lz operators and resulting eigenvalues

- Angular momenta: Orbital L and Spin S
  - Addition of angular momenta
  - Magnetic moments and Zeeman effect
  - Spin-orbit coupling and Stern-Gerlach (Proof of electron spin s)

- Periodic table
  - Relationship to quantum numbers *n, l, m*
  - Trends in radii and ionization energies

<u>Schrödinger Equation</u>: Coordinate Systems

<u>1D Cartesian</u>

Kinetic energy Potential energy Total energy

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x)$$

<u>3D Cartesian</u>

Kinetic energy Potential energy Total energy

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

Convert to spherical using: $x=r\sin\theta\cos\phi,\ y=r\sin\theta\sin\phi,\ z=r\cos\theta$

<u>3D Spherical</u>

Kinetic energy Potential energy

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

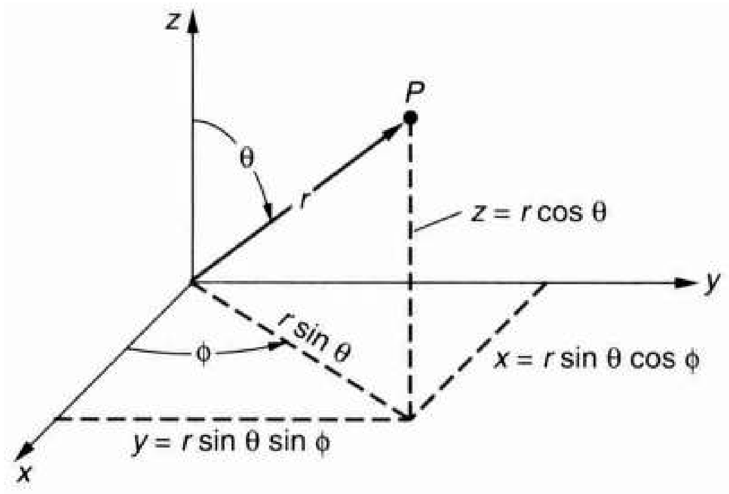
$$=E\psi$$ Total energy

Hydrogen Atom: 3D Spherical Schrödinger Equation

“Rewritten” Schrodinger Eqn.:

$$\frac{\hat{p}^2}{2\mu}\psi(r,\theta,Q)+V_{eff}\psi(r,\theta,Q)=E_n\psi(r,\theta,Q)$$

where $\hat{p}^2=-\hbar^2\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right]$



Eigenfunctions:

$$\psi_{nlm}(r,\theta,\phi)=\underline{R_n(r)}\;\underline{\underline{Y_{lm}(\theta,\phi)}}$$

Laguerre Polynomials

Spherical Harmonics

Eigenvalues: $E_n=\frac{-z^2E_0}{n^2}$ where $E_0=\frac{1}{2}\left(\frac{ke^2}{\hbar}\right)^2\mu\approx 13.6eV$

Hydrogen Atom: 3D Spherical Schrödinger Equation

3 Quantum Numbers (3-dimensions)

n = energy level value (average radius of orbit)

n = 1, 2, 3 …

l = angular momentum value (shape of orbit)

l **= 0, 1, 2, … (n – 1)**

m = z component of *l* (orientation of orbit)

m = -*l*,(-*l* + 1) ..0,1,2,..+*l*

How many quantum states (n, l, m) exist for n = 3? Is there a general formula?

Wave Functions : Formulas

$n = 1$

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$l = 0$

$$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

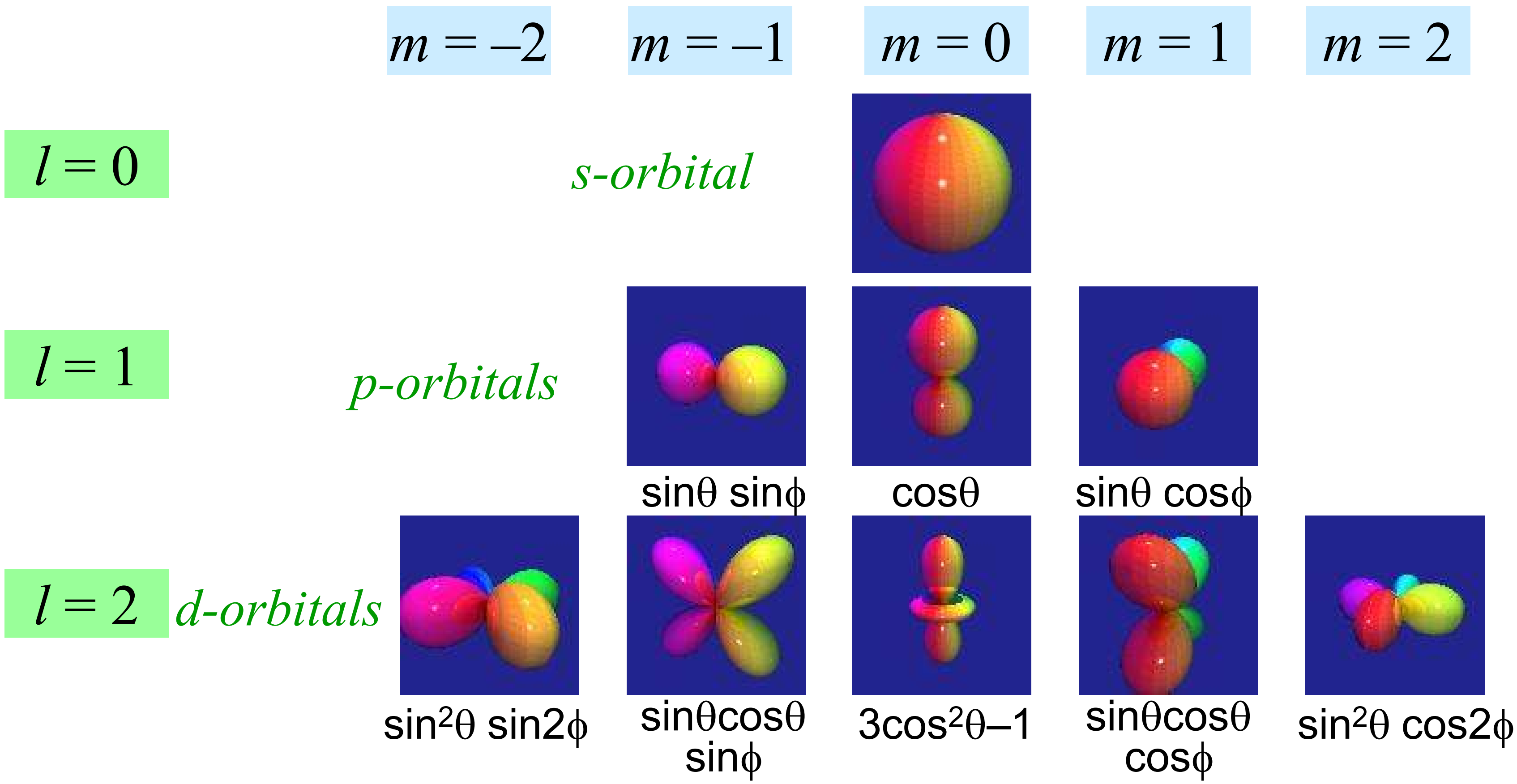
$n = 2$

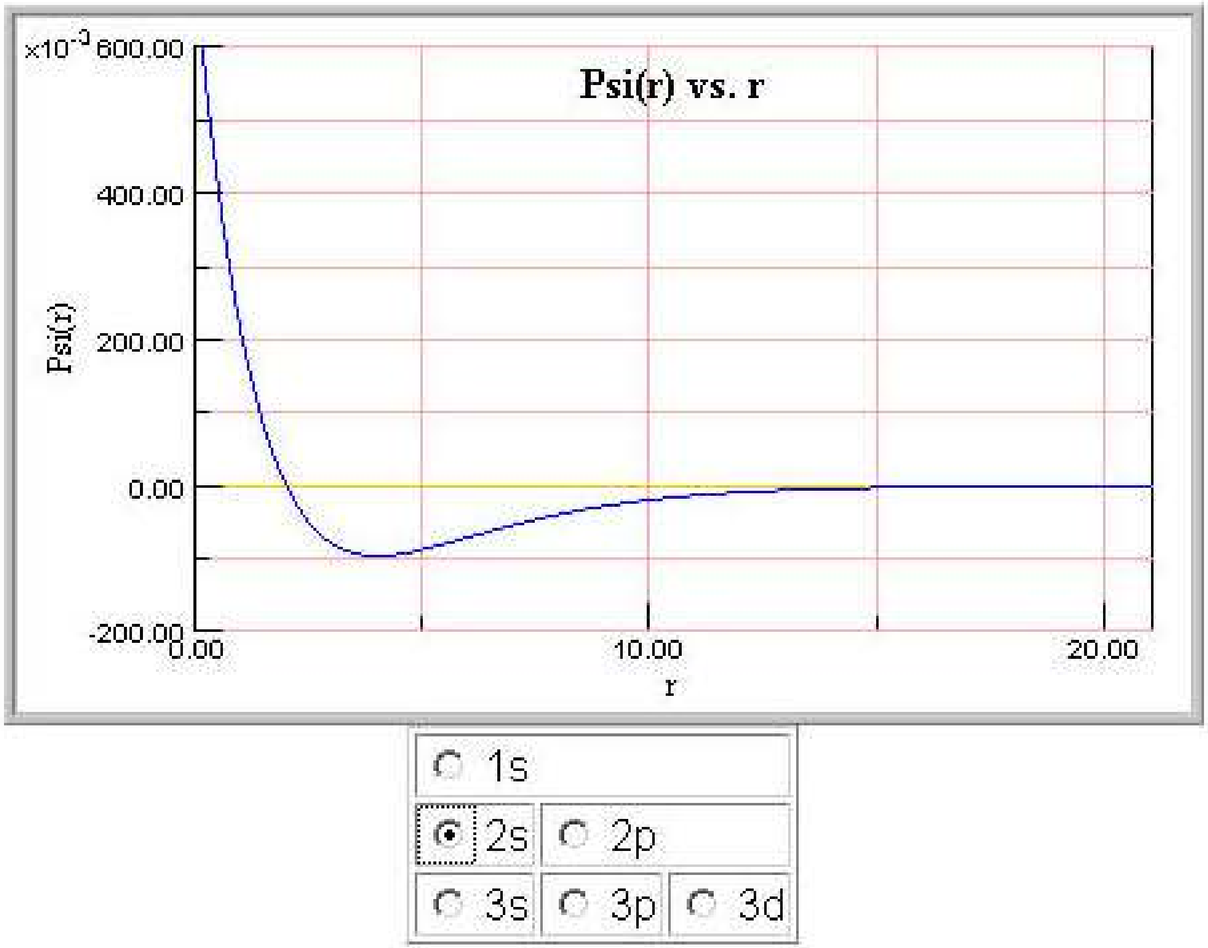
$$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta$$

$l = 1$

$$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin\theta \, e^{\pm i\phi}$$

<u>Wave Functions</u>: Angular Component



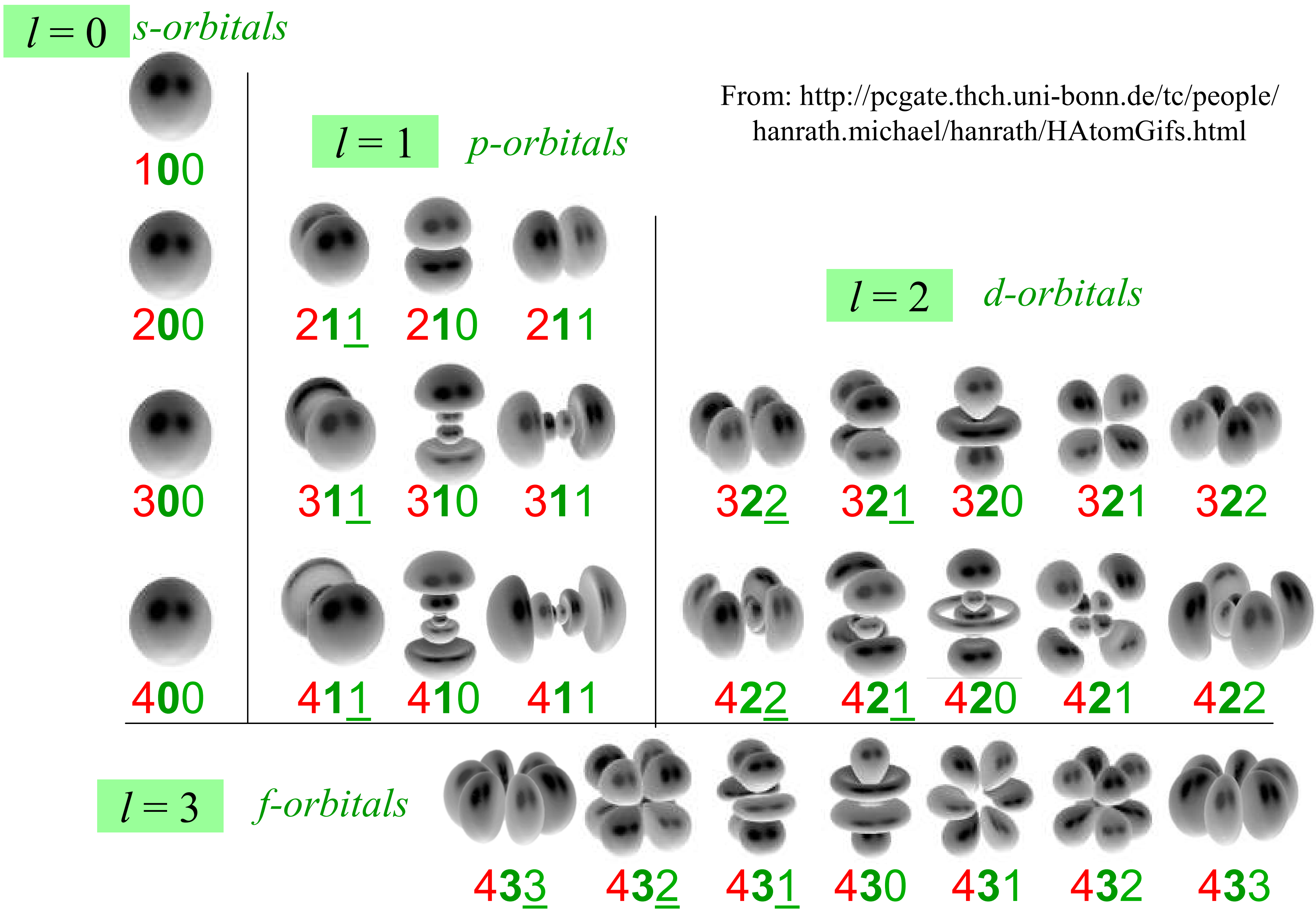


http://cwx.prenhall.com/bookbind/pubbooks/giancoli3/chapter40/multiple3/deluxe-content.html

What is the relationship between the number of zero crossings for the radial component of the wave function and the quantum numbers n and l?

Wave Functions: Angular & Radial Components

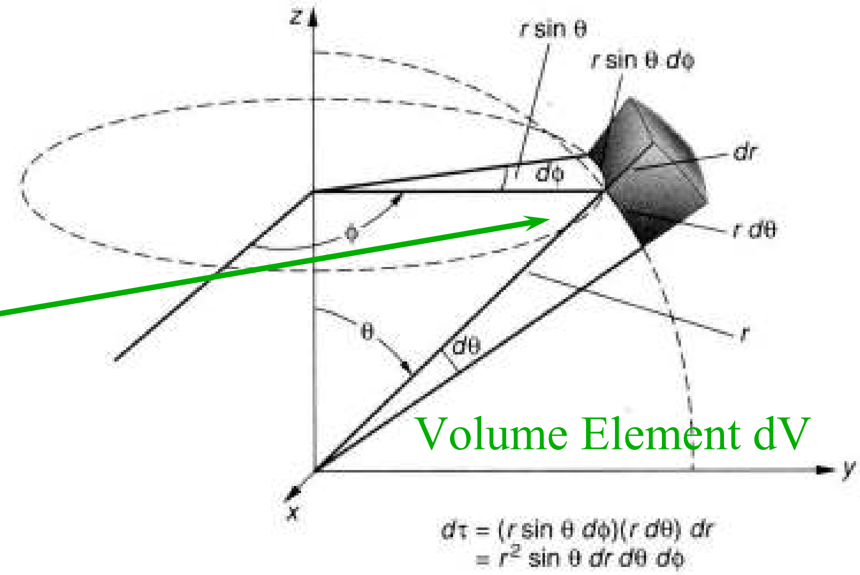
From: http://pcgate.thch.uni-bonn.de/tc/people/hanrath.michael/hanrath/HAtomGifs.html



Probability Density: Formula

$$P = \int \psi^* \psi(r,\theta,\phi) dV$$

$$= \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi^* \psi \boxed{r^2 \sin\theta d\varphi d\theta dr}$$



$$P = 4\pi \int_0^\infty \psi^* \psi r^2 dr \text{ for spherically symmetric } \psi$$

$$\boxed{P = \int_0^\infty P(r) dr \quad \text{where} \quad P(r) = \left(4\pi r^2\right) \psi^* \psi}$$

$\Rightarrow$For small Δr, can use P = P(r) Δ r (analogous to 1D case)

Probability Density: "Density" Plots

$$\left|\psi_{200}\right|^2$$

$n = 2$

s-orbital

$l = 0$

$$\left|\psi_{210}\right|^2$$

$n = 2$

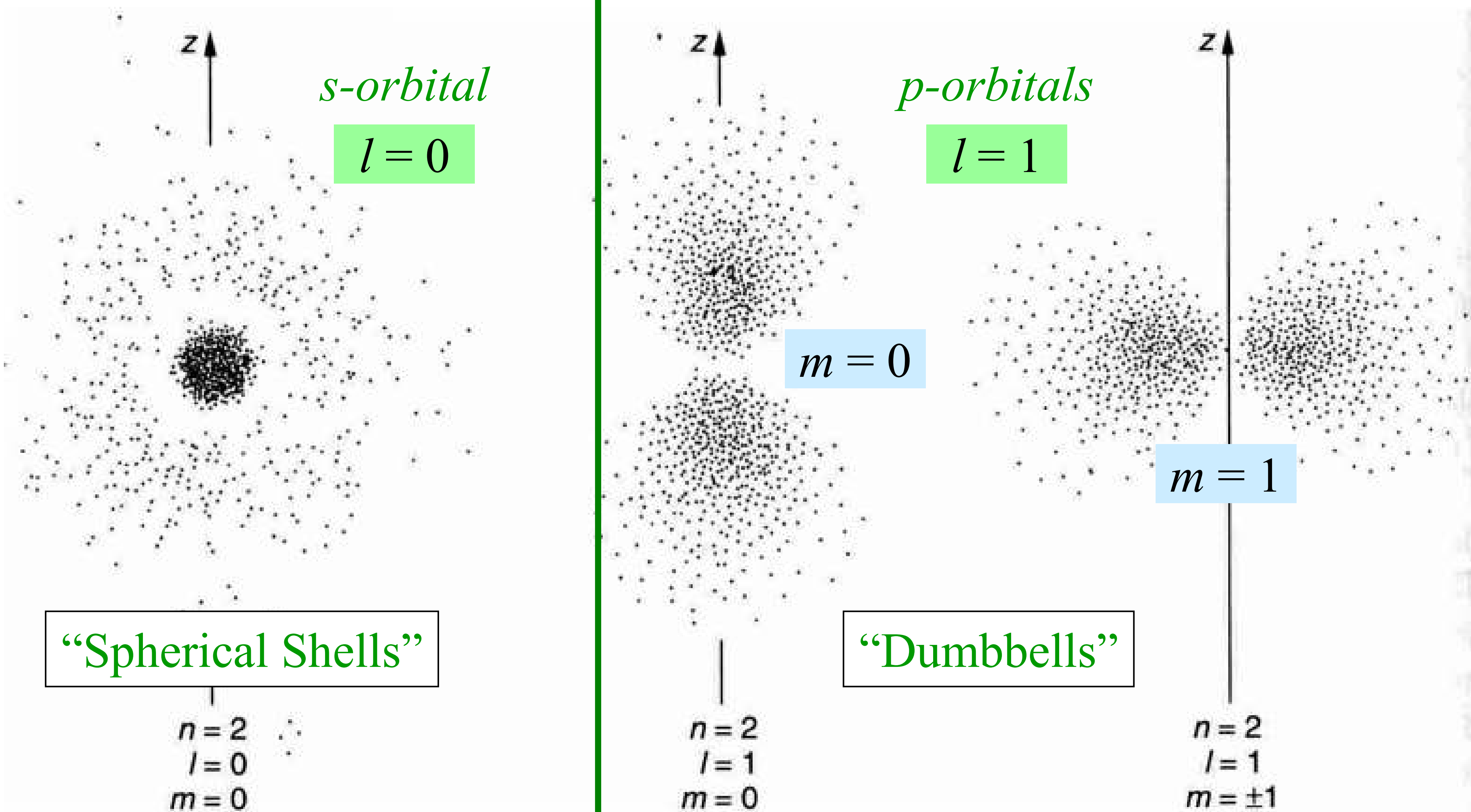
$$\left|\psi_{21\pm1}\right|^2$$

p-orbitals

$l = 1$

$m = 0$

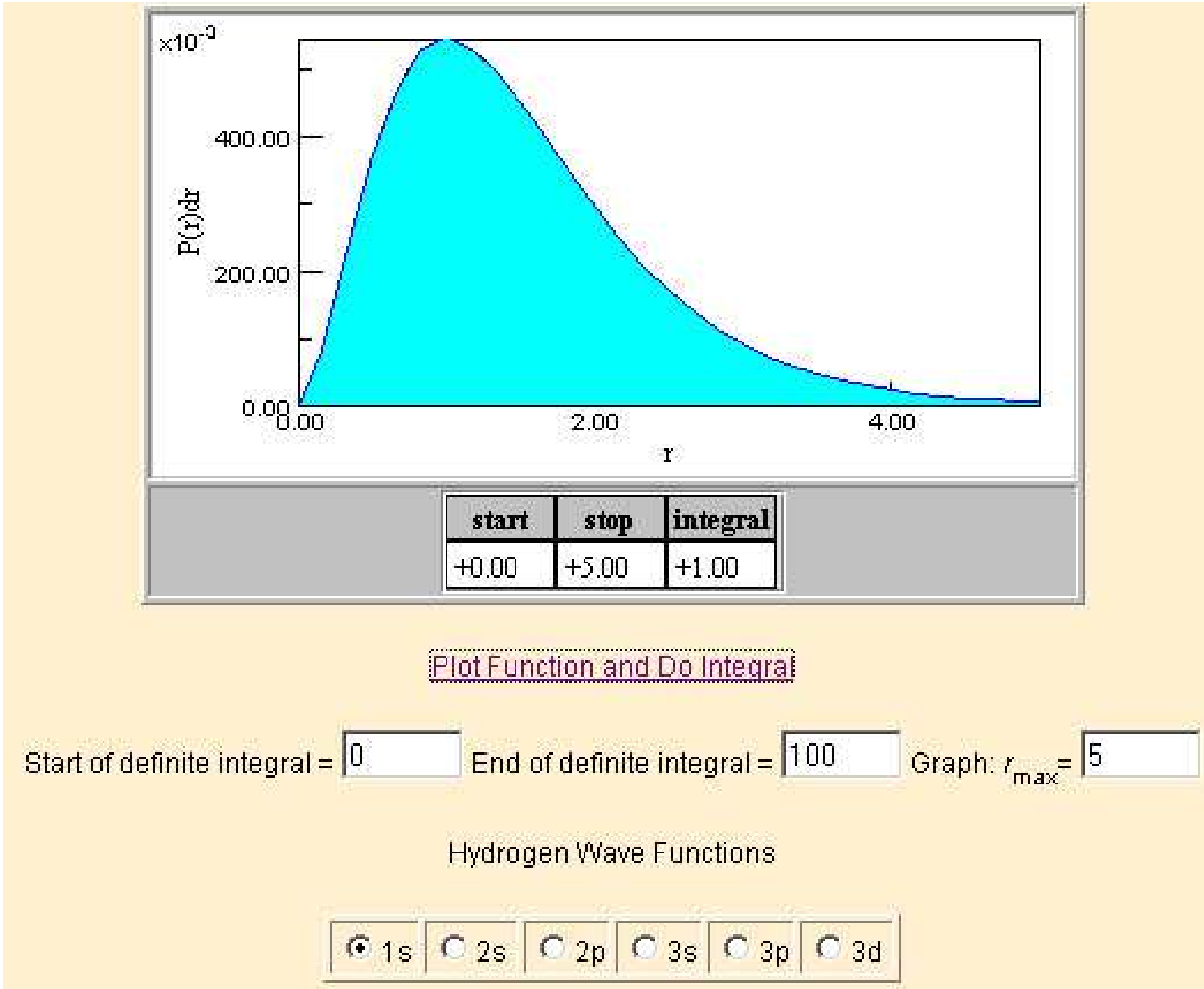
$m = 1$



"Spherical Shells"

"Dumbbells"

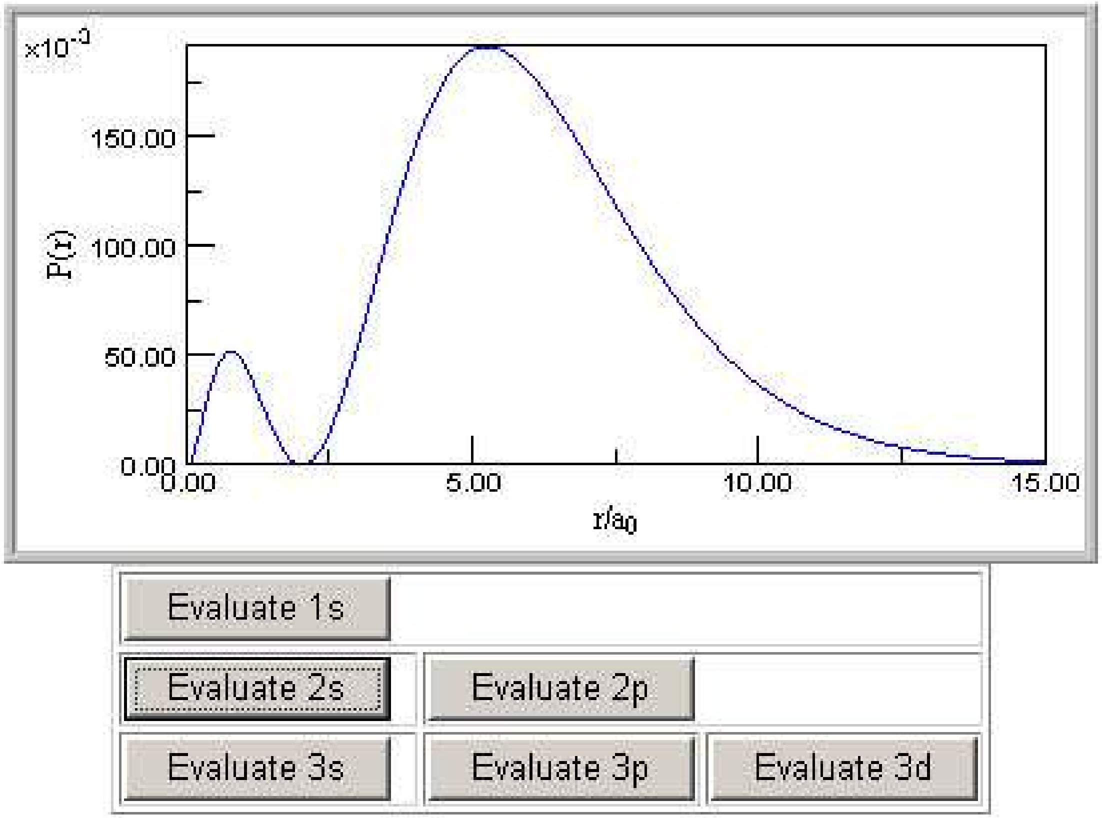
<u>Probability Density</u>: Cross Sections



http://webphysics.davidson.edu/faculty/dmb/hydrogen/default.html

Can you draw the radial probability functions for the 2s to 3d wave functions?

<u>Probability Density</u>: Cross Sections



http://cwx.prenhall.com/bookbind/pubbooks/giancoli3/chapter40/multiple3/deluxe-content.html

Rank the states (1s to 3d) from smallest to largest for the electron's most PROBABLE radial position.

For which state(s) do(es) the most probable value(s) of the electron's position agree with the Bohr model?

Probability Density: Problem

For the ground state $n = 1$, $l = 0$, $m = 0$ of hydrogen, calculate the probability $P(r)\Delta r$ of finding the electron in the range $\Delta r = 0.05a_o$ at $r = a_o/2$

$$P_{100}(r)\Delta r = (4\pi r^2)\left[\Psi_{100}(r)\right]^2 \Delta r$$

$$where\ \Psi_{100}(r) = \frac{e^{-r/a_o}}{\sqrt{\pi}a_o^{1.5}} \quad and \quad \left[\Psi_{100}(r)\right]^2 = \frac{e^{-2r/a_o}}{\pi a_o^3}$$

$$P_{100}(a_o)\Delta r = (\pi a_o^2)\left(\frac{e^{-a_o/a_o}}{\pi a_o^3}\right)(0.05a_o)$$

$$after\ substitution\ of\ r, \Psi_{100}, and\ \Delta r$$

$$\boxed{P_{100}(a_o)\Delta r} = e^{-1}(0.05) = \boxed{0.018}$$

Orbital Angular Momentum L:
Related to Orbital "Shape"

- Magnitude of Orbital Angular Momentum L

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

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

- Z-component of L

$$\hat{L}_z\psi(r,\theta,\phi) = -i\hbar\frac{\partial}{\partial\phi}\psi = m\hbar\psi$$

Eigenvalues: $\boxed{L_z = m\hbar}$

Orbital Momentum L: Vector Diagram

For ***l* = 2**, find the magnitude of the angular momentum **L** and the possible *m* values. Draw a vector diagram showing the orientations of **L** with the z axis.

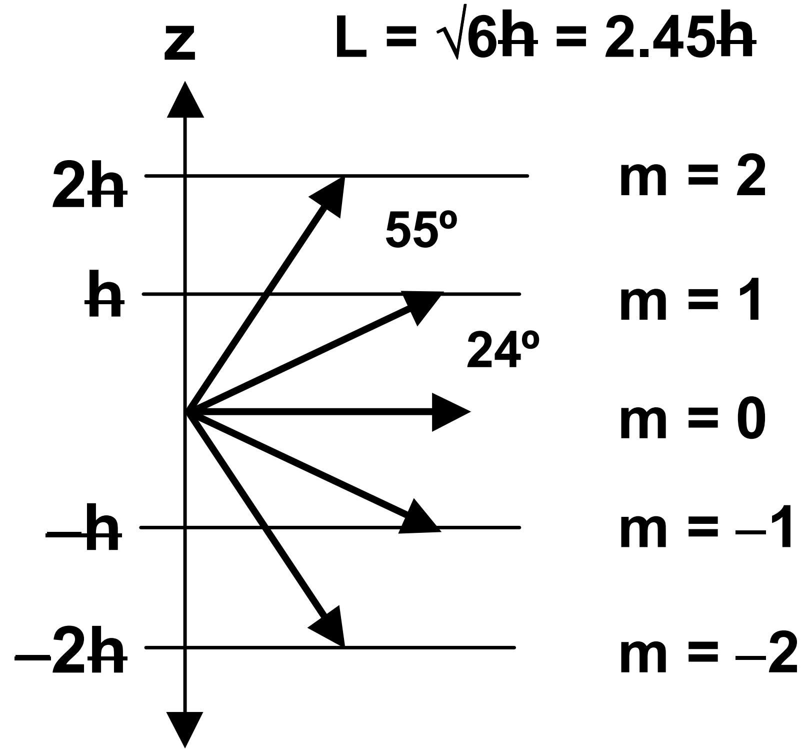
$$l = 2$$

$$L = \sqrt{l(l+1)}\,\hbar = \sqrt{2(2+1)}\,\hbar$$

$$L = \underline{\sqrt{6}\,\hbar} \;\; or\ 2.45\,\hbar$$

$$m = -l \;\; to \;\; l = 0,\ \pm 1\ \pm 2$$

$$L_z = m\,\hbar = 0,\ \pm 1\hbar,\ \pm 2\hbar$$



Can you draw the vector diagram for l = 3? For j = 3/2?

Spin Angular Momentum S:
Property of Electron

- Magnitude of Spin Angular Momentum S

Eigenvalues: $\boxed{S = \sqrt{s(s+1)}\ \hbar}$

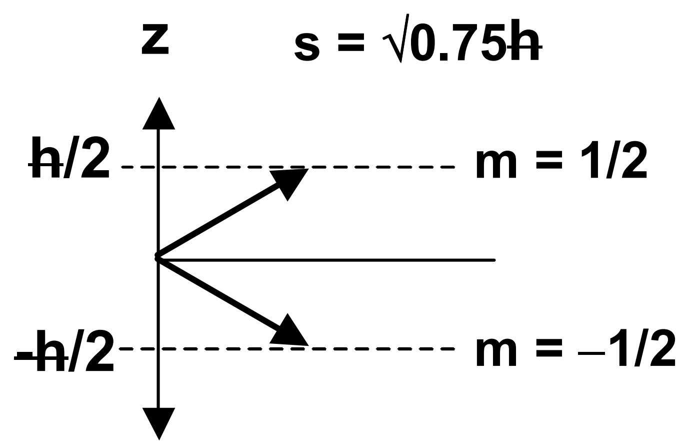
For one electron: $S = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\ \hbar = \sqrt{\frac{3}{4}}\ \hbar$

Example for $s = 1/2$

- Z-component of S

Eigenvalues: $\boxed{S_z = m_s \hbar}$

For one electron: $S_z = \frac{\hbar}{2}$



Angular Momentum: Link to Magnetic Moments

- Orbital angular momentum L and spin angular momentum s of electrons result in magnetic moments μ_l and μ_s.

Remember that $\vec{\boldsymbol{\mu}} = i\vec{A} \rightarrow \left(\frac{qv}{2\pi r}\right)\pi r^2 = \frac{q}{2}(vr) = \frac{q}{2}\left(\frac{\mathbf{L}}{m}\right)$ where $L = mvr$

Orbital $l = 0, 1, 2, \ldots$

$$\vec{\mu}_l = \frac{-g_L \mu_B}{\hbar}\vec{L} = \sqrt{l(l+1)}\,g_L \mu_B$$

z-component $\mu_{lz} = -m_l g_L \mu_B$

Spin: $s = ½$

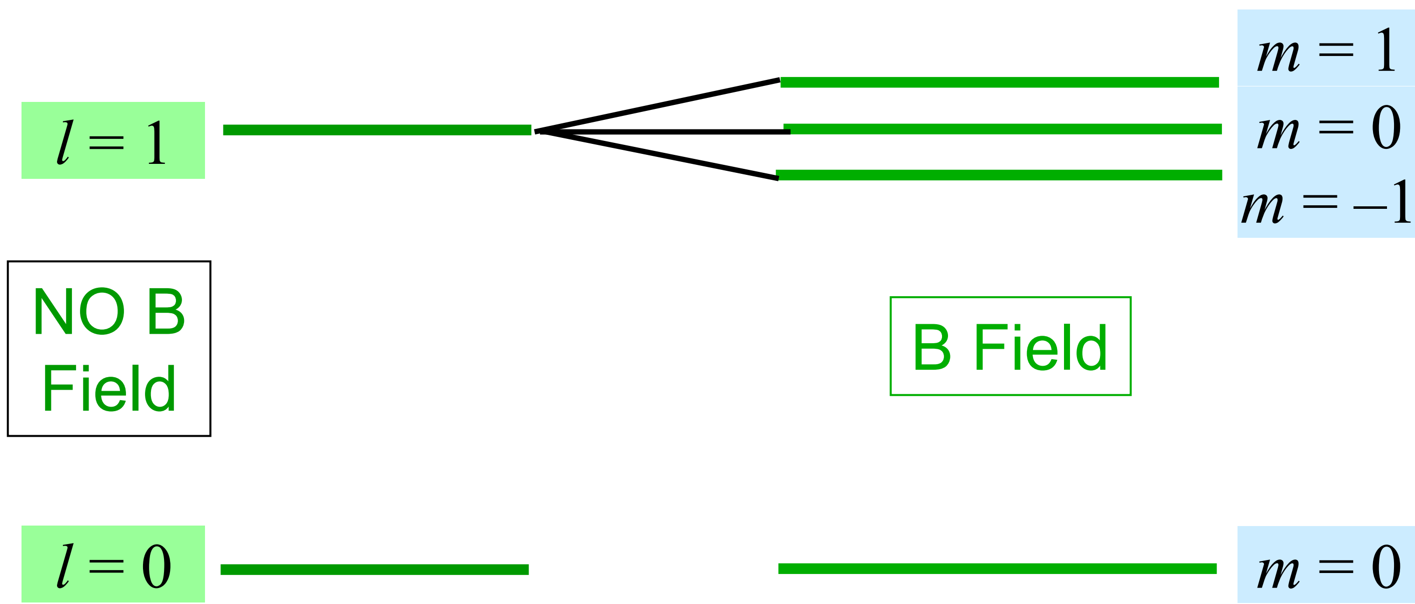
$$\vec{\mu}_s = \frac{-g_s \mu_B}{\hbar}\vec{s} = \sqrt{s(s+1)}\,g_s \mu_B$$

z-component $\mu_{sz} = -m_s g_s \mu_B \approx \pm\mu_B$

where $\vec{\mu}_B = \frac{e\hbar}{2m_e} = 5.79\times10^{-5}\ \frac{\text{eV}}{\text{T}}$ and g_L, g_s = gyromagnetic ratios

Zeeman Effect: Splits *m* values

- Orbital magnetic moment μ_L interacts with an external magnetic field B and separates degenerate energy levels.

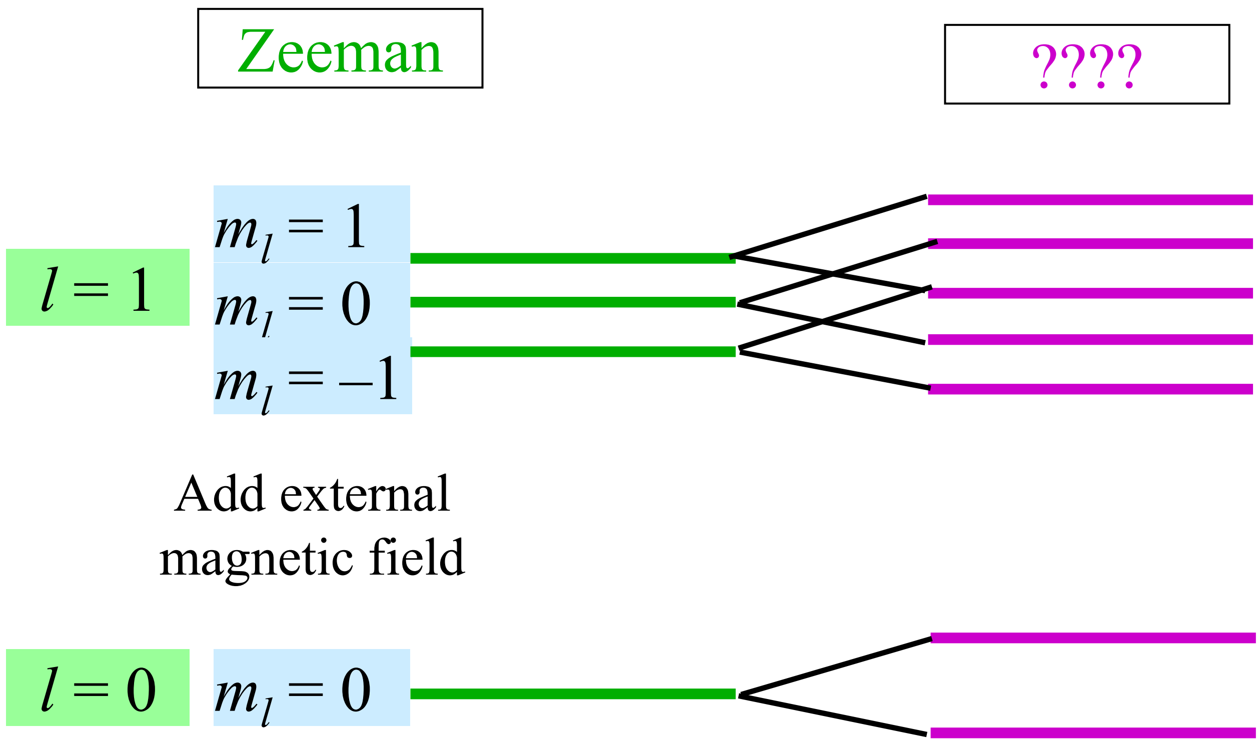


$$U = -\vec{\mu} \cdot \vec{B}_{ext} \Rightarrow \boxed{U = -\mu_{lz} B}$$

assume z direction

Different energies for different m_l values!

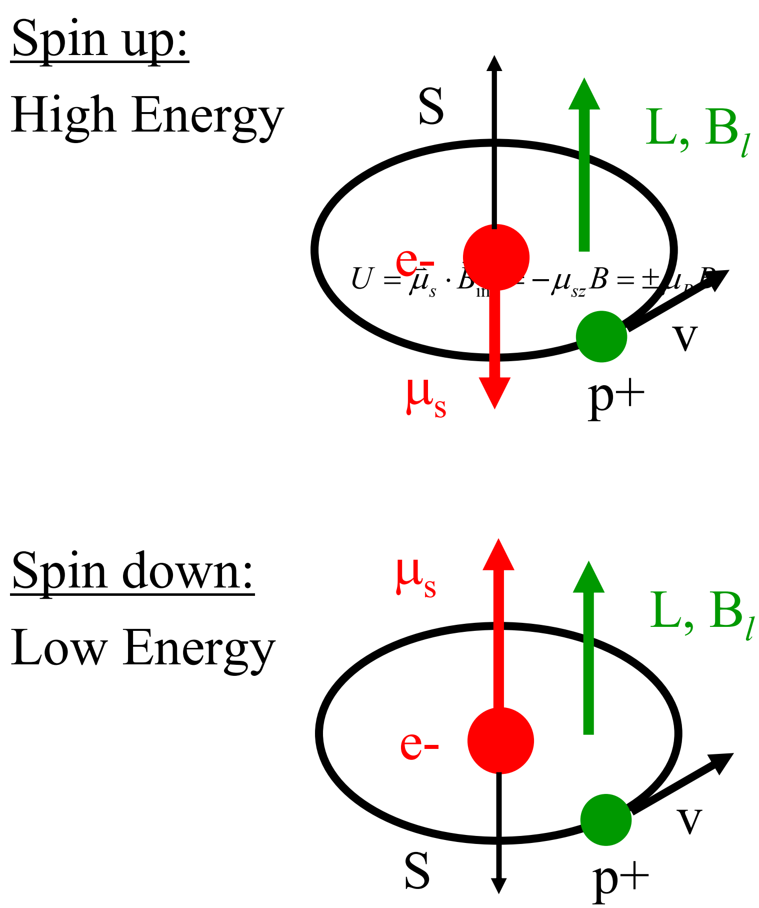
“<u>Anomalous” Zeeman Effect</u>: More Lines??

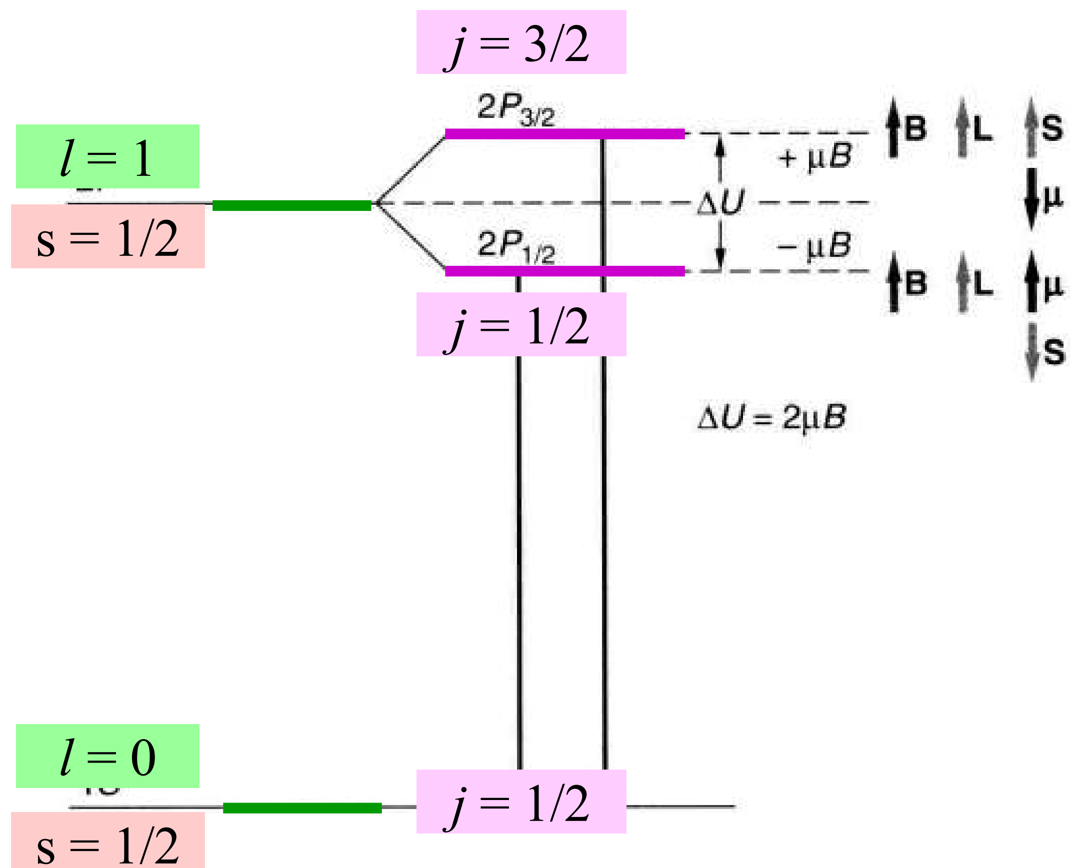


Why are there more energy levels than expected from the Zeeman effect?

- Electron's spin magnetic moment μ_s interacts with internal B field caused by its orbital magnetic moment μ_l and separates energy levels.

Spin-Orbit Coupling: Splits j values





Angular Momentum Addition: L + S gives J

- Special Case: $\boxed{\vec{L}+\vec{S}}$

Vectors

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

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

Quantum Numbers

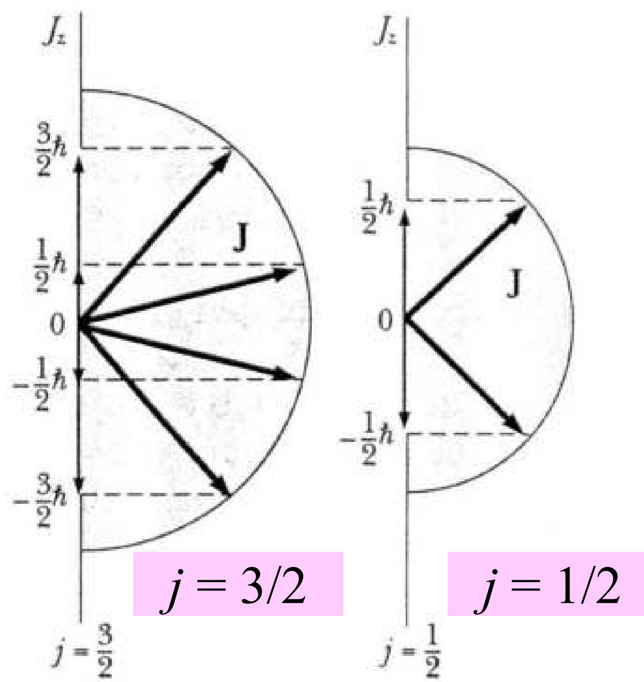
$$j=l+s,\ |l-s|$$

$$m_j=-j,-j+1,\ldots j-1,j$$

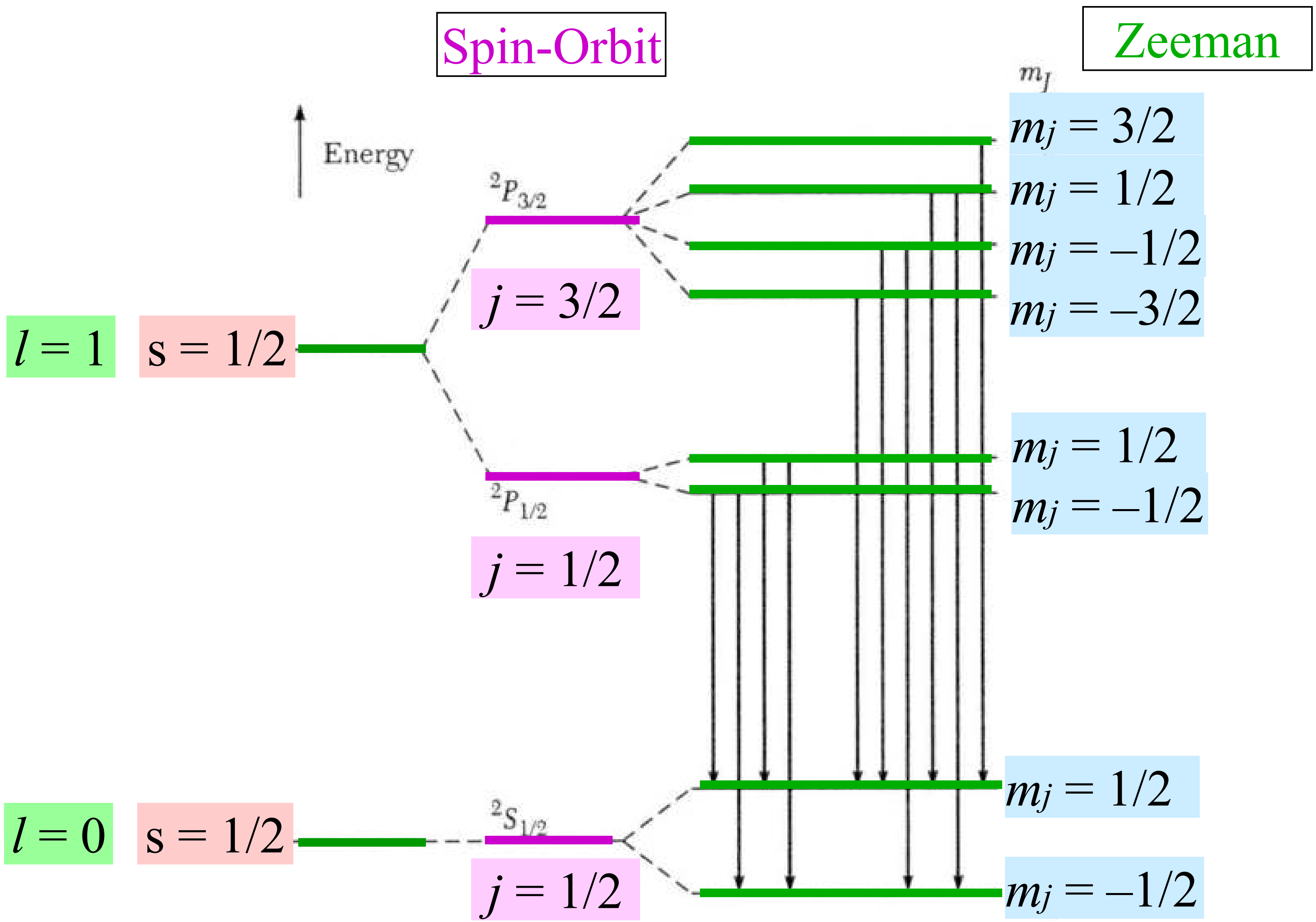
Example: $l=1,\ s=½$

$$j=1+\tfrac{1}{2}=\tfrac{3}{2} \quad \text{and} \quad j=\left|1-\tfrac{1}{2}\right|=\tfrac{1}{2}$$

$$m_j=-\tfrac{3}{2},-\tfrac{1}{2},\tfrac{1}{2},\tfrac{3}{2} \quad \text{and} \quad m_j=-\tfrac{1}{2},\tfrac{1}{2}$$



“Anomalous” Zeeman Effect: Spin-Orbit + Zeeman



- Quantum numbers m_j (j-j coupling) for HIGHER Z elements.

Angular Momentum Addition: General Rules

- **General Case:** $\boxed{\vec{J}_1 + \vec{J}_2}$

Vectors

$$\vec{J}_{tot} = \vec{J}_1 + \vec{J}_2$$

$$\left|\vec{J}_{tot}\right| = \sqrt{j(j+1)}\hbar$$

Quantum Numbers

$$j = (j_1 + j_2), (j_1 + j_2 - 1), \ldots |j_1 - j_2|$$

$$m_j = -j, -j+1, \ldots j-1, j$$

Example: $j_1 = 3/2,\ j_2 = 3/2$

$$j_{\max} = \tfrac{3}{2} + \tfrac{3}{2} = 3 \quad \text{and} \quad j_{\min} = \left|\tfrac{3}{2} - \tfrac{3}{2}\right| = 0$$

$$j = 3,\ 2,\ 1,\ 0$$

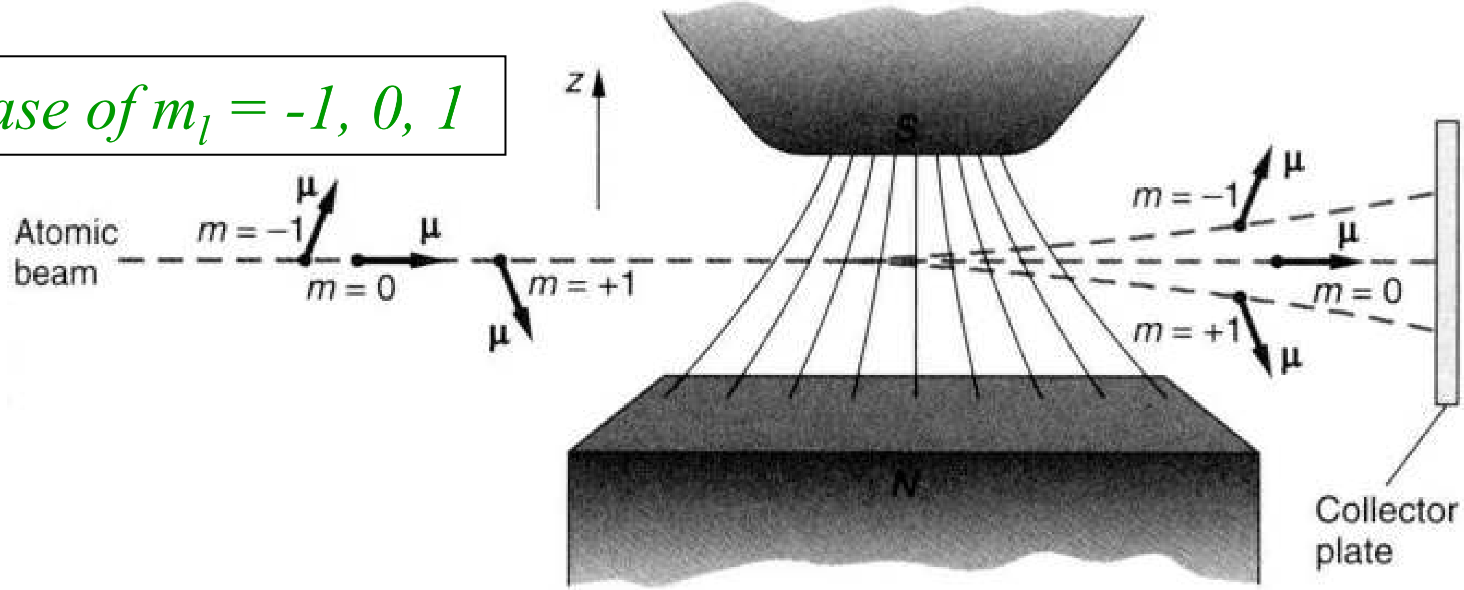
$$m_j = -3, -2, -1, 0, 1, 2, 3 \quad \text{for } j = 3$$

Stern-Gerlach Experiment: ALSO splits *m* values

- A magnetic force $\left(F_z = \mu_z \frac{dB}{dz} \right)$ deflects atoms up or down by an amount that depends on its magnet moment and the B field gradient.

- For hydrogen ($m_{lz} = 0$), two lines are observed (spin up, spin down).
  - Since $l = 0$, this experiment gave direct evidence for the existence of spin.

Case of m_l = -1, 0, 1



What is the "story" of this experiment? Did Stern & Gerlach know about

Stern-Gerlach Experiment: Problem

The angular momentum of the yttrium atom in the ground state is characterized by the quantum number $j = 5/2$. How many lines would you expect to see if you could do a Stern-Gerlach experiment with yttrium atoms?

Remember that in the Stern-Gerlach experiment all of the atoms with different m_j values are separated when passing through an inhomogeneous magnetic field, resulting in the presence of distinct lines.

How many lines would you expect to see if the beam consisted of atoms with $\boldsymbol{l = 1}$ and $\boldsymbol{s = 1/2}$?

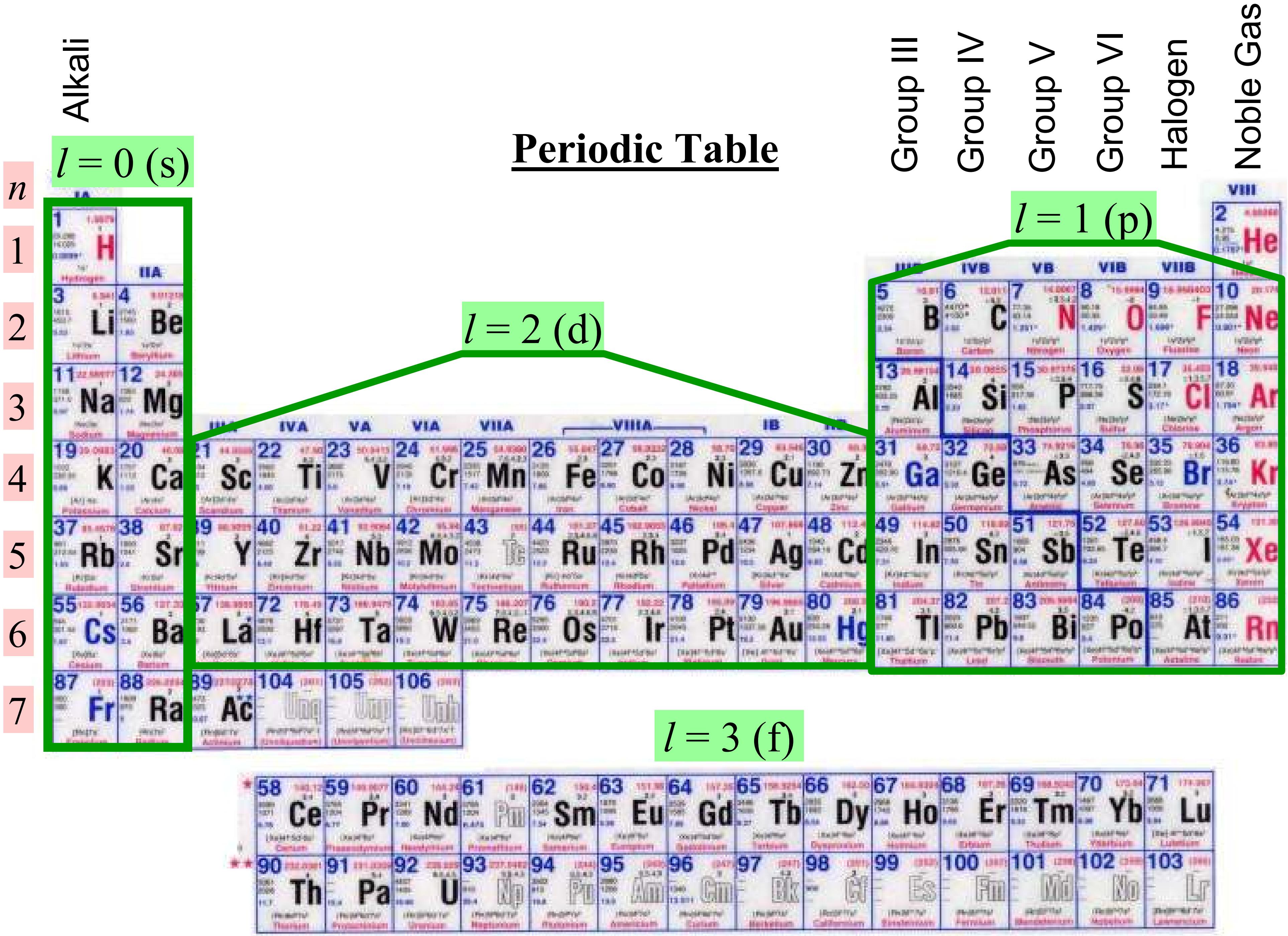
Multi-electron Atoms

$$V_{\text{int}} = \frac{ke^2}{|\vec{r}_2 - \vec{r}_1|}$$

- Schrödinger equation cannot be solved exactly for multi-electron atoms because Coulombic repulsion "mixes" variables.
  - Estimate energies using single-electron wave functions and "correcting" energies with 1$^{\text{st}}$-order perturbation theory.

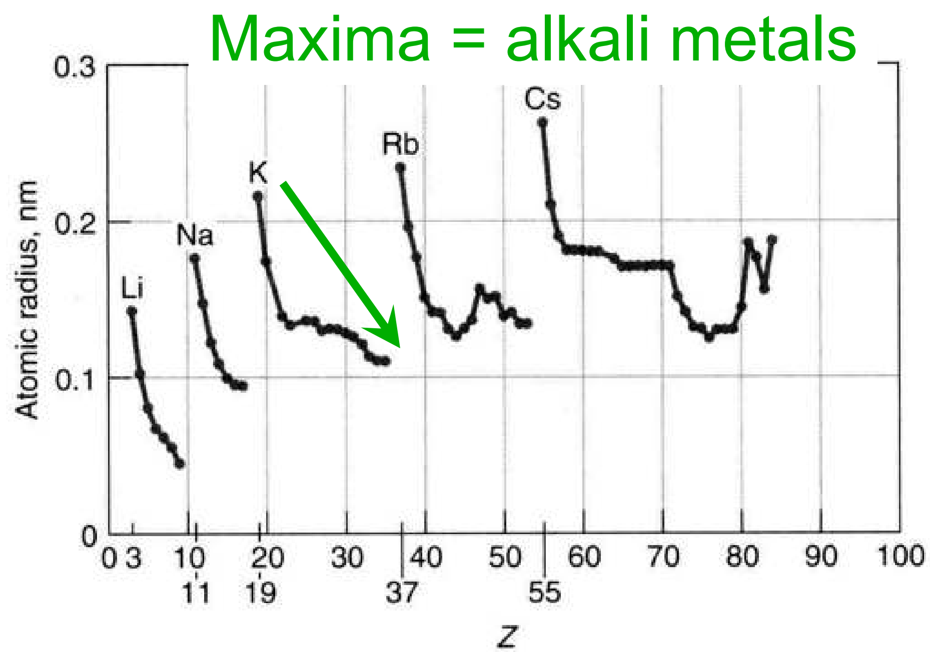
- Orbitals "fill" in table as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p . .
  - Only ONE electron per state (n, l, m_l, m_s) - *Pauli Exclusion Rule!*
  - Why is 4s filled before 3d? $\Rightarrow$ *4s orbital has a small bump near origin and "penetrates" shielding of core electrons better than 3d orbital, resulting in a larger effective nuclear charge and lower energy.*

Periodic Table

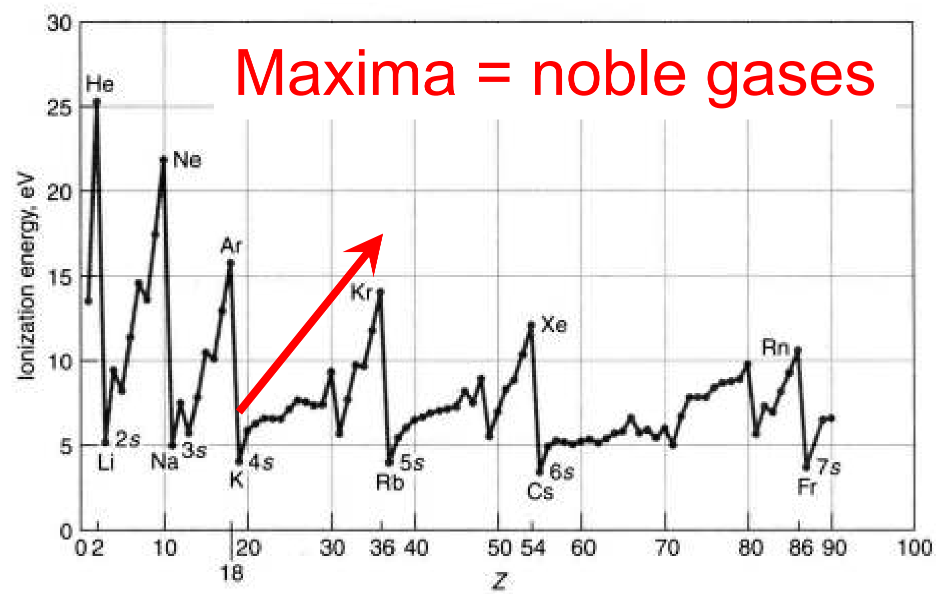


Periodic Table: Trends for Radii and Ionization Energies

- Effective atomic radii decrease across each row of table.
  - Why? Effective nuclear charge increases and more strongly attracts outer electrons, decreasing their radius.



- Ionization energies increase across each row of table until the complete "shell" is filled.
  - Alkali atoms easily give up s-orbital electrons.
  - Halogens have strong affinity for outer electrons.



APPENDIX: Wave Functions Formulas

Spherical Component $Y_{l,m}$

$Y_\ell^{m_\ell}(\theta, \phi)$

s-orbital $l = 0$

$$Y_0^0 = \frac{1}{2\sqrt{\pi}}$$

p-orbital $l = 1$

$$Y_1^0 = \frac{1}{2}\sqrt{\frac{3}{\pi}} \cdot \cos\theta$$

$m = \pm 1$

$$Y_1^{\pm 1} = \mp\frac{1}{2}\sqrt{\frac{3}{2\pi}} \cdot \boxed{\sin\theta}\,\boxed{e^{\pm i\phi}}$$

d-orbital $l = 2$

$$Y_2^0 = \frac{1}{4}\sqrt{\frac{5}{\pi}} \cdot (3\cos^2\theta - 1)$$

$$Y_2^{\pm 1} = \mp\frac{1}{2}\sqrt{\frac{15}{2\pi}} \cdot \sin\theta \cdot \cos\theta \cdot e^{\pm i\phi}$$

$$Y_2^{\pm 2} = \frac{1}{4}\sqrt{\frac{15}{2\pi}} \cdot \sin^2\theta \cdot e^{\pm 2i\phi}$$

f-orbital $l = 3$

$$Y_3^0 = \frac{1}{4}\sqrt{\frac{7}{\pi}} \cdot (5\cos^3\theta - 3\cos\theta)$$

$$Y_3^{\pm 1} = \mp\frac{1}{8}\sqrt{\frac{21}{\pi}} \cdot \sin\theta \cdot (5\cos^2\theta - 1) \cdot e^{\pm i\phi}$$

$$Y_3^{\pm 2} = \frac{1}{4}\sqrt{\frac{105}{2\pi}} \cdot \sin^2\theta \cdot \cos\theta \cdot e^{\pm 2i\phi}$$

$$Y_3^{\pm 3} = \mp\frac{1}{8}\sqrt{\frac{35}{\pi}} \cdot \sin^3\theta \cdot e^{\pm 3i\phi}$$

Complete Wave Function $\psi_{n,l,m}$

$n = 1$ $l = 0$

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$n = 2$ $l = 0,1$

$$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta$$

$$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin\theta\, e^{\pm i\phi}$$

$n = 3$ $l = 0,1,2$

$$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0}$$

$$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0} \cos\theta$$

$$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\boxed{\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0}}\,\boxed{\sin\theta}\,\boxed{e^{\pm i\phi}}$$

$l = 1$ $m = \pm 1$

$$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}(3\cos^2\theta - 1)$$

$$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin\theta\cos\theta\, e^{\pm i\phi}$$

$$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin^2\theta\, e^{\pm 2i\phi}$$