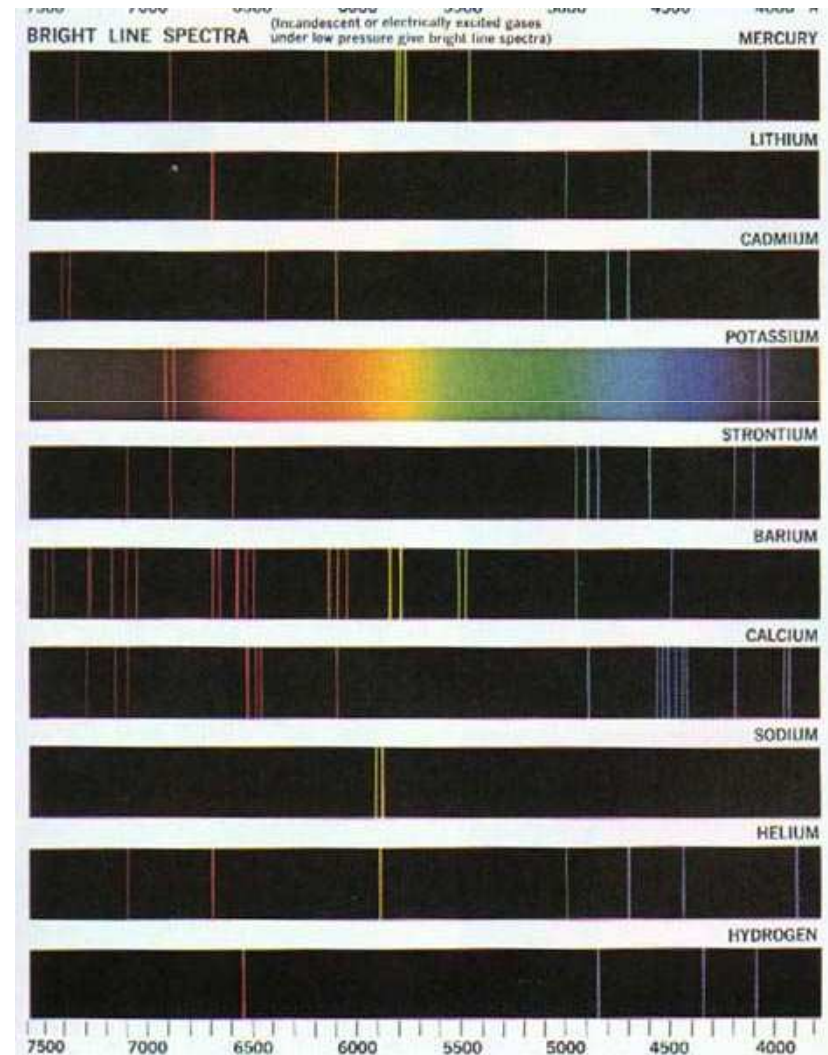
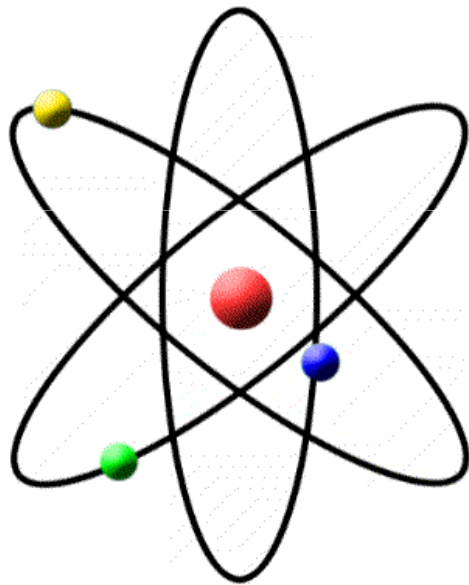


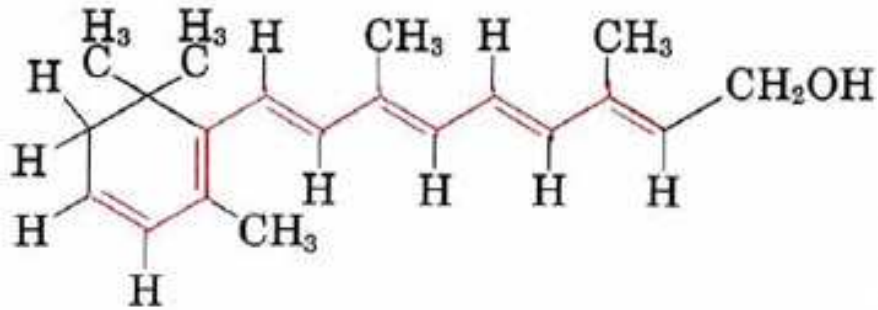
# Repetition: Atomic Structure

Classical physics fails to explain the atomic structure and spectra.



## Particle in a box: conjugated systems

Vitamin A2: 12 delocalized electrons



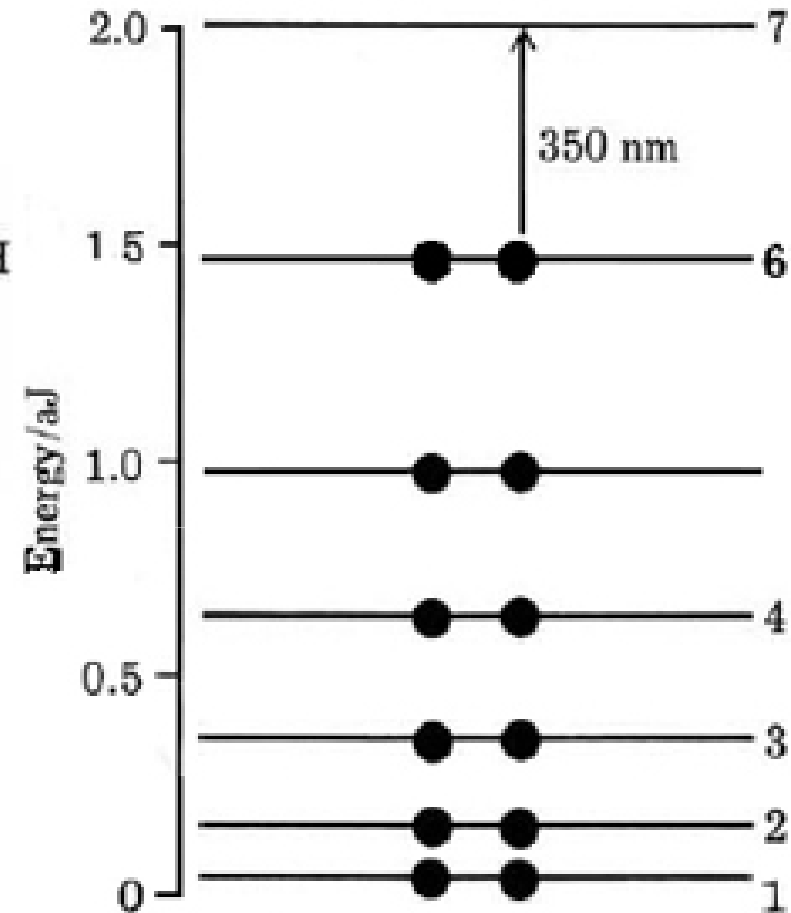
$$m = 9.110 \times 10^{-31} \text{ kg}$$

$$L = 1210 \times 10^{-12} \text{ m}$$

$$n = 6 \text{ to } n = 7$$

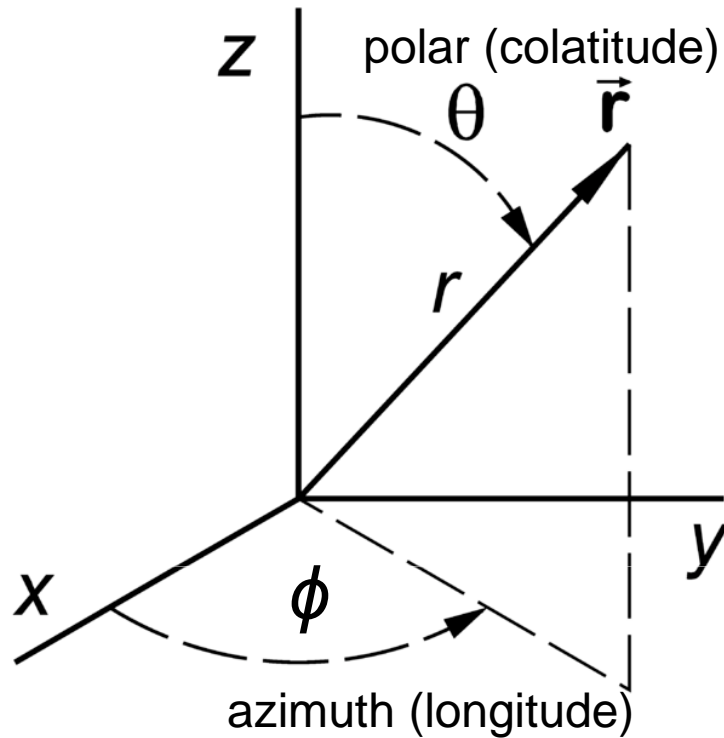
$$\Delta E = E_7 - E_6 = 5.34 \times 10^{-19} \text{ J}$$

$$\lambda = hc/\Delta E = 327 \text{ nm}$$



$$E_n = \frac{n^2 h^2}{8mL^2}$$

# Spherical polar coordinates



Restrictions:

$$r \in [0, \infty) \quad 0 \leq \theta \leq \pi \quad 0 \leq \phi \leq 2\pi$$

Relationship with cartesian coordinates:

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

Volume element:  $dV = r^2 \sin \phi d\phi d\theta dr$ .

Laplacian in spherical polar coordinates:

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

# Solving Schrödinger equation for H-like atoms

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

- Separation of variables:  $\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$

$$\frac{-\hbar^2}{R(r)} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R(r)}{\partial r} \right) + 2mr^2(V(r) - E) - \frac{\hbar^2}{Y(\theta, \phi)} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} \right) = 0.$$

*radial part*

*angular part*

- Separation of variables:  $\psi(\mathbf{r}) = R(r)\Theta(\theta)\Phi(\phi)$

$$\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2} - E \right] R = 0 \quad \text{radial}$$

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left[ l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right] \Theta = 0. \quad \text{polar}$$

$$\frac{d^2\Phi}{d\phi^2} - m_l^2\Phi = 0, \quad \text{azimuthal}$$

# Solving Schrödinger equation for H-like atoms

**Energy:**  $E_n = -\frac{Z^2}{n^2} \left( \frac{me^4}{8\epsilon_0^2 h^2} \right)$   $n =$  principal quantum number

**Wavefunction:**  $\Psi_{n,l,m_l}(r, \theta, \phi) = R_{n,l}(r) Y_{l,m_l}(\theta, \phi)$

$l =$  orbital angular quantum number

$m_l =$  magnetic quantum number

**Radial wavefunction:**

$$R_{nl}(r) = N_{nl} \left( \frac{\rho}{n} \right)^l L_{n,l}(r) e^{-\rho/2n}$$

**Normalization**

associated Laguerre

**Polynomial**

**Exponential**

$$\rho = \frac{2Zr}{a_0}$$

$$a_0 = \frac{\hbar^2}{(e^2/4\pi\epsilon_0) m_e} \quad (\text{Bohr radius})$$

**Angular wavefunction:**

$$Y_{l,m_l}(\theta, \phi) = P_{m_l}^l(\cos \theta) e^{im_l\phi}$$

spheric harmonic

associated Legendre polynomial

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} |\psi_{n,l,m_l}(r, \theta, \phi)|^2 dr \cdot r d\theta \cdot r \sin \theta d\phi = 1$$

# Hydrogenic wavefunctions:

<https://faculty.washington.edu/seattle/physics227/reading/reading-26-27.pdf>

## Radial wavefunctions:

$$R_{1,0} = \left(\frac{Z}{a_0}\right)^{3/2} 2 e^{-\rho}$$

$$R_{2,0} = \left(\frac{Z}{2a_0}\right)^{3/2} 2(1-\rho) e^{-\rho}$$

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

$$R_{3,0} = \left(\frac{Z}{3a_0}\right)^{3/2} 2 \left(1 - 2\rho + \frac{2}{3}\rho^2\right) e^{-\rho}$$

$$R_{3,1} = \left(\frac{Z}{3a_0}\right)^{3/2} \frac{4\sqrt{2}}{3} \rho \left(1 - \frac{1}{2}\rho\right) e^{-\rho}$$

$$R_{3,2} = \left(\frac{Z}{3a_0}\right)^{3/2} \frac{2\sqrt{2}}{3\sqrt{5}} \rho^2 e^{-\rho}$$

## Angular wavefunctions:

$$Y_{0,0} = \sqrt{\frac{1}{4\pi}}$$

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$$

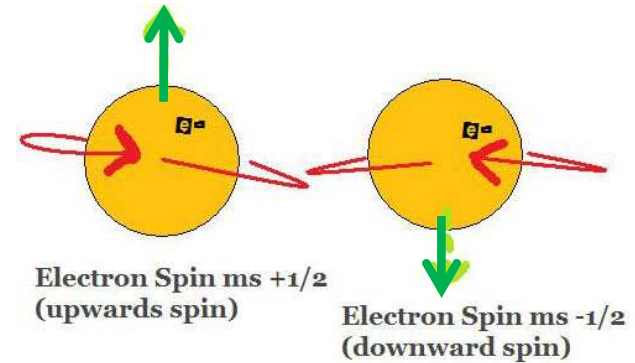
$$Y_{2,0} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

$$Y_{2,\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi}$$

$$Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$$

# The Aufbau principle

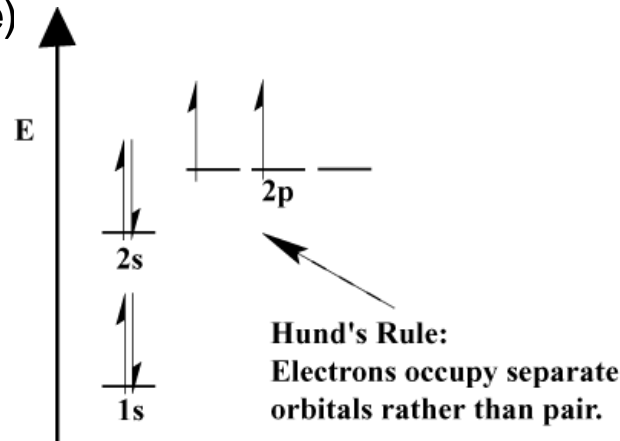
- ✓ No more than two electrons may occupy any given orbital and, if they do so, then their spin must be paired. (**Pauli exclusion principle: the electronic eigenfunction must be antisymmetric with respect to electron change**).



- ✓ The order of orbital occupation in many electron atoms is:  
**1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s...**

- ✓ Electrons occupy different orbitals of a given subshell before doubly occupying any one of them.

- ✓ An atom in its ground state adopts a configuration with the greatest number of unpaired electrons. (**Hund's rule**)



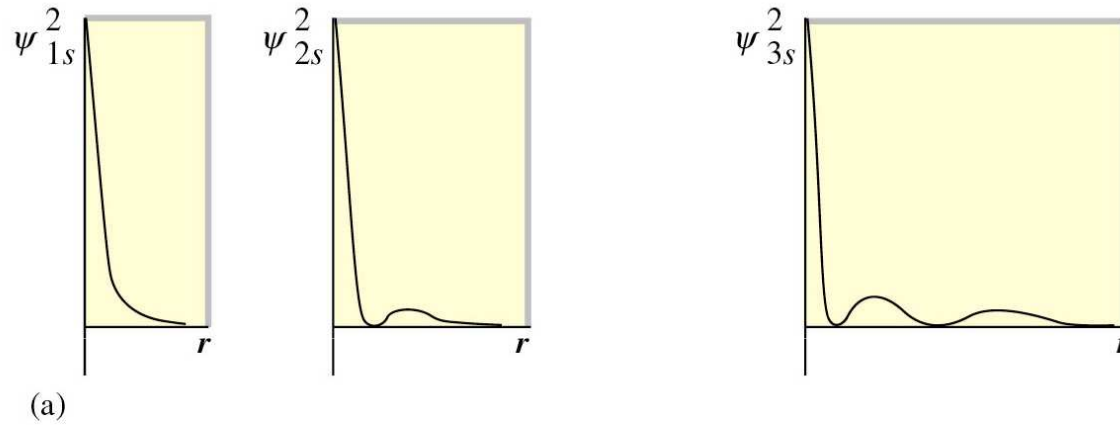
# Orbital shapes: s orbitals

$$n = 1, 2, 3 \dots$$

$$l = 0$$

$$m_l = 0$$

probability distribution

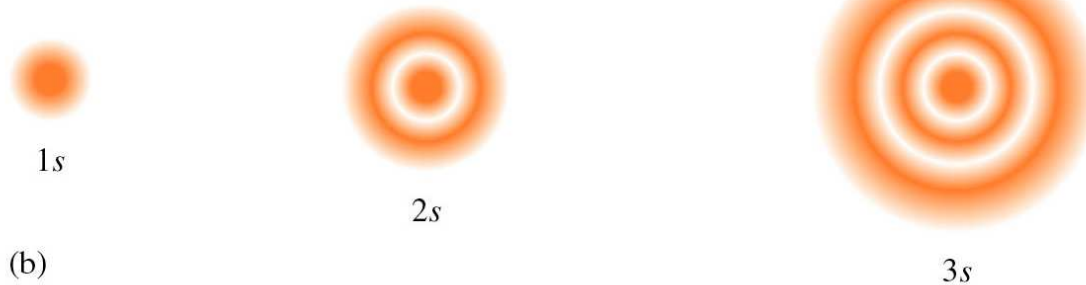


$$R_{n,0} \sim e^{-\rho}$$

$$\rho = \frac{2Zr}{a_0} \quad a_0 = \frac{\hbar^2}{(e^2/4\pi\epsilon_0) m_e}$$

nr. of radial nodes:  $n-1$

$n$  increases, orbital radius increases

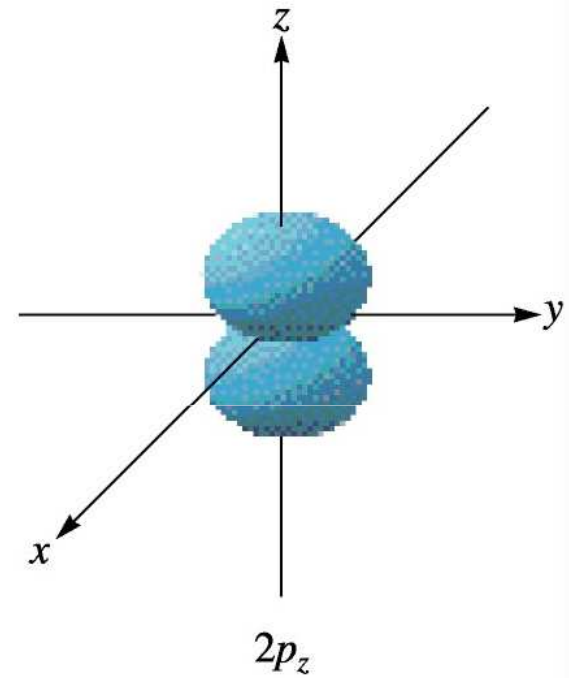
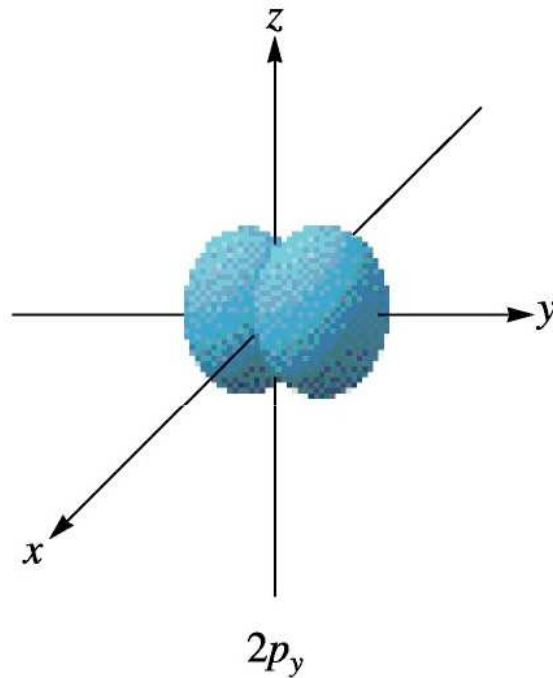
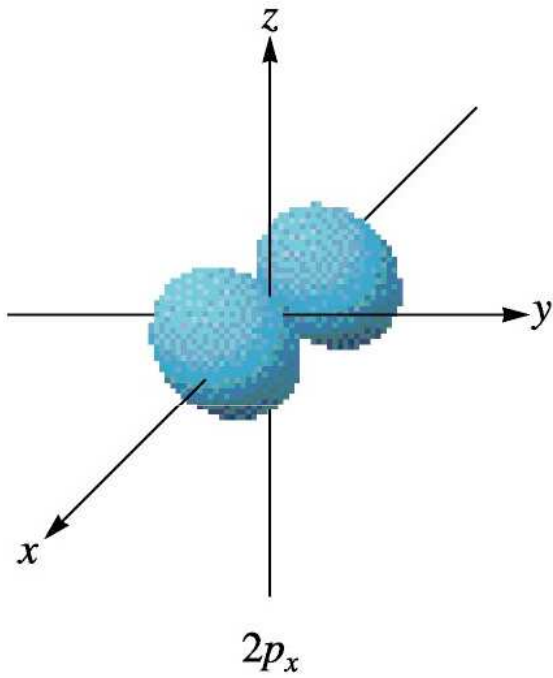


electron density distribution



# Orbital shapes: p orbitals

$n = 2$   
 $l = 1$   
 $m_l = -1, 0, 1$   
one angular node



$m_l = \pm 1$

$m_l = 0$

boundary surface

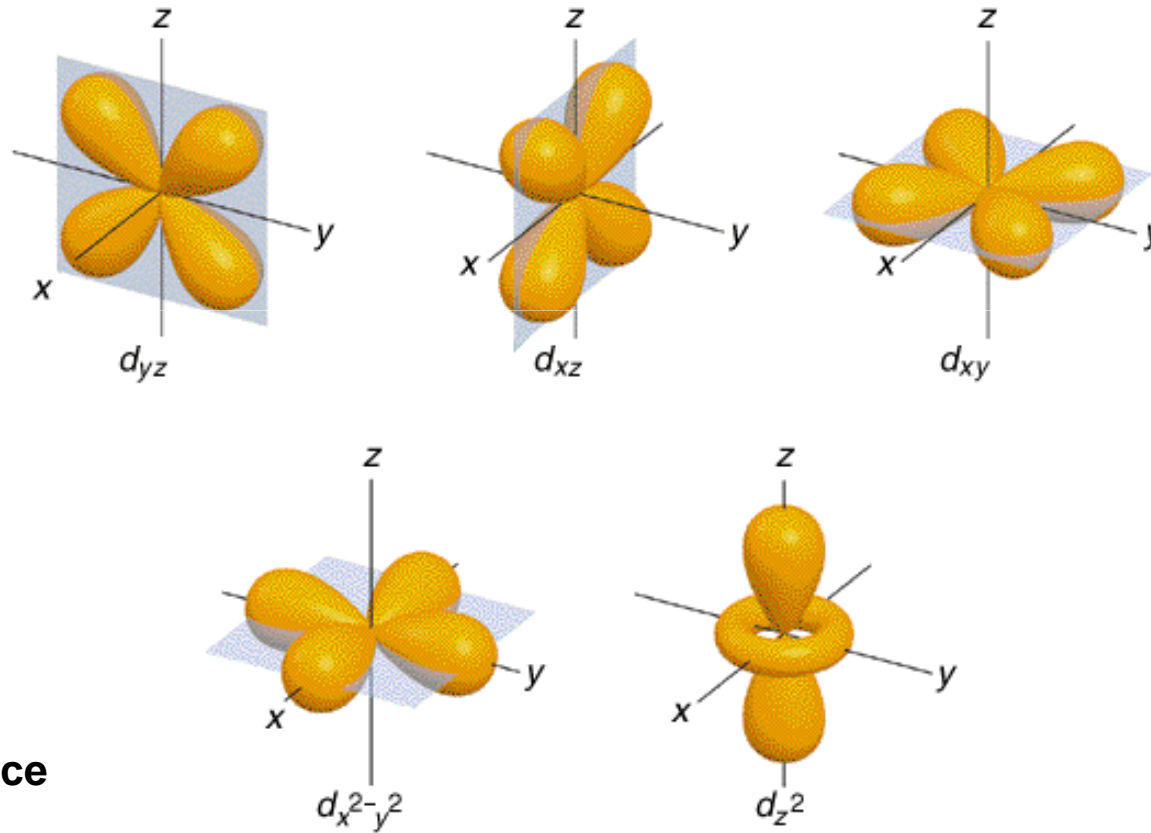
# Orbital shapes: d orbitals

$n = 3$

$l = 2$

$m_l = -2, -1, 0, 1, 2$

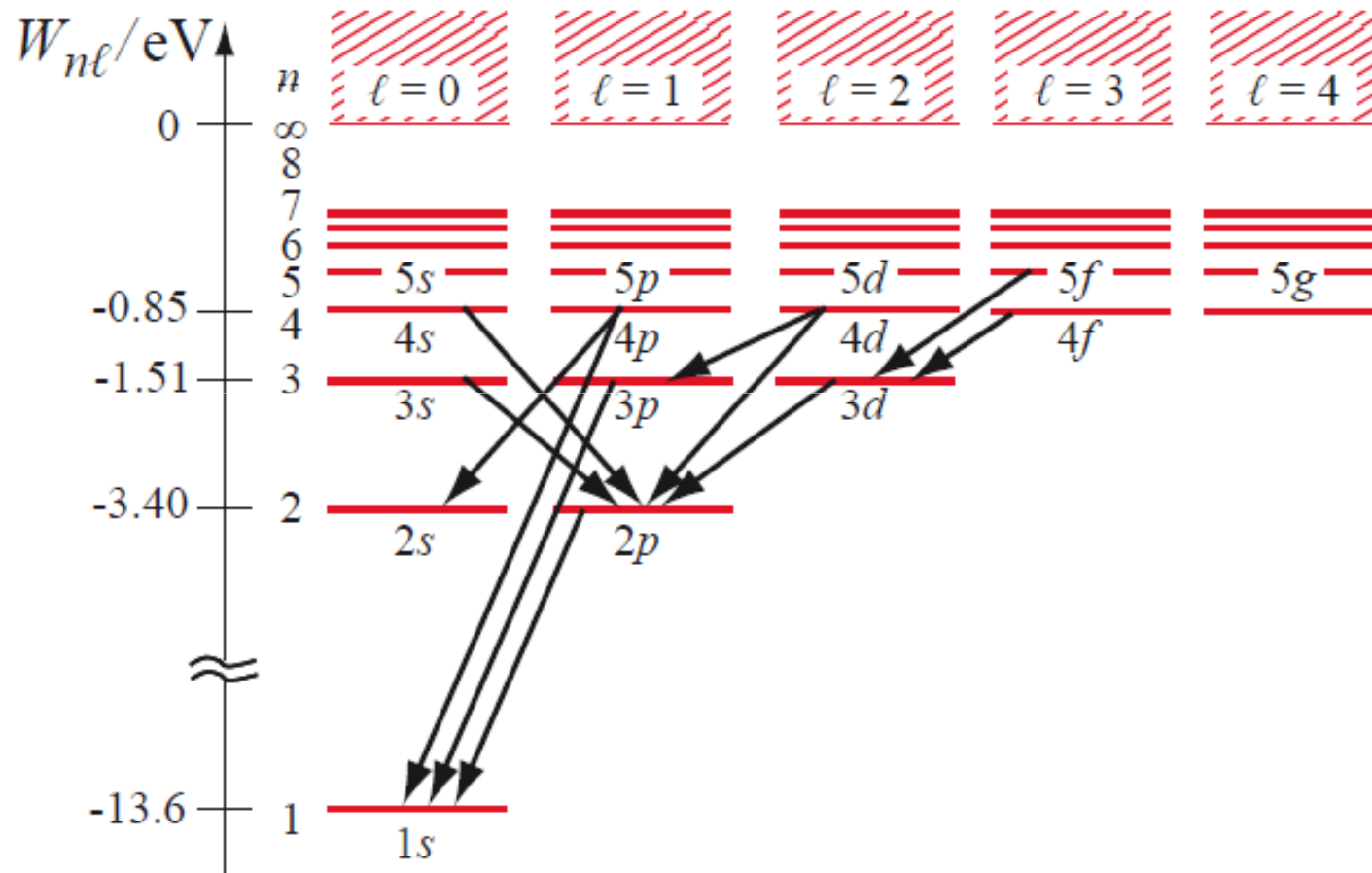
two angular nodes



boundary surface

# Energy diagram of H atom

$$\Delta l = \pm 1$$



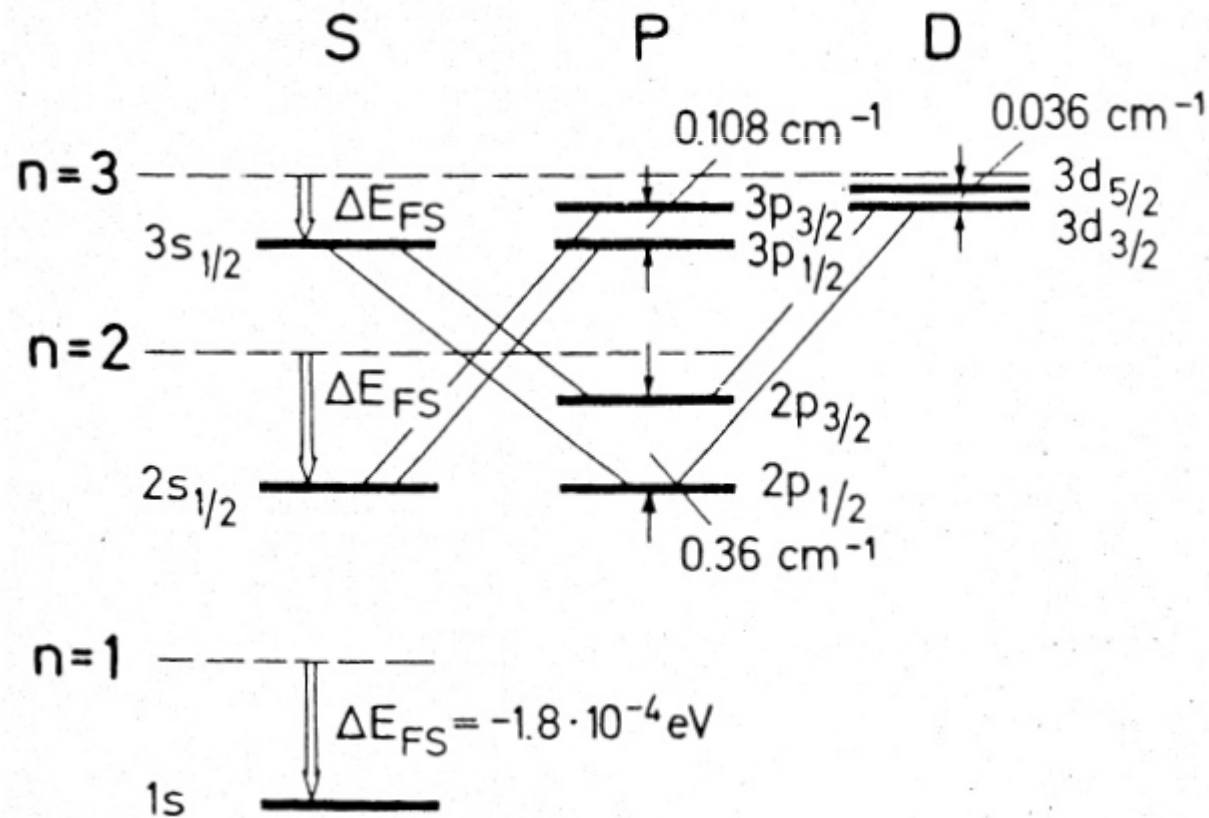
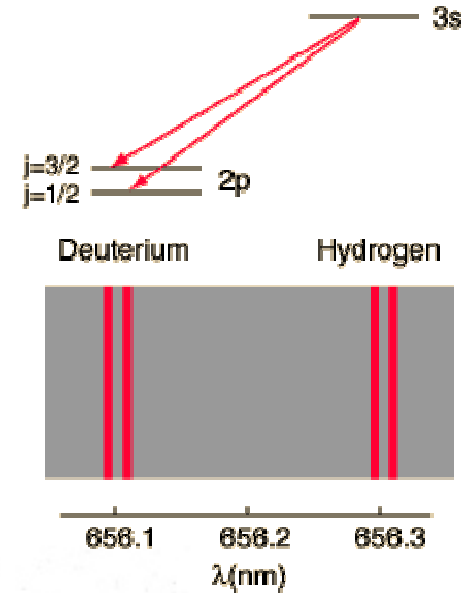
# Fine structure of H atom

$$E_{nlj} = E_n + \Delta E_{FS}$$

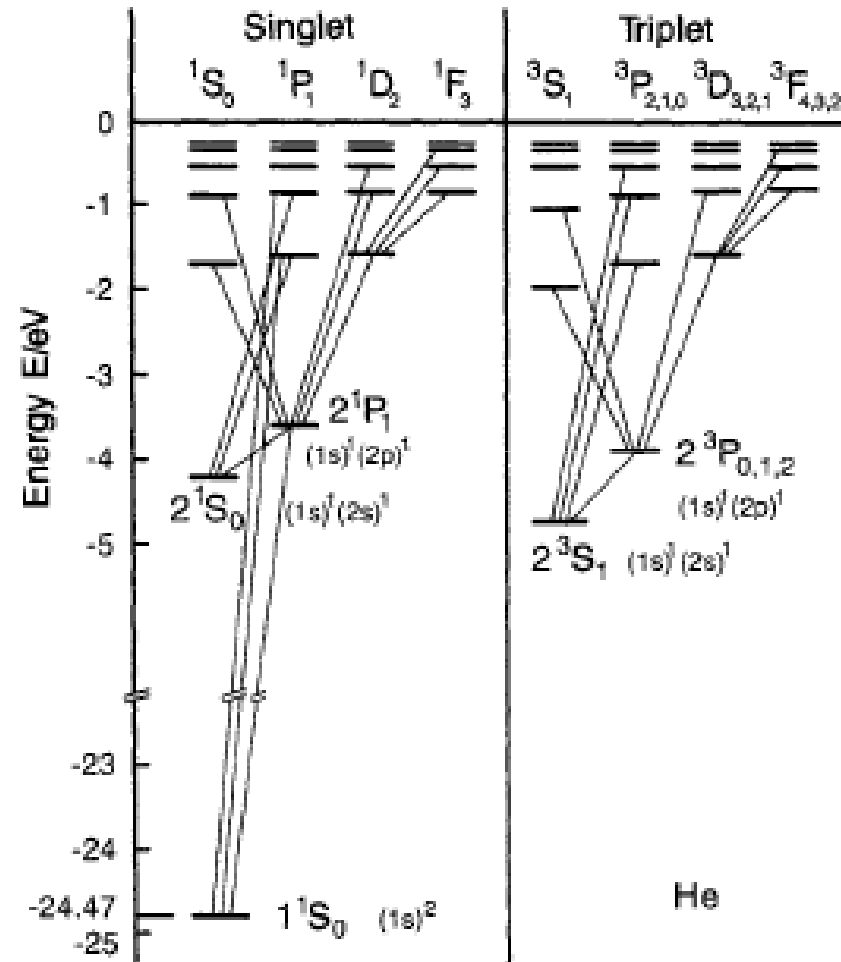
$$\Delta E_{FS} = \Delta E_{so} + \Delta E_{rel}$$

$$E_{H-atom} = -\frac{Z^2 E_0}{n^2} \left( 1 + \frac{Z^2 \alpha^2}{n} \left( \frac{1}{j+1/2} - \frac{3}{4n} \right) \right)$$

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c}$$



# Term scheme of the He atom



## Transition from LS coupling to jj coupling

