

# Hydrogenic atoms

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PHYSICAL CHEMISTRY I

## 1 Schrödinger's equation for hydrogenic atoms

- Hamiltonian
- Energy levels
- Atomic orbitals
- Electronic spin
- Pauli exclusion principle



# Hamiltonian

- Hydrogenic atoms  $\Rightarrow$  Only one electron. Ej. H, He<sup>+</sup>, Li<sup>2+</sup>, ...
- Hamiltonian

$$\hat{H}(x, y, z) = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - k \underbrace{\frac{Ze^2}{\sqrt{x^2 + y^2 + z^2}}}_r$$

- Point particles
- Nucleus fixed at the origin of coordinates  $m_{\text{nucleus}} \gg m_e$

$$\mu = \frac{m_{\text{nucleus}} m_e}{m_{\text{nucleus}} + m_e} \simeq m_e$$

- Spherical polar coordinates

$$\hat{H}(r, \theta, \phi) = -\frac{\hbar^2}{2\mu} \left( \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2(\theta, \phi)}{2\mu r^2} - k \frac{Ze^2}{r}$$



# Quantum numbers

- Eigenfunctions  $\Rightarrow \hat{H}\psi_{n,l,m}(r, \theta, \phi) = E\psi_{n,l,m}(r, \theta, \phi)$

$$\psi_{n,l,m}(r, \theta, \phi) = \underbrace{R_{n,l}(r)}_{\text{radial}} \underbrace{Y_l^m(\theta, \phi)}_{\text{angular}}$$

- Origin of the quantum numbers

- $\psi(r, \theta, \phi) = \psi(r, \theta + 2\pi, \phi)$
- $\psi(r, \theta, \phi) = \psi(r, \theta, \phi + 2\pi)$
- $\lim_{r \rightarrow \infty} \psi(r, \theta, \phi) = 0$

- Discrete values

- $n = 1, 2, 3, \dots \Rightarrow \hat{H}\psi = E\psi \Rightarrow E = -\frac{\mu e^4 k^2}{2\hbar^2} \frac{Z^2}{n^2}$
- $l = 0, 1, 2, \dots, n-1 \Rightarrow \hat{L}^2\psi = L^2\psi \Rightarrow L^2 = l(l+1)\hbar^2$
- $m = -l, -l+1, \dots, 0, \dots, l-1, l \Rightarrow \hat{L}_z\psi = L_z\psi \Rightarrow L_z = m\hbar$



# Energy levels

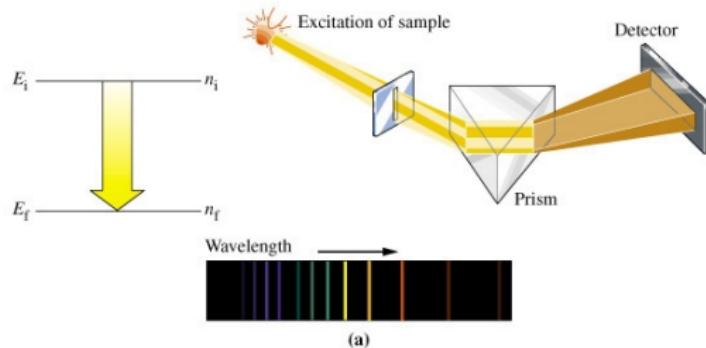
$$\bullet \quad E_n = -\underbrace{\frac{\mu e^4 k^2}{2\hbar^2}}_{R_H} \frac{Z^2}{n^2}$$

Energy levels diagram for hydrogenic atoms:

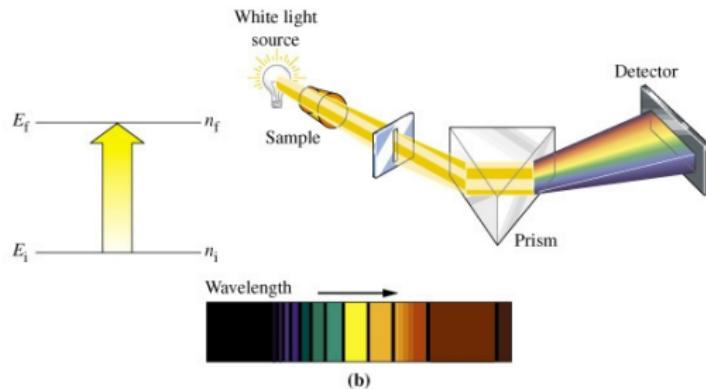
- Vertical axis: Energy (increasing upwards).
- Horizontal dashed lines: Discrete energy levels for  $n = \infty$ , 5, 4, 3, 2, 1.
- Transitions (vertical arrows):
  - $n = \infty \rightarrow n = 1$ : Four arrows, labeled  $E_1 = -R_H/1^2 = -2.179 \times 10^{-18} \text{ J}$ .
  - $n = 2 \rightarrow n = 1$ : Three arrows, labeled  $E_2 = -R_H/2^2 = -5.45 \times 10^{-19} \text{ J}$ .
  - $n = 3 \rightarrow n = 1$ : One arrow, labeled  $E_3 = -R_H/3^2 = -2.42 \times 10^{-19} \text{ J}$ .
  - $n = 4 \rightarrow n = 1$ : Two arrows, labeled  $E_4 = -R_H/4^2 = -1.36 \times 10^{-19} \text{ J}$ .
  - $n = 5 \rightarrow n = 1$ : One arrow, labeled  $E_5 = -R_H/5^2 = -8.72 \times 10^{-20} \text{ J}$ .
- Labels:
  - $n = \infty$ :  $E_\infty = 0$
  - $n = 5$
  - $n = 4$
  - $n = 3$
  - $n = 2$ :  $E_2 = -R_H/2^2 = -5.45 \times 10^{-19} \text{ J}$
  - $n = 1$ :  $E_1 = -R_H/1^2 = -2.179 \times 10^{-18} \text{ J}$
  - Ionization
  - Balmer series



# Spectroscopy



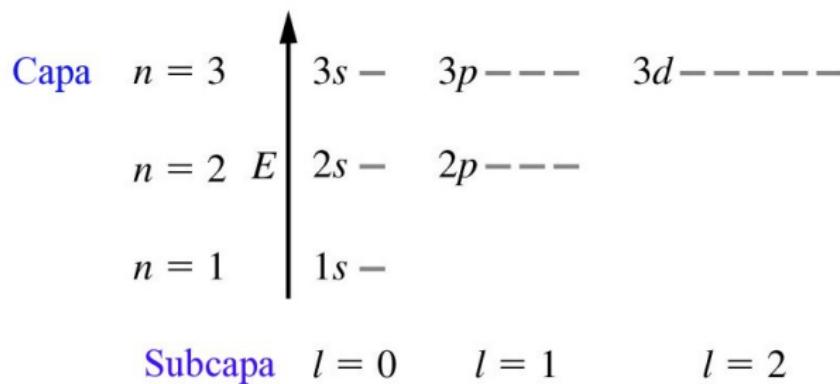
- Emission



- Absorption



# Shells and subshells



- Subshell degeneracy  $\Rightarrow 2l + 1$

- Shell degeneracy  $\Rightarrow \sum_{l=0}^{n-1} (2l + 1)$



# Atomic orbitals

- Probability density

$$|\psi_{n,l,m}(r, \theta, \phi)|^2 = \underbrace{|R_{n,l}(r)|^2}_{\text{radial}} \underbrace{|Y_l^m(\theta, \phi)|^2}_{\text{angular}}$$

- Radial functions

| $n$ | $l$ | $R_{n,l}(r)$   |
|-----|-----|--|
| 1   | 0   | $2 \left( \frac{Z}{a'_o} \right)^{3/2} e^{-Zr/a'_o}$   |
| 2   | 0   | $\frac{1}{2\sqrt{2}} \left( \frac{Z}{a'_o} \right)^{3/2} \left( 2 - \frac{Zr}{a'_o} \right) e^{-Zr/2a'_o}$ |
| 2   | 1   | $\frac{1}{2\sqrt{6}} \left( \frac{Z}{a'_o} \right)^{3/2} \frac{Zr}{a'_o} e^{-Zr/2a'_o}$                    |

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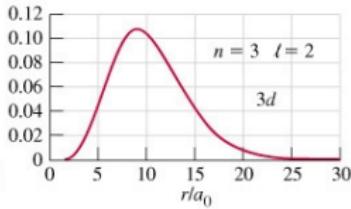
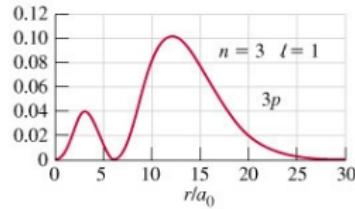
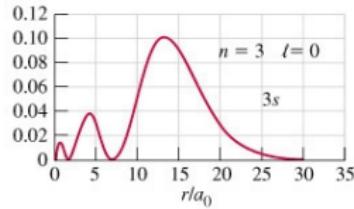
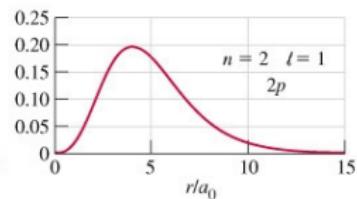
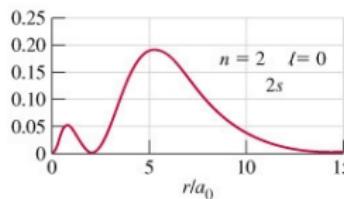
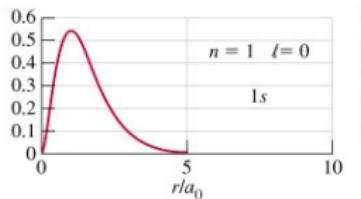

$$a'_o = \hbar^2 / k\mu e^2 = a_o m_e / \mu$$



# Radial distribution

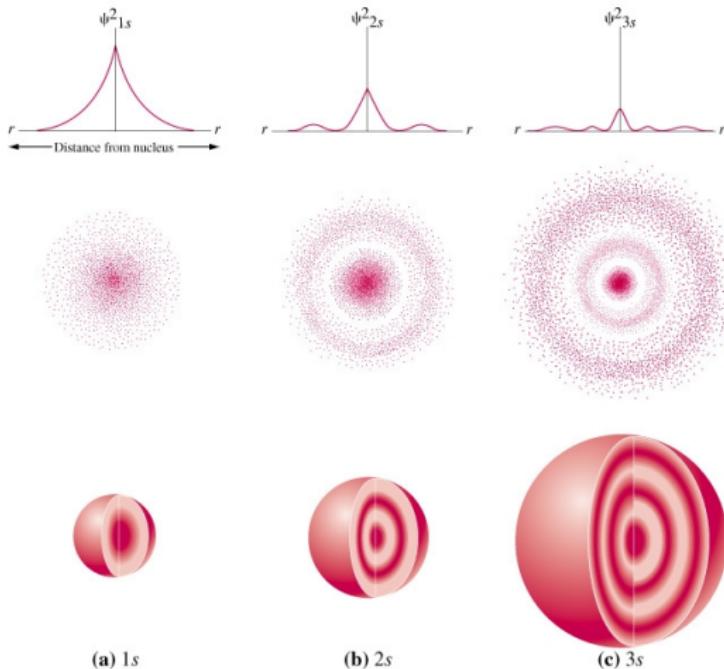
- Radial distribution function  $\Rightarrow |R_{n,l}(r)|^2 r^2$

$$P(r \in (a, b)) = \int_a^b |R_{n,l}(r)|^2 r^2 dr$$



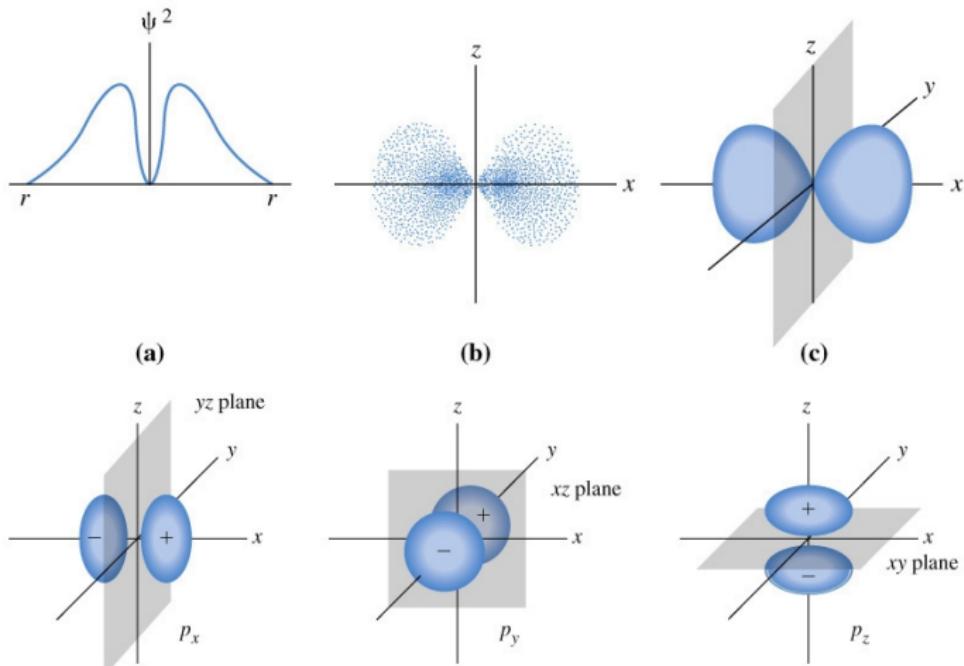


## s orbitals



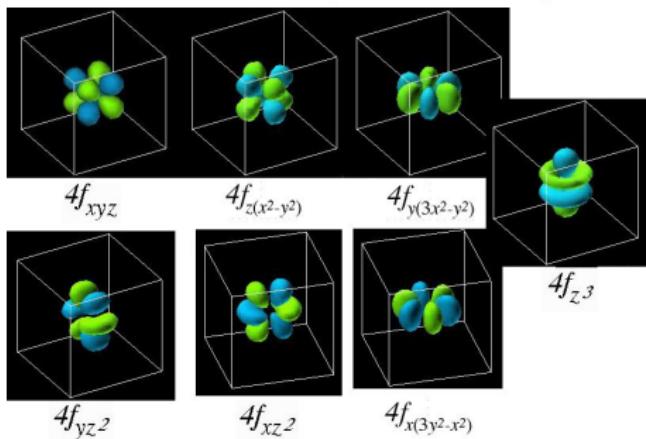
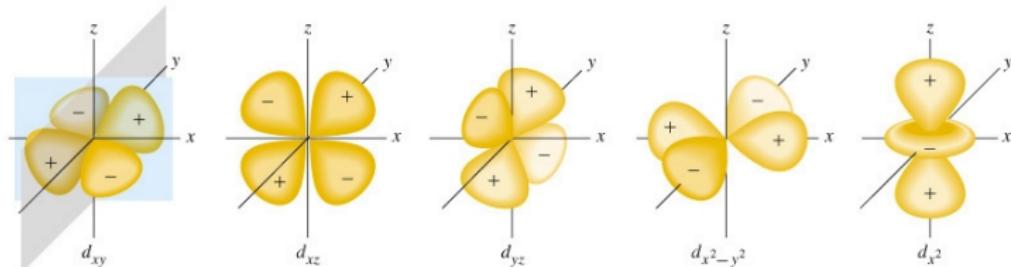


## p orbitals





# *d* and *f* orbitals





## Electronic spin

- Experimental measurements of energy level splitting
- Dirac  $\Rightarrow$  Relativistic effects  $\Rightarrow$  Intrinsic angular momentum

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$$

$$\hat{S}^2 f = s(s+1)\hbar^2 f; \quad s = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots \left\{ \begin{array}{l} \text{bosons} \Rightarrow \text{integer} \\ \text{fermions} \Rightarrow \text{half-integer} \end{array} \right.$$

$$\hat{S}_z f = m_s \hbar f; \quad m_s = -s, -s+1, \dots, s-1, s$$

- $e^- \Rightarrow s = \frac{1}{2} \Rightarrow m_s = \pm \frac{1}{2} \Rightarrow \left\{ \begin{array}{l} \hat{S}_z \alpha = \frac{1}{2} \alpha \\ \hat{S}_z \beta = -\frac{1}{2} \beta \end{array} \right.$

$$\psi_{n,l,m,m_s} = \psi_{n,l,m}(r, \theta, \phi) S_{m_s}$$



## Pauli exclusion principle

- Indistinguishable particles  $\left\{ \begin{array}{l} q_1 = (x_1, y_1, z_1, m_{s,1}) \\ q_2 = (x_2, y_2, z_2, m_{s,2}) \\ \vdots \\ q_n = (x_n, y_n, z_n, m_{s,n}) \end{array} \right.$

$$\psi(q_1, q_2, \dots, q_i, \dots, q_j, \dots, q_n) \quad \psi(q_1, q_2, \dots, q_j, \dots, q_i, \dots, q_n)$$

$\downarrow$      $\downarrow$

$$|\psi(q_1, q_2, \dots, q_i, \dots, q_j, \dots, q_n)|^2 \equiv |\psi(q_1, q_2, \dots, q_j, \dots, q_i, \dots, q_n)|^2$$

- The state function of a system of electrons (fermions) must be antisymmetric with respect to the exchange of any two electrons.

$$\psi(q_1, q_2, \dots, q_i, \dots, q_j, \dots, q_n) = -\psi(q_1, q_2, \dots, q_j, \dots, q_i, \dots, q_n)$$



## Pauli exclusion principle

- Consequence. If the electron  $e^- 2$  has the same spacial coordinates than electron  $e^- 1$  then

$$\psi(q_1, q_1, \dots, q_i, \dots, q_j, \dots, q_n) = -\psi(q_1, q_1, \dots, q_i, \dots, q_j, \dots, q_n)$$

$$\psi(q_1, q_1, \dots, q_i, \dots, q_j, \dots, q_n) = 0$$

$$|\psi(q_1, q_1, \dots, q_i, \dots, q_j, \dots, q_n)|^2 = 0 \Rightarrow \text{Pauli's repulsion}$$