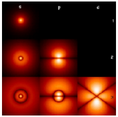


Hydrogenic atoms

Adolfo Bastida

Physical Chemistry I

Index

Hamiltonian

- Hydrogenic atoms ⇒ Only one electron. Ej. H, He^{+}, Li^{2+}, ...
- Hamiltonian

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

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

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

  - Spherical polar coordinates

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

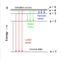
Quantum numbers

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

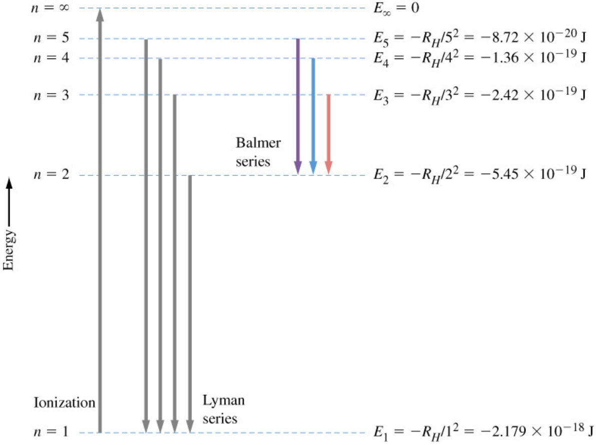
$$\psi_{n,l,m}(r,\theta,\phi) = \underbrace{R_{n,l}(r)}_{\text{radial}}\ \underbrace{Y_l^m(\theta,\phi)}_{\text{angular}}$$

- Origin of the quantum numbers
  - $\psi(r,\theta,\phi) = \psi(r,\theta+2\pi,\phi)$
  - $\psi(r,\theta,\phi) = \psi(r,\theta,\phi+2\pi)$
  - $\lim\limits_{r\to\infty} \psi(r,\theta,\phi) = 0$

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

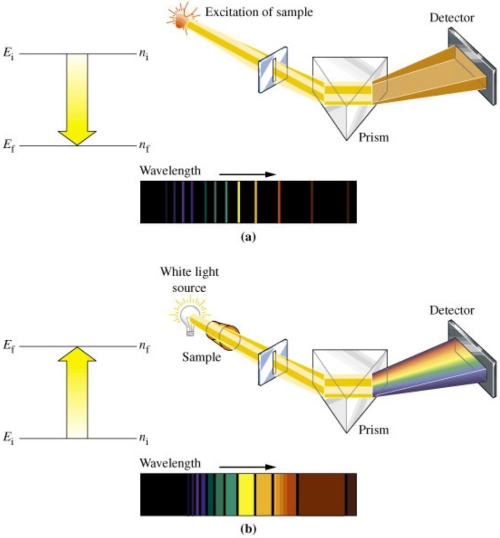


Energy levels

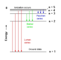


- $$E_n = -\underbrace{\frac{\mu e^4 k^2}{2\hbar^2}}_{R_H}\frac{Z^2}{n^2}$$

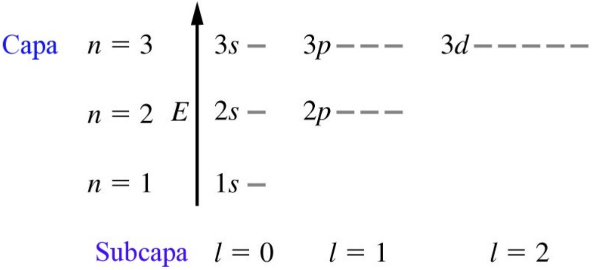
Spectroscopy



- 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

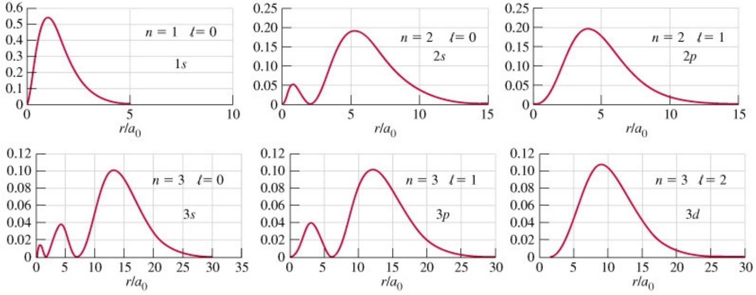
n	l	$R_{n,l}(r)$
1	0	$2\left(\frac{Z}{a'_o}\right)^{3/2} e^{-Zr/a'_o}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a'_o}\right)^{3/2}\left(2-\frac{Zr}{a'_o}\right) e^{-Zr/2a'_o}$
2	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a'_o}\right)^{3/2} \frac{Zr}{a'_o} e^{-Zr/2a'_o}$

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

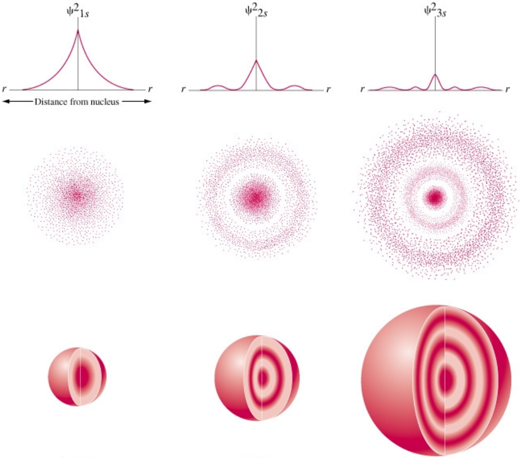
Radial distribution

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

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

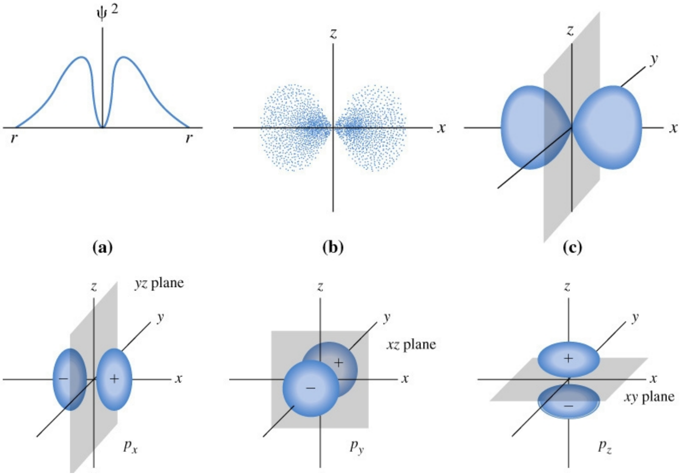


s orbitals

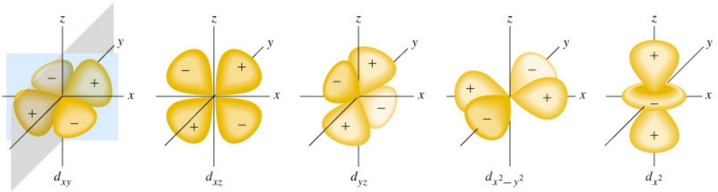


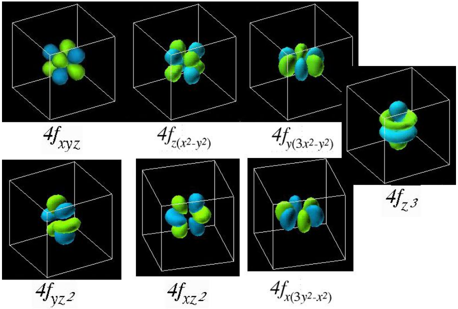
(a) 1s (b) 2s (c) 3s

p orbitals



d and *f* orbitals





Electronic spin

- Experimental measurements of energy level splitting
- Dirac ⇒ Relativistic effects ⇒ Intrinsic angular momentum

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

$$\hat{S}^2 f = s(s+1)\hbar^2 f; \quad s = 0, \tfrac{1}{2}, 1, \tfrac{3}{2} \ldots \begin{cases} \text{bosons} \Rightarrow \text{integer} \\ \text{fermions} \Rightarrow \text{half-integer} \end{cases}$$

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

- $e^- \Rightarrow s = \frac{1}{2} \Rightarrow m_s = \pm\frac{1}{2} \Rightarrow \begin{cases} \hat{S}_z \alpha = \frac{1}{2}\alpha \\ \hat{S}_z \beta = -\frac{1}{2}\beta \end{cases}$

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

Pauli exclusion principle

- Indistinguible particles $\begin{cases} q_1 = (x_1, y_1, z_1, m_{s,1}) \\ q_2 = (x_2, y_2, z_2, m_{s,2}) \\ \vdots \\ q_n = (x_n, y_n, z_n, m_{s,n}) \end{cases}$

$$\begin{array}{ccc} \psi(q_1, q_2, ..., q_i, ..., q_j, ..., q_n) & & \psi(q_1, q_2, ..., q_j, ..., q_i, ..., q_n) \\ \downarrow & & \downarrow \\ |\psi(q_1, q_2, ..., q_i, ..., q_j, ..., q_n)|^2 & \equiv & |\psi(q_1, q_2, ..., q_j, ..., q_i, ..., q_n)|^2 \end{array}$$

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

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

Pauli exclusion principle

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

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