CHE 349 - Physical Chemistry for Life Sciences

Lecture 19

Schrödinger equation:

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\theta,\phi) - \frac{e^2}{4\pi\varepsilon_0 r}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

- $\varepsilon_0 = permittivity\ constant = 8.854 * 10^{-12}\,\frac{C^2}{Nm^2}$

Quantized energy of the hydrogen atom equation:

$$E_n = -\frac{\mu e^4}{32\pi^2\varepsilon_0^{\,2}\hbar^2 n^2}$$

Simplistic energy of the hydrogen atom equation:

$$E_n = -\frac{R_\infty}{n^2}$$

- R_∞: Rydberg constant
- This constant can be expressed in many unit systems like:
  - $2.179 * 10^{-11}\,\frac{erg}{molecule}$
  - $2.179 * 10^{-18}\,\frac{J}{molecule}$
  - $1312\,\frac{kJ}{mol}$
  - $13.60\,\frac{eV}{molecule}$

Hydrogenic Wavefunctions

n	l	m_l	
1	0	0	$\psi(1s) = \frac{1}{\sqrt{\pi}}(\frac{Z}{a_0})^{\frac{3}{2}}e^{-(\frac{Zr}{a_0})}$
2	0	0	$\psi(2s) = \frac{1}{4\sqrt{2\pi}}(\frac{Z}{a_0})^{\frac{3}{2}}(2-\frac{Zr}{a_0})e^{-(\frac{Zr}{2a_0})}$
2	1	0	$\psi(2p_z) = \frac{1}{4\sqrt{2\pi}}(\frac{Z}{a_0})^{\frac{5}{2}}(z)e^{-(\frac{Zr}{2a_0})}$
2	1	± 1	$\psi(2p_x) = \frac{1}{4\sqrt{2\pi}}(\frac{Z}{a_0})^{\frac{5}{2}}(x)e^{-(\frac{Zr}{2a_0})}$

			$\psi(2p_y) = \frac{1}{4\sqrt{2\pi}}(\frac{Z}{a_0})^{\frac{5}{2}}(y)e^{-(\frac{Zr}{2a_0})}$

$z = rcos\theta$ $x = rsin\theta cos\phi$ $y = rsin\theta sin\phi$ $r^2 = x^2 + y^2 + z^2$

$Z = charge\ on\ nucleus$

$a_0 = Bohr\ radius = \frac{\varepsilon_0 h^2}{\pi m_e e^2} = 0.529\ Å = 0.529 * 10^{-10}\ m$

n = principle quantum number

l = orbital angular momentum quantum number

m_l = magnetic quantum number

Hydrogen atom

The permissible values of the quantum numbers are:

- n: positive integers 1, 2, 3, …;
- l: for a given n, zero and positive integers up to $n - 1$
- m_l: for a given l, integers from $-\ l$ to $+\ l$
- The symbols s, p, d and f are assigned to functions with l = 0, 1, 2, and 3, respectively.

Many-Electron Atoms

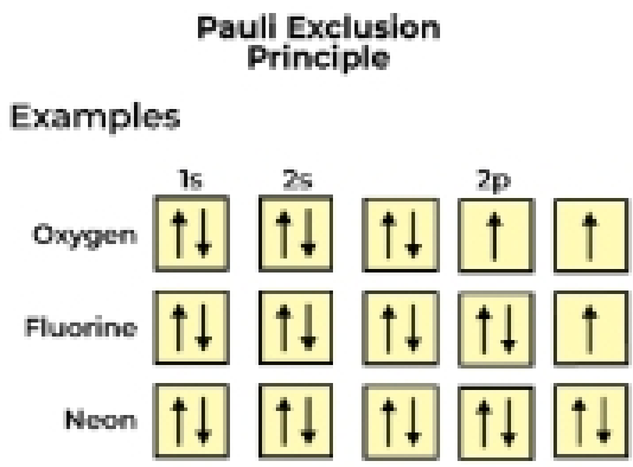
Hamiltonian operator for two electrons formula:

$$\hat{H} = -\frac{\hbar^2}{2\mu}(\nabla_1^2 + \nabla_2^2) - (\frac{2e^2}{4\pi\varepsilon_0 r_1} + \frac{2e^2}{4\pi\varepsilon_0 r_2} - \frac{e^2}{4\pi\varepsilon_0 r_{12}})$$

- μ: $the\ mass\ of\ an\ electron$
- r_1: $the\ distance\ from\ the\ nucleus\ to\ electron\ 1$
- r_2: $the\ distance\ from\ the\ nucleus\ to\ electron\ 2$
- r_{12}: $the\ distance\ between\ the\ electrons$

Pauli Exclusion Principle

- This principle states at most two electrons can be in each orbital.
- Two electrons in the same orbital must have opposite spins.
- No two electrons in an atom can have the same four quantum numbers: $n,\ l,\ m_l,\ and\ m_s$.
- To ensure this, the wave function describing the system of electrons must be antisymmetric upon the exchange of any pair of electrons. In simpler terms, if you swap the positions of two electrons, the overall wave function must change its sign.
- This antisymmetry helps prevent the violation of the Pauli exclusion principle and is crucial for understanding the behavior of electrons in atoms and molecules.



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Ionization Energy

- **The first ionization energy** (I_1) is the minimum energy required to remove an electron from a many-electron element.
- **The second ionization energy** (I_2) is the energy required to remove the second electron.
- ***The ionization energy generally increases upon going from left to right in a row of the periodic table. Similarly, it increases as you move across groups in the periodic table (like from the bottom of Group 2 all the way to the top of Group 17). In contrast, it decreases going down a column of the periodic table.***

Electron affinity

- **Electron affinity** (E_a) is defined as the energy released upon binding of an electron to a gas-phase atom.
- ***The electron affinity increases upon going from left to right in a row of the periodic table. Similarly, it increases as you move across groups in the periodic table (like from the bottom of Group 2 all the way to the top of Group 17). In contrast, it decreases going down a column of the periodic table.***

Ionization energy and electron affinity directly reflects the orbital energies of many-electron atoms.

Electronegativity is defined as the tendency of an atom participating in a covalent bond to attract the shared electrons to itself.

Mulliken electronegativity definition: $X = \frac{1}{2}(I_1 + E_a)$

- According to Mulliken, the electronegativity is one half of the sum of the first ionization energy and electron affinity of an atom.
- NOTE: X is the symbol for electronegativity.

<u>Hybridization</u>