

Inorganic Chemistry (CY11001)

Chemical Bonding: Part-I

Covering: Intro, Plank's eqn, Photoelectric Effect, de Broglie eqn, Heisenberg uncertainty principle, Schrödinger Equation

Books to Refer:

Inorganic Chemistry by Shriver & Atkins

Inorganic Chemistry by James E. Huheey

Physical Chemistry: Atkins

Prof. Madhab Chandra Das

Department of Chemistry

High Pressure Lab (Ground Floor)

Ph: 03222-282894

Email: mcdas@chem.iitkgp.ernet.in

What is Inorganic Chemistry?

MODERN PERIODIC TABLE OF THE ELEMENTS																	
LONG FORM																	
Groups ↓ Periods →																	
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The Overall FLOW

Theory Marks = 25 and class test Marks = 7Total 32

- 1. Chemical Bonding: Part -1, Part-II (bonding in s,p,d systems, MO theory) & Part-III (metallic bonding)**
- 2. CFT: Oh, Td and square planar complexes , JT distortion, Application of CFT**
- 3. Chelate effect and chelation therapy**
- 4. Organometallics: EAN rule, Wilkinson's catalyst – alkene hydrogenation, Monsanto process for the manufacture of acetic acid**
- 5. Redox Chemistry: Oxidation reduction, redox potential, Latimer and Frost diagram**
- 6. Bio-Inorganic: Hemoglobin, myoglobin, hemocyanin**

Atomic Structure

1896: A. H. Becquerel

Radioactivity of uranium

1897: J. J. Thompson

Electrons having –ve charge

1909: R. A. Millikan

Measured electronic charge (1.60×10^{-19} C; mass = 9.11×10^{-31} kg, 1/1836 of the mass of H atom

1911: E. Rutherford

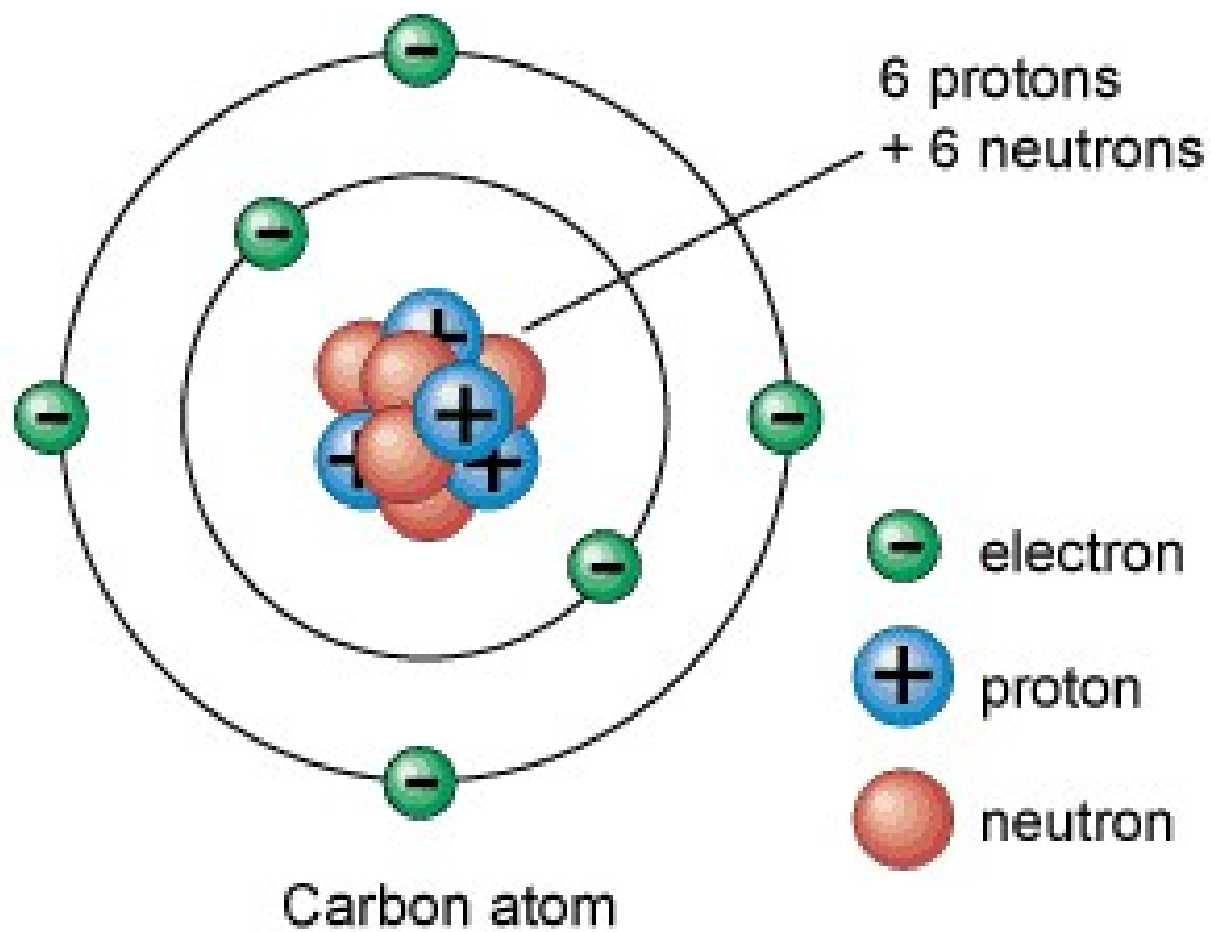
Established the nuclear model of the atom

1913: Bohr's theory

N Prize

1913: H. G. J. Moseley

Determined nuclear charge by X-ray emission, establishing atomic number



Failure of Classical Mechanics

- **Classical Mechanics:** The mechanistic properties of macro-objects
- Total energy, $E = \frac{1}{2} mv^2 + V_x$ (x & v are function of time)
- $p = mv = m (dx/dt)$ (p = momentum)
- $E = p^2/2m + V_x \dots \dots \dots \text{Eq.1}$
- You get both position & momentum of a particle



Macroscopic world





- **Certain experiments done in late 19th century and early 20th century gave results, totally different (or at variance) with the predictions of classical physics.**
- **For example, photoelectric effect.**

Max Planck $E = h\nu$

1900 German physicist

E = Quantum of Energy
 ν = Frequency of emitted radiation
 h = Planck's constant



A young Max Planck was to give a lecture on radiant heat. When he arrived he inquired as to the room number for the Planck lecture. He was told, "You are much too young to be attending the lecture of the esteemed professor Planck."

Proposed his quantum theory and explains the results of black body radiation by assuming that a black body radiates energy discontinuously in discrete energy packets called quanta and given by the equation above.....

Particle nature of electron was established by:

- Black body radiation
- Photoelectric effect ✓
- Compton effect

PHOTOELECTRIC EFFECT

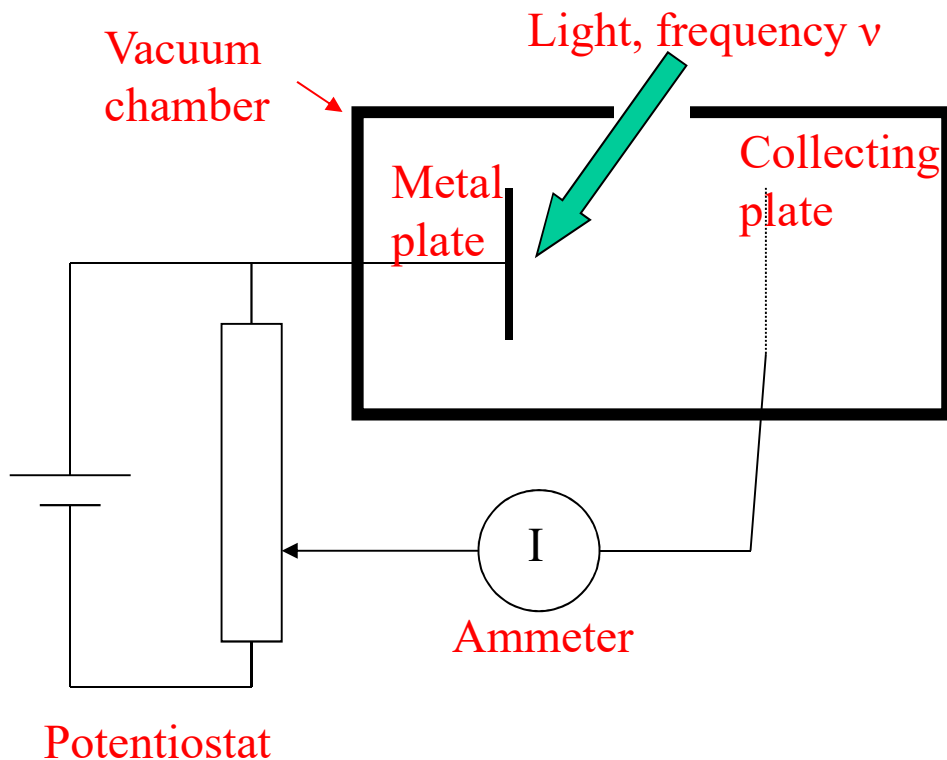
Hertz



J.J. Thomson



When UV light is shone on a metal plate in a vacuum, it emits charged particles (Hertz 1887), which were later shown to be electrons by J.J. Thomson (1899).



Classical expectations

As intensity of light increases, KE of ejected electrons should increase.

Electrons should be emitted whatever the frequency ν of the light.

Actual results:

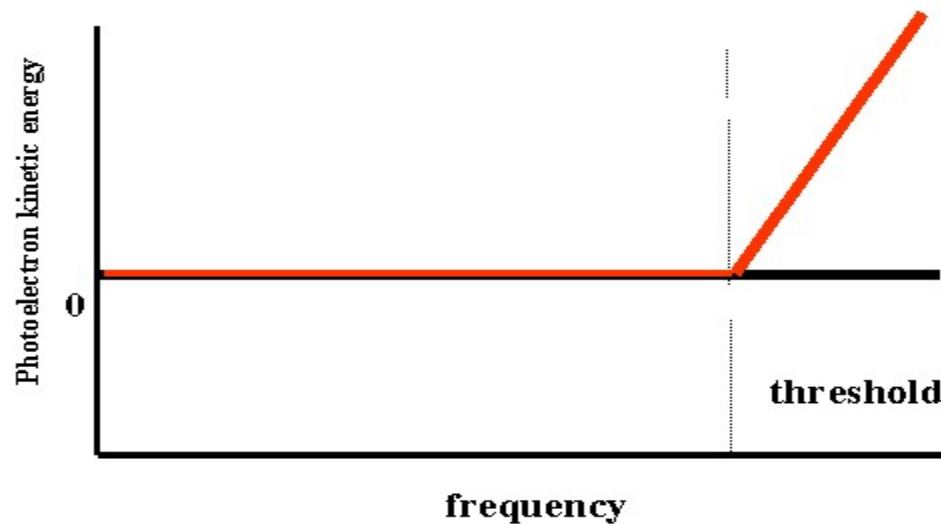
Maximum KE of ejected electrons is independent of intensity, but dependent on ν

For $\nu < \nu_0$ (i.e. for frequencies below a cut-off frequency) no electrons are emitted

Classical electromagnetic theory of light can't explain

Observations

- (i) No electrons are ejected, regardless of the intensity of the radiation, unless its frequency exceeds a threshold value characteristic of the metal.
- (ii) The kinetic energy of the electron increases linearly with the frequency of the incident radiation but is independent of the intensity of the radiation.
- (iii) Even at low intensities, electrons are ejected immediately if the frequency is above the threshold.

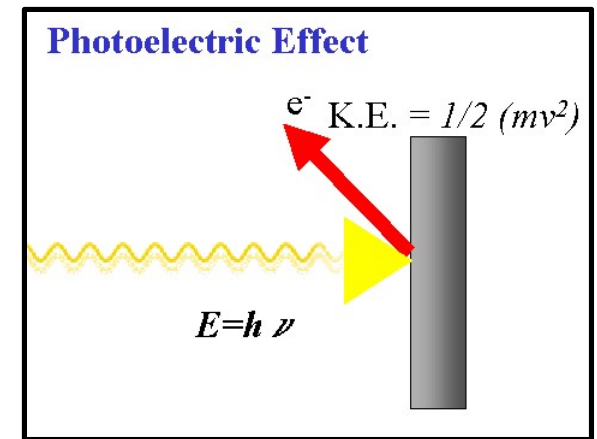


Einstein

- Classical electromagnetic theory of light fails
- He explained this phenomenon 1905 by quantum theory of radiations.
- Proves the particle nature of e

$$h \nu = \frac{1}{2} m v^2 + \phi$$

- $KE = \frac{1}{2}(mv^2) = h\nu - \phi$
- ϕ is the work function
- $h\nu$ is the energy of the incident light.
- Light can be thought of as a bunch of particles which have energy $E = h\nu$ (Max Planck). The light particles are called photons.
- When these photon encounter with e it gives up its E to e
- A part of E is used to eject out of e overcoming its BE (ϕ)
- The rest appears as KE



Math problem by TA

Louis de Broglie (1924)

The Nobel Prize in Physics 1929

French physicist (1892-1987)

- e like light or photon behaves both as a particle and a wave.
- Relation between wavelength λ and the mass and velocity of the particles.
- $E = h\nu$ and also $E = mc^2$,
- E is the energy
- m is the mass of the particle
- c is the velocity.



Wave \longleftrightarrow Particle Duality

- $E = mc^2$ Einstein Eqn.
- $E = h\nu$ Planck Eqn.
- $mc^2 = h\nu$

$$\Rightarrow mc^2 = hc/\lambda \quad \{ \text{since } \nu = c/\lambda \}$$

$$\Rightarrow \lambda = h/mc = h/p$$

p = momentum of electron

λ = de-Broglie wave length of electron

Physical significance?
Macroscopic vs Microscopic

Math problem by TA

Major objections to the Rutherford-Bohr model

- We are able to define the position and velocity of each electron precisely.
- It is difficult to measure both quantities at the same time
- No justification of angular momentum of e
i.e. $mvr = nh/2\pi$

Werner Heisenberg

Heisenberg's name will always be associated with his theory of quantum mechanics, published in 1925, when he was only 23 years (Nobel on 1932).



1887-1961

- It is impossible to specify the exact position and momentum of a particle simultaneously.
- **Uncertainty Principle.**
- $\Delta x \Delta p \geq h/4\pi$ where h is **Plank's Constant**, a fundamental constant with the value 6.626×10^{-34} J s.

Rader Speed gun:

Math problem by TA

Significance of Uncertainty Principle

- Bohr's picture of an e in an atom that gives the e a fixed position and fixed velocity is no longer correct
- This concept should be replaced by PROBABILITY....
- Thus the 3D space or region round the nucleus where there is a higher **probability** of finding an e with a probable velocity and with specific E is called an atomic orbital
- **Schrödinger** wave Equation gives a satisfactory description of an e in an atom in these terms i.e. with a probable velocity & with a particular E in a given region of space at a time

Wave equation?

Schrödinger Equation.



- Solutions to wave equations are called wave functions/Eigen functions ψ
- The probability of finding an e at a point in space whose coordinates are x,y,z is $\psi^2(x,y,z)$
- It is the differential equation of 2nd order

1933: Nobel

Derivation: Not required but you may try out (for any difficulty contact me or check Atkins)

$$\nabla^2 \psi + (8\pi^2 m / h^2)(E - V) \psi = 0$$

- This can be rearranged as

$E = \text{Total } E$ $V = \text{Potential } E$
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- $\{(-\hbar^2/8\pi^2 m) \nabla^2 + V\} \psi = E \psi$

- $H \psi = E \psi$

- $H = \{(-\hbar^2/8\pi^2 m) \nabla^2 + V\}$ **Hamiltonian operator**

- When operate H on ψ it gives the E

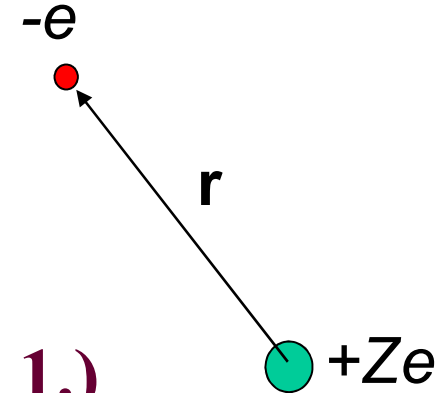
$$\{(-\hbar^2/8\pi^2 m)(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2) + V\} \Psi = E \Psi$$

∇^2 Laplacian operator

How to write Hamiltonian for different systems?

$$\{(-\hbar^2/8\pi^2m)\nabla^2 + V\} \Psi = E \Psi$$

H atom



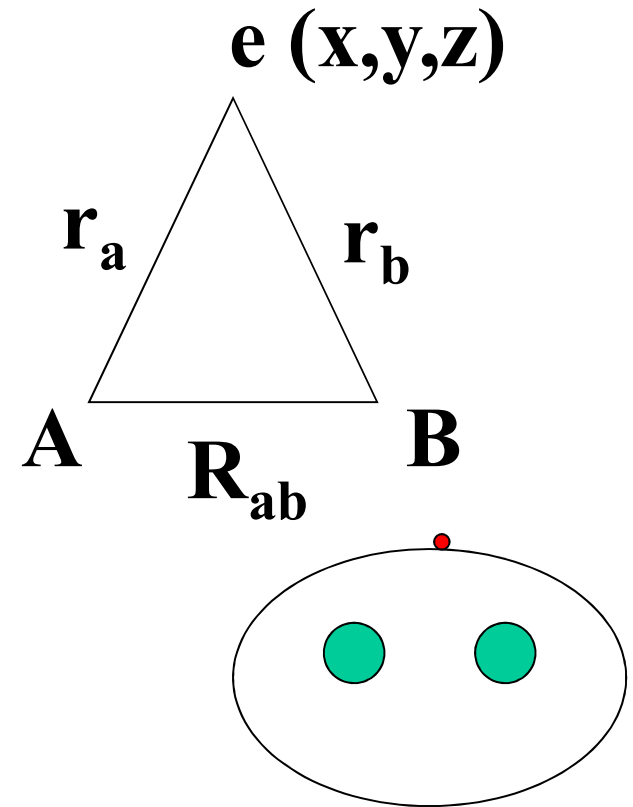
- $PE = -e^2/r$, (r = distance between the electron and the nucleus; for H, $Z = 1$.)
- $H = \{(-\hbar^2/8\pi^2m) \nabla^2 - e^2/r\}$
- Wave eqn: $\nabla^2 \Psi + (8\pi^2 m/\hbar^2)(E + e^2/r) \Psi = 0$

- If the effective nuclear charge is Ze

$$H = \{(-\hbar^2/8\pi^2m) \nabla^2 - Ze^2/r\}$$

H_2^+ Molecule

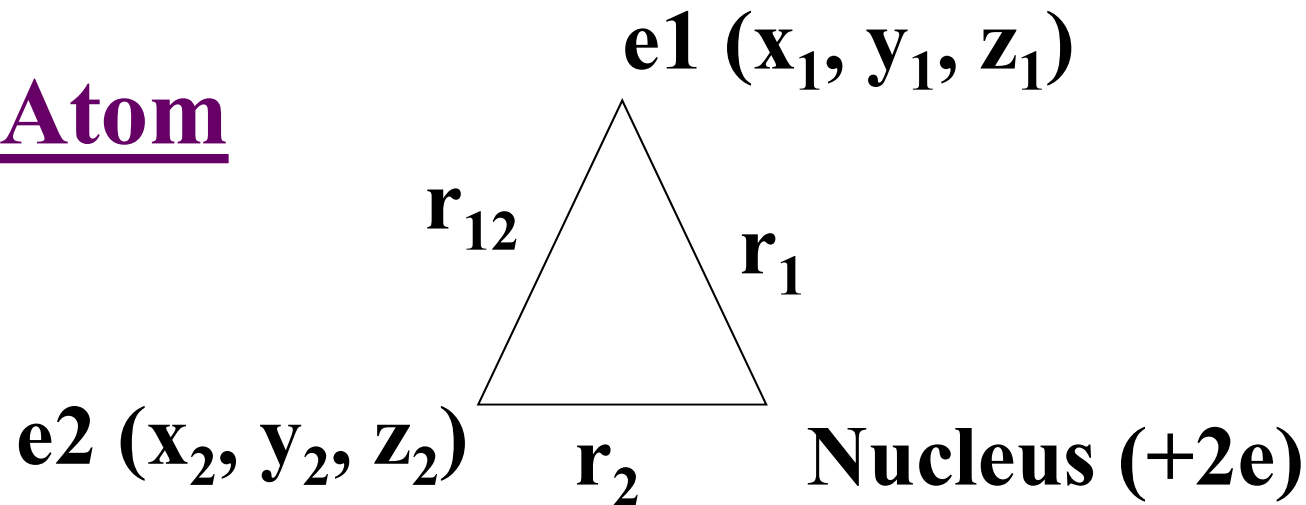
$$\{(-\hbar^2/8\pi^2m)\nabla^2 + V\} \Psi = E \Psi$$



- $\text{PE} = V = -e^2/r_a - e^2/r_b + e^2/R_{ab}$
- $H = (-\hbar^2/8\pi^2m)\nabla^2 + (-e^2/r_a - e^2/r_b + e^2/R_{ab})$
- The Wave equation is

$$\nabla^2 \Psi + (8\pi^2 m/\hbar^2) (E + e^2/r_a + e^2/r_b - e^2/R_{ab}) \Psi = 0$$

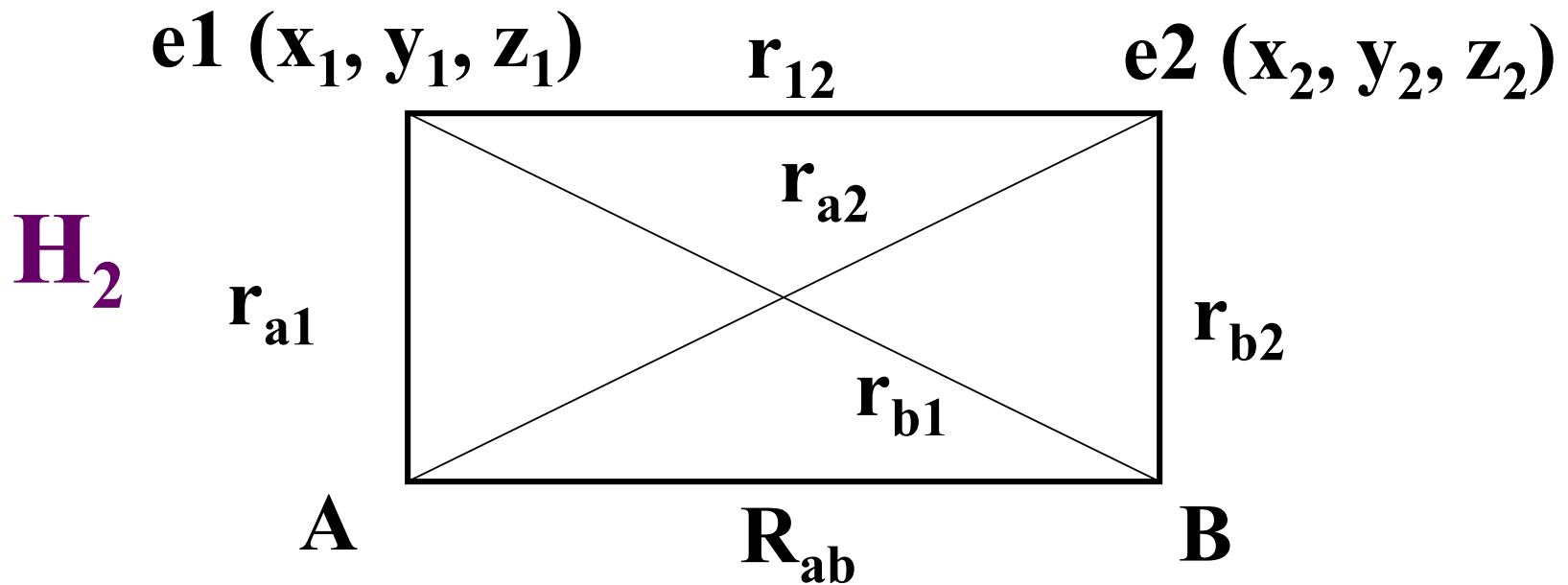
He Atom



$$\{(-\hbar^2/8\pi^2m)\nabla^2 + V\} \Psi = E \Psi$$

- $V = -2e^2/r_1 - 2e^2/r_2 + e^2/r_{12}$
- $H = (-\hbar^2/8\pi^2m) (\nabla_1^2 + \nabla_2^2) + V$
- The Wave equation is

$$(\nabla_1^2 + \nabla_2^2) \Psi + (8\pi^2 m/\hbar^2)(E-V) \Psi = 0$$



- **PE = V = ?**
- **$H = (-\hbar^2/8\pi^2m)(\nabla_1^2 + \nabla_2^2) + V$**
- **The Wave equation is**
- **$(\nabla_1^2 + \nabla_2^2)\Psi + (8\pi^2 m/\hbar^2)(E-V)\Psi = 0$**

Contd....

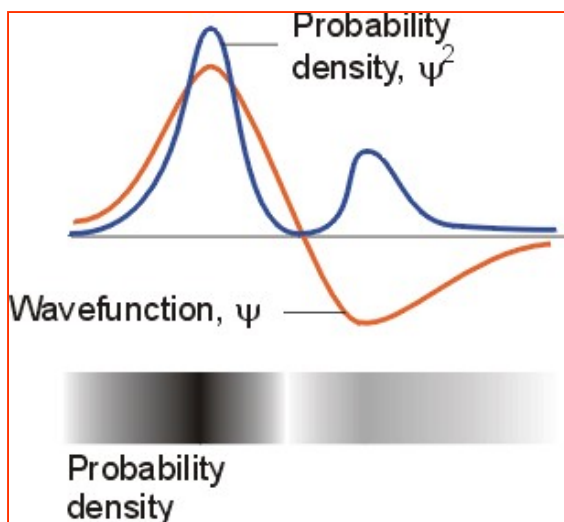
$$V = -e^2/4\pi\epsilon_0 [1/r_{a1} + 1/r_{b1} + 1/r_{a2} + 1/r_{b2} - 1/r_{12} - 1/R_{ab}]$$

SI Unit instead of CGS)

attractive potential energy

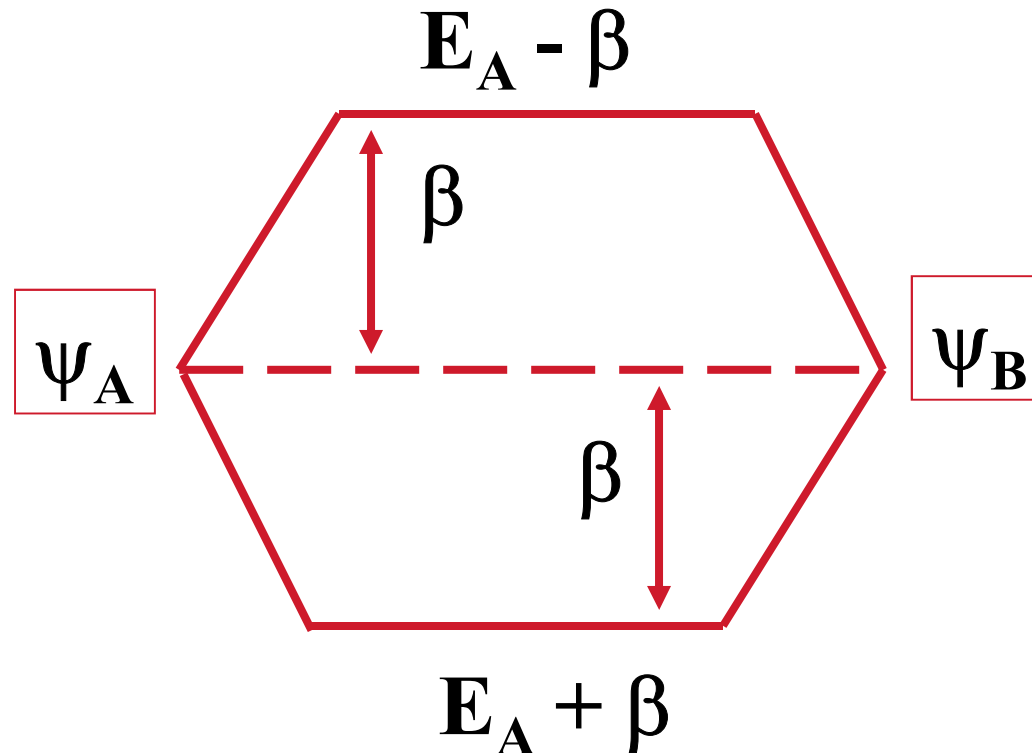
Electron-electron repulsion

Internuclear repulsion



The sign of the wave function has no direct physical significance: the positive and negative regions of this wave function both corresponds to the same probability distribution.

Energy level diagram



Eigen functions (ψ): No physical significance

ψ^2 : bears a meaningful significance $\int \psi^2 d\tau = 1$

Only If you are interested: Schrödinger Equation in polar coordinates (Atkins)

Solutions to ψ : Born Oppenheimer Principle, Variation Theorem (Atkins)

