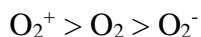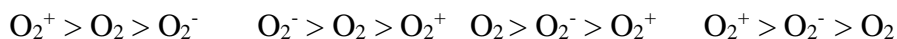# ATOMIC AND MOLECULAR STRUCTURE

1.Which of the following is called Schrodinger Equation?

$E = h\nu$ $E = mc^2$ $H\Psi = E\Psi$ none

$H\Psi = E\Psi$

2. Which of the following is correct order of stability?

$O_2^+ > O_2 > O_2^-$ $O_2^- > O_2 > O_2^+$ $O_2 > O_2^- > O_2^+$ $O_2^+ > O_2^- > O_2$

$O_2^+ > O_2 > O_2^-$

3.Which of the following is paramagnetic?

O_2 F_2 C_2 N_2

O_2

4.n – type semiconductor is formed due to doping of Si with

Phosphorous   Sodium   Boron   Oxygen

Phosphorous

5.For a semiconductor, the conductivity _____ with increase in temperature.

Increases   Decreases   Remain same   None

Increases

6. For n type semiconductor which metal is doped with Silicon?

Arsenic.

7. What is e/m ratio for electron?

5.27×10^{17} esu/gm.

8. What is the value of Bohr radius a_0 ?

0.0529 nm.

9. Classical mechanics explain which phenomenon?

diffraction

10. What happen when Indium is doped with silicon?

It generates p type semiconductor.

11. If uncertainty in position and momentum are equal then what will be the uncertainty in velocity?

$1/2m \sqrt{h/\pi}$.

12. What is the bonding molecular orbital from the atomic orbitals having wave functions Ψ_A and Ψ_B?

$\Psi_A + \Psi_B$.

5 marks question

Moderate

Prove that $\left(V - \frac{h^2}{8\pi^2 m \nabla^2}\right)\Psi = E\Psi$ π $(V - h^2/8\pi^2 m \nabla^2)\,\Psi = E\Psi$

This equation is Schrodinger wave equation for a particle of mass m in three dimension. In this equation V is potential energy, E is kinetic energy of the particle of mass m. ∇^2 is Laplacian operator. Ψ is wave function for the particle, h is Planck's constant.

Total energy operator (Hamiltonian operator) $\hat{H}$ in three dimension is

$\hat{H} = - h^2/8\pi^2 m \nabla^2 + V (x,y,z)$ ------ (1)

V (x,y,z) in three dimension is simply written as V.

$\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$

Following eigenvalue equation for the energy we write

$\hat{H}\Psi = E\Psi$ ------- (2)

Using equation (1) in equation (2)

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

$(V - h^2/8\pi^2 m \nabla^2) \Psi = E\Psi$ (Proved)

Easy

Why does germanium act as n-type semiconductor? What is the difference between n- type and p-type semiconductor?

Germanium belongs to Group IV. It is a semiconductor and contains four valence electrons. If atoms with 5 valence electrons such as antimony, arsenic or phosphorous are added to germanium, then it adds extra electrons to germanium. This leads to increase in free electrons in the conduction band, as a result, the forbidden gap decreases and the conduction process is increased. This is called n- type semiconductor.

n- type semiconductor	p- type semiconductor
This type of semiconductor is formed by doping of Group IV with pentavalent elements such as Phosphorous, Arsenic etc.	This type of semiconductor is formed by doping of Group IV element with trivalent elements such as Boron, Aluminium etc.
This type of doping causes increase in free electrons.	This type of doping causes increase in positive holes.
This type of doping causes decrease in energy of conduction band of the Group IV element.	This type of doping causes decrease in energy of valence band of the Group IV element.

Hard

An electron is confined in 1 – d box of length 10^{-10} m with potential energy equal to 0 inside (V = 0) and V = ∞ outside the box. Calculate the ground state energy and separation between the levels with quantum number 2 and 3. [mass of electron = 9.11×10^{-31} kg, Planck's constant = 6.627×10^{-34} Js].

The energy of electron inside one – dimensional box is given by, $E = n^2 h^2/ 8 m_e a^2$ where m_e is mass of electron, 'a' is box length, h is Planck's constant and n is quantum number (n = 1, 2, 3, 4.....)

For ground state n = 1, so ground state energy $E_1 = 1^2 \times h^2 / 8 m_e a^2$

So, $E_1 = (6.627 \times 10^{-34} \text{ J s})^2 / 8(9.11 \times 10^{-31} \text{ kg})(10^{-10} \text{ m})^2 = 6.026 \times 10^{-18}$J (Since J = kg m^2 s^{-2})

Ground state energy of electron = 6.026×10^{-18} J

Energy in level 3 = $E_3 = 3^2 h^2/ 8 m_e a^2 = 9 \times h^2 / 8 m_e a^2 = 9 \times 6.026 \times 10^{-18}$ J

Energy in level 2 = $E_2 = 2^2 h^2/ 8 m_e a^2 = 4 \times h^2 / 8 m_e a^2 = 4 \times 6.026 \times 10^{-18}$ J

So, $\Delta E = E_3 - E_2 = (9 - 4) \times 6.026 \times 10^{-18}$ J $= 5 \times 6.026 \times 10^{-18}$ J $= 30.13 \times 10^{-18}$ J $= 3.013 \times 10^{-18}$ J

Modarate

Set up the Schrodinger equation for a particle in a one – dimensional box.   5

Show how the model of particle in a box can be applied to calculate the energy spectra of polyene.   4

What is zero point energy of a particle in one dimensional box? Why the energy of this particle cannot be zero at zero point energy? If the zero point energy of a particle in one dimensional box is 2.5 eV, what is the next higher energy value?   2 + 2 + 2

Schrodinger equation for a particle in a one – dimensional box is written as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E\psi = 0$$

Where Ψ is wave function of the particle, m is mass of the particle, h is Planck's constant, E is Kinetic energy of the particle. (The particle moves along x – direction).
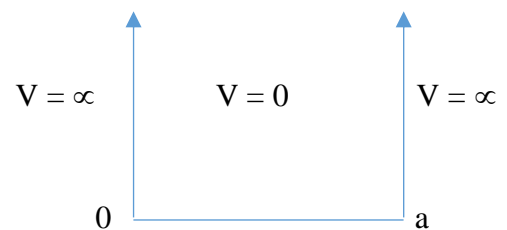
E of the particle is quantized and is given by $E = \frac{n^2 h^2}{8ma^2}$, n = 1, 2, 3…..

Where n is quantum number and 'a' is length of the box. The potential energy outside the box is ∝ and inside the box is 0.

Outside the box potential energy V = ∝

Out side the box we have

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - \infty)\psi = 0$$

E can be considered negligible in comparison to ∝, so we get,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (-\infty)\,\psi = 0$$

$$\frac{d^2\psi}{dx^2} - \infty\,\psi = 0$$

$$\frac{d^2\psi}{dx^2} = \infty\,\psi$$

$$\Psi = \frac{1}{\infty}\, d^2\Psi/dx^2 = 0$$

Ψ =0 means the particle is absent outside the box.

Within the box

Schrodinger wave equation for1 – d particle within the box where V = 0 is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E\psi = 0$$

We write the equation as

$$\frac{d^2\Psi}{dx^2} + \alpha^2\Psi = 0$$

Where,

$$\alpha^2 = \frac{8\pi^2 mE}{h^2}$$

b. π – electron in polyene may be identified with the system of particle in one – dimensional box. The length of the box may be taken as the end to end distance of the molecule. The electronic energy levels in polyenes can be obtained by using expression for the energy $E = n^2h^2/8m_e a^2$

Electrons of polyenes (e.g. butadiene, hexatriene) are distributed over the energy levels following Pauli Exclusion Principle and aufbau principle. The electron transition energy is equal to the energy difference between the highest occupied level (n) and lowest unoccupied level (n + 1).

$$\Delta E = E_{n+1} - E_n = \frac{(n+1)^2 h^2}{8m_e a^2} - \frac{n^2 h^2}{8m_e a^2} = \frac{(2n+1)h^2}{8m_e a^2}$$

We discuss below the transition energy and the frequency of transition for CH_2=CH- CH=CH_2 (butadiene). π – electrons of butadiene are assumed to move freely from one end of the molecule to the other as in the case of one-dimensional box. End to end distance of butadiene can be obtained from the single and double bond length which for butadiene is 578 pm. According to free electron model, the four π electrons in the ground state are present in the lowest two energy levels (n =1, n =2), so transition will occur from level 2 to level 3.

The transition energy,

$$\Delta E = E_3 - E_2 = 5\left(\frac{h^2}{8m_e a^2}\right) = 5 \times \frac{(6.626 \times 10^{-34}\ Js)^2}{8(9.11 \times 10^{-31}kg)(578 \times 10^{-12}m)^2} = 9.02 \times 10^{-19}J$$

Energy of transition is 9.02 x 10^{-19} J

Frequency of transition, $v = \frac{\Delta E}{h} = 9.02 \times \frac{10^{-19}J}{6.626 \times 10^{-34}Js} = 1.36 \times 10^{15}s^{-1}$.

c. The lowest value of kinetic energy of a particle in one - dimensional box is called zero – point energy.

Kinetic energy of a particle in one –dimensional box is given by $E = n^2 h^2/ 8ma^2$, n = 1, 2, 3…..

Zero point energy is obtained by putting n= 1 in above expression for energy $E_{zero-point} = h^2 / 8ma^2$

Minimum energy is not zero but greater than zero. This is in accordance with the uncertainty principle. If the kinetic energy is zero then velocity v_x is zero and momentum $p_x = mv_x = 0$.

From uncertainty principle $\Delta x \Delta p_x \geq h$. If $p_x = 0$ the uncertainty in Δp_x is zero, consequently Δx is ∞. But the particle is somewhere between x = 0 and x = a and Δx cannot exceed a. Hence kinetic energy equal to zero is impossible for a particle in one dimensional box.

For level n = 1, energy is zero point energy = $h^2/8ma^2$ = 2.5 eV.

Next higher level is for n = 2

Energy in level n = 2 is given by $2^2\left(\frac{h^2}{8ma^2}\right) = 4 \times 2.5\ eV = 10eV$.

Easy

(a) Show the hybridization and calculate the CFSE of $[Fe(H_2O)]^{2+}$ and $[Fe(H_2O)]^{3+}$ complex ions.　4

(b) Explain the paramagnetic behaviour of oxygen molecule (O_2) under the light of M.O. theory.　　3

(c) Determine the bond order of each member of the following groups, and determine which member of each group is predicted by the molecular orbital model to have the strongest bond:

(i) H_2, H_2^+, H_2^-

(ii) O_2, O_2^+, O_2^- 4

(d) What is Pauli Exclusion Principle?   2

(e) What is an operator?

(a) The electronic configuration of Fe^{2+} ion in the firat complex is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^6$.

$[Fe(H_2O)]^{2+}$ is an inner orbital complex with sp^3d^2 configuration.

The electronic configuration of Fe^{2+} is $t_{2g}^4e_g^2$. H_2O being a weak field ligand in +2 state of Fe.

The electronic configuration of Fe^{3+} ion in the firat complex is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^5$.

$[Fe(H_2O)]^{3+}$ is an outer orbital complex with d^2sp^3 configuration.

The electronic configuration of Fe^{2+} is $t_{2g}^5e_g^0$. H_2O being an strong field ligand in +3 state of Fe.

The CFSE of $[Fe(H_2O)]^{2+}$: $4 \times (-0.4\Delta_0) + 2 \times (-0.6\Delta_0) = -0.4\Delta_0$

The CFSE of $[Fe(H_2O)]^{3+}$: $5 \times (-0.4\Delta_0) + 0 \times (-0.6\Delta_0) = -2.0\Delta_0$

(b) Each oxygen atom has electronic configuration $1s^2\,2s^2\,2p^4$. So each oxygen atom contains 8 electrons and total 16 electrons are there in O_2 molecule. The arrangement are as follows:

(σ_{1s}^2), (σ_{1s}^{*2}), (σ_{2s}^2), (σ_{2s}^{*2}),(π_{2pz}^2), (π_{2px}^2), (π_{2py}^2), (π_{2px}^{*1}), (π_{2py}^{*1}),

Bond order $= \frac{1}{2}(10 - 6) = 2$

From MO diagram, it is evident that O_2 molecule possess two unpaired electrons in π_{2px}^*,π_{2py}^* antibonding molecular orbitals. Therefore O_2 molecule would be paramagnetic in nature.

(c) Hydrogen molecule (H_2): Hydrogen molecule is formed by the overlap of 1s atomic orbitals of two hydrogen atoms having one electron each. From the overlap of these atomic orbitals, two molecular orbitals viz. bonding and antibonding are generated. In a hydrogen molecule the total two electrons are accommodated in lower energy, bonding (σ_{1s}) molecular orbital.

Hence bond order $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2 - 0) = 1$.

H_2^+: It has only one electron in bonding (σ_{1s} orbital.

Bond order $= \frac{1}{2}(1 - 0) = \frac{1}{2}$

H_2^- : This is formed when a hydrogen atom having one electron in 1s atomic orbital combines with a hydride ioh H^- having two electrons. H_2^- possess total 3 electrons. Electronic configuration σ_{1s}^2, σ_{1s}^{*1}

Bond order $= \frac{1}{2}(2 - 1) = \frac{1}{2}$

O_2: Each oxygen atom has electronic configuration $1s^2\,2s^2\,2p^4$. So each oxygen atom contains 8 electrons and total 16 electrons are there in O_2 molecule. The arrangement are as follows:

(σ_{1s}^2), (σ_{1s}^{*2}), (σ_{2s}^2), (σ_{2s}^{*2}),(π_{2pz}^2), (π_{2px}^2), (π_{2py}^2), (π_{2px}^{*1}), (π_{2py}^{*1}),

Bond order $= \frac{1}{2}(10 - 6) = 2$

O_2^+: Total number of electrons $= 15$

Bond order $= \frac{1}{2}(10 - 5) = 2.5$

O_2^-: Total number of electrons $= 17$

Bond order = ½ (10 – 7) =1.5

(d) Pauli Exclusion Principle states that no two electrons in an atom can have all four quantum number same. So from Pauli Exclusion Principle no more than two electrons can occupy the same atomic orbital. In the same orbital two electrons have same n, l and m values but one has spin quantum number s = +1/2 and the other has s = -1/2. Thus the two electrons in a orbital has opposite spin.

An operator is a symbol that tells to do something to whatever follows the symbol. Thus an operator is a rule for converting a given function into another function.

$\frac{d}{dx}, \frac{d^2}{dx^2}$, addition, subtraction, multiplication, square, square root .... are operator.