2021
CHEMISTRY
(Quantum Chemistry and Chemical Bonding II)
Paper: 2.3
Full marks: 60
Time: 3 hr

The figures in the margin indicate full marks for the questions

1. Answer the following questions: 1x5=5

   a) What is overlap integral?

   b) Predict the relative stabilities of N_2, N_2^+ and N_2^-

   c) Why resonance integral is always a positive quantity?

   d) State whether the statement is true or false "In the potential energy curve for antibonding orbital there is a minimum point"

   e) Energy difference between bonding $MO,(E_+)$ and ant bonding $MO(E_-)$ in H_2 molecules is given by $E_+-E_- = 2H_{ab}$ when S_{ab} is neglected. it means that

   i) $E_+ < E_-$ ii) $E_+ = E_-$ iii) $E_+ > E_-$ iv) None of the above

2. Answer **any five** from the following questions $3x5 = 15$

   a) Explain *Molecular* Orbital Theory by considering each electron in a molecule is described by certain wave function Ψ.

b) Draw Molecular Orbital energy level diagram for CO. Show which orbital's are occupied and work out the bond orders and magnetic property of this molecule?

c) Explain Walsh diagram using suitable example?

d) Compare the MO and VB treatment of the hydrogen molecule in the ground state.

e) Explain INVERSION in terms of symmetry of molecular orbitals in homonuclear diatomic molecules .

f) "The energy level of a bonding MO is lower than the combining AO and that of an ABMO is higher than the corresponding AO".Give reason?

g) Using MO theory write electronic configuration of O_2^{2-}, O_2, O_2^+ and O_2^- and hence arrange them in the order of bond order and calculate number of unpaired electron in O_2^{2-}, O_2, O_2^+ and O_2^-

h) Using Huckel approximation, estimate the delocalization energy of benzene?

3. Answer **any ten** from the following questions $4 \times 10 = 40$

a) Briefly explain the features of Extended Huckel Theory?

b) Using Huckel approximation, find the energies and HMO function of butadiene?

c) What are the types of Hybridization in the central atom in the following compounds?

$$H_2O, \ CH_4$$

d) What is Born-Openheimer approximation? Under what condition is this approximation applicable?

e) Setup the Huckel determinant for methyleneimine ($CH_2=NH$) taking β_{CN} as $^1\beta$ and $\acute{a}_N=\acute{a} +0.5\beta$ where $\acute{a}$ and β represents usual coulomb and resonance integral respectively and obtain the Huckel MO energy level?

f) Using Walsh diagram predict the shapes of the following
   i) H_2O ii)BH_2

g) Using the Huckel approximation determine whether linear H_3^+ or the triangular H_3^+ is more stable?

h) Using MO treatment, find energy and wave Function of H_2^+ molecules?

i) Show that for hydrogen molecule ion

$$I)\ H_{aa} \ = \ E_H +j +\frac{1}{R}$$

$$II)\ H_{ab} \ = \ E_H \ S_{ab} + K +\frac{1}{R} S_{ab}$$

j) Show that the four antisymmetric wave functions representing the excited states of the hydrogen molecule have one singlet and three triplet state.

k) Construct sp hybrid orbitals by combing one 2s and one 2p atomic orbitals.

l) Using Huckel approximation , find the energies and molecular orbitals of the allyl radical CH_2- CH-CH_2

m) If 2s and 2p are orthonormal orbitals then show that the hybrid orbitals

$(s + \sqrt{p}) \sqrt{3}$ is also normalised .

n) Calculate the delocalisation energy of

1) CH_2- $CH = CH_2$ 2) cyclopropane

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