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December 2022

M.Sc. (Chemistry) - III SEMESTER

Physical Chemistry Special-I (CH-325B)

Time : 3 Hours] [Max. Marks : 75

Instructions :

1. *It is compulsory to answer all the questions (1.5 marks each) of Part-A in short.*
2. *Answer any four questions from Part-B in detail.*
3. *Different sub-parts of a question are to be attempted adjacent to each other.*
4. *All the symbols represent usual meaning related to physical chemistry.*

PART-A

1. (a) Describe Born-Oppenheimer approximation with its significance in quantum mechanics. [CO:1-4, PO:2-5] (1.5)

(b) Write a short note on Density functional theory (DFT). [CO:1, PO:2-5] (1.5)

(c) Write Sackur-Tetrode equation and explain its significance in statistical thermodynamics. [CO:3, PO:2-5] (1.5)

(d) How many microstates are possible for the $3d^2$ electronic configuration? [CO:1-2, PO:2-5]
(1.5)

(e) What are the possible term symbols for p^3 electronic configuration? [CO:1-2, PO:2-5]
(1.5)

(f) Calculate vibrational contribution to the molar heat capacity of $N_2(g)$ at 1000 K. (The experimental value is 3.43 JK^{-1} mol^{-1}) [CO:3, PO:2-5]
(1.5)

(g) Discuss '*orthonormality*' in the quantum mechanics. [CO:1-4, PO:2-5]
(1.5)

(h) Differentiate the term '*molecular partition function*' and '*partition function*'. [CO:3, PO:2-5]
(1.5)

(i) Find the relation for the commutators **[Lz, Lx]** and **[Ly, Lz]**. [CO:1-2, PO:2-5]
(1.5)

(j) Define '*Ladder Operator*' and derive relationship for $[\hat{J}_+, \hat{J}_-]$. [CO:1-4, PO:2-5]
(1.5)

PART-B

2. (a) Describe n-bond and delocalization energies of cyclopropenyl system. Calculate HMO coefficients and sketch molecular orbitals to describe symmetry of each energy level. [CO:4, PO:2-5]
(10)

(b) Find out the coefficients of atomic orbitals in sp^2 hybrid orbitals. [CO:1-2, PO:2-5]
(5)

3. (a) Describe π-bond and delocalization energies of 1,3-butadiene system. Calculate HMO coefficients and sketch molecular orbitals to describe symmetry of each energy level. [CO:4, PO:2-5]
(10)

(b) Find out the coefficients of atomic orbitals in sp^3 hybrid orbitals. [CO:1-2, PO:2-5]
(5)

4. (a) Prove variation theorem and its significance in multielectron system. Use the Φ_1 and Φ_2 as orthonormal trial functions and derive the relation for the ground state energy using variation method? [CO:1-2, PO:2-5]
(10)

(b) Write a note on "vibrational partition function". [CO:3, PO:2-5]
(5)

5. (a) Derive expression for first order perturbation and find the correction in wave function & energy? [CO:1-2, PO:2-5]
(10)

(b) Write a short note on *'Configuration Interaction'*. [CO:1-2, PO:2-5]
(5)

6. (a) Explain how the form of the Rotational Partition function of molecule depends on the shape of the molecule (with suitable examples)? [CO:3, PO:2-5] (10)

(b) Calculate the contribution of each normal mode to the vibrational heat capacity of CO_2 at 400 K [θ_{vib} = 954 K (Bending Mode), θ_{vib} = 1890 K (Asymm. Mode), θ_{vib} = 3360 K (Symm. Mode)]. [CO:3, PO:2-5] (5)

7. (a) Sketch the molecular orbital diagram for the valence electron in $\mathbf{CH_4}$. [CO:4, PO:2-5] (7.5)

(b) Sketch the 'Walsh Correlation' diagram for the valence electron in a $\mathbf{AH_2}$ molecule. [CO:4, PO:2-5] (7.5)
