Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
II Semester, 2016-2017

CHEMF 244 Physical Chemistry III

Quiz Test - 01; Time: 30 mins. Date: 14.02.2017 [25 M]

Name: ID: Marks obtained:

Q1. On the basis of symmetry, which of the following molecule(s) cannot have a dipole moment: CH_4, CH_3Cl, CH_2D_2, H_2S, SF_6. Explain briefly. **[2]**

Q2. Consider ethylene molecule and answer the following:

a) What are the symmetry operations present in the molecule? **[2]**

b) How many classes of symmetry operations are there in the molecule? **[4]**

c) What would be the dimension of the irreducible representations? **[2]**

d) Construct the character table. **[2]**

e) Determine the Mulliken symbols for each of the irreducible representation. **[2]**

Q3. (i) Consider $2p_x$ and $2p_y$ orbitals of N atom in NH_3 molecule. Use $2p_x$ and $2p_y$ orbitals as the bases function to represent all the transformation operators of the point group to which NH_3 belongs. What would be the irreducible representation? Do mention all the relevant assumption. **[7]**

(ii) Comment with brief explanation:

(a) Orbital overlap integral of $2p_x$ and $2p_y$ orbitals. **[2]**

(b) Orbital overlap integral of $2p_x$ and $2p_z$ orbitals. **[2]**

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Quiz Test - 02; Time: 25 mins. Date: 05.04.2017 [25 M]

Name: ID: Marks obtained:

Q1. Given that D_e = 4.75 eV and R_e = 0.741 Å for the ground electonic state of H_2. Find $U(R_e)$, and $\langle T_{el} \rangle_{Re}$ **in eV**. Ground state energy of H-atom is -13.598 eV. [4]

Q2. A particle is subject to the potential energy $V = ax^4 + by^4 + cz^4$. If its ground state energy is 10 eV, calculate <T> and <V> for the ground state. [4]

Q3. Apply Hellmann-Feynman theorem to 1-D simple harmonic oscillator to evaluate $\langle x^2 \rangle$. [5]

Q4. Determine the number of basis functions for CH_3OH for a calculation using the following basis sets: (i) STO-3G, (ii) 3-21G, (iv) 6-31G, (v) 6-31G*, (vii) 6-31G**, and (viii) 6-31+G* [12]

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Quiz Test - 03; Time: 30 mins. Date: 26.04.2017 [25 M]

Name: ID: Marks obtained:

Q1. Consider simple model system, H_2, in minimal basis molecular orbital treatment using linear combination of atomic orbitals. The hydrogen atom 1s orbitals are ϕ_1 and ϕ_2 centered on H-atom 1 and 2, respectively.

(a) Represent all spin orbitals of H_2 using molecular orbitals, Ψ_1 and Ψ_2. **[4]**

(b) What would be the form of ground state wave function of H_2 molecule if you take into considerations determinants upto double excitations? Justify your answer. **[4]**

(c) Assume, the Hartree Fock approximated ground state wave function of H_2 is Ψ_0. Determine the matrix element $\langle\Psi_0|\widehat{O_1}|\Psi_0\rangle$. $\widehat{O_1}$ is the one electron operator. **[7]**

Q2. Perturbation theory for non-degenerate state is not useful for degenerate states: Explain in brief. **[3]**

Q3. Use the concepts of Moller-Plesset perturbation theory to answer the following questions for a molecular system of 3 electrons:

(a) What would be the form of the unperturbed Hamiltonian? Need to explain all the terms in brief. *Answer, without proper description would not be considered.* **[3]**

(b) What would be the form of the zeroth order wavefunction? **[2]**

(c) What would be the eigen value of the state represented in previous question. **[2]**