SEAT No. [126] No. of Printed Pages : 02

SARDAR PATEL UNIVERSITY

M.Sc. (SEMESTER-II) EXAMINATION
Saturday, 16th November,2019
Time: 10 :00 a.m. to 01:00 p.m.
CHEMISTRY: PS02CCHE21
(QUANTUM CHEMISTRY)

Note: -Figures to the right indicate full marks: **Total marks: 70**

Q.1.Answer the following: **[8]**

1. The sum of kinetic energy and potential energy is _____
   a) Laplacian operator b) Hamiltonian operator
   c) Momentum operator d) Hermitian operator
2. The symbol corresponds to Laplacian operator is_____
   a) ∇^2 b) ∇ c) L d) L^2
3. An angle between rotational axis and Z-axis known as_____
   (a) Azimuthal angle (b) rotation angle (c) Zenith angle (d) theta angle
4. Perturbation method is applied to the system if:
   (a) For the unperturb state E^0 not known & Ψ^0 known.
   (b) For the unperturb state E^0 known & Ψ^0 not known.
   (c) For the unperturb state E^0 & Ψ^0 known.
   (d) For the unperturb state E^0 & Ψ^0 are not known.
5. At the equilibrium point (X=0) of oscillation all the energy corresponds to_____
   (a) Kinetic Energy (b) Rotational Energy
   (c) Potential energy (d) Electronic Energy
6. Which of the following indicates non degenerate states _____
   (a) E_{222} (b) E_{212} (c) E_{221} (d) E_{122}
7. The expression for the fourth order perturbation energy is _____
   a) $\langle\Psi^0|\hat{V}|\Psi^3\rangle$ c) $\langle\Psi^1|\hat{V}|\Psi^2\rangle$
   b) $\langle\Psi^2|\hat{V}|\Psi^2\rangle$ d) $\langle\Psi^0|\hat{V}|\Psi^4\rangle$
8. The energy required by H_2^+ for dissociation is .....
   (a) 2.79 eV (b) 1.06 eV (c) 2.97eV (d) 1.60 eV

Q.2 Attempt any SEVEN of the following: **[14]**

1. Evaluate the commutator [Y,d/dz].
2. Explain the total wave functions for hydrogen like atom.
3. Explain the symmetric and asymmetric wave functions.
4. What are the application of quantum mechanical tunneling?
5. Derive the n^{th} order perturbation energy equation.
6. Explain the σ and π-molecular orbitals.
7. Derive the Laguerre polynomial for n=2 & l=1.
8. Explain the bonding in HeH molecule.
9. The $\pi_u 2Py$ orbital is lower is energy than $\sigma_g 2Pz$ for the N_2 system. Explain.

Q.3.A. Butadiene contain $4\pi e$, each of which moves freely from one end of the molecules to the other. Treat the molecules as a one dimensional box whose length is equal to the length of C-C bond plus half of the C-C bond length on either side. The average C-C bond length is 0.14 nm. **[06]**

(i) Calculate the total ground state energy of the molecule.

(ii) Calculate lowest absorption frequency (in cm^{-1}) and wavelength (in nm) of light absorbed.

(Given: $h=6.26 \times 10^{-34}$ Js, $1J = 6.24 \times 10^{18}$ eV and $1\ eV = 8.06 \times 10^3\ cm^{-1}$)

(P.T.O.)

Q.3.B. Write a note quantum mechanical tunneling and write its two applications. **[06]**

OR

B. Answer the following: **[06]**

1. Show that set-down operator commute with square of angular momentum operator but set-down operator does not commute with component of angular momentum operator($\widehat{Lx}$) and set-up operator.
2. Show that [Lx, Ly] ≠ 0.

Q.4.A. Answer the following: **[06]**

1. Derive the fourth degree of Hermit's polynomial.
2. Derive the energy equation and Schrodinger equation for the vibrational motion of a particle in a one dimensional harmonic oscillator

B. Considering nitric oxide as a rigid rotator rotates in a xy-plane and in a space **[06]** ① calculate 1st three energy level & angular momentum ② calculate wavelength & frequency of radiation emittion when transition takes places from n = 2 to n = 1. [Radius is 1.15×10^{-10} M]

OR

B. Answer the following: **[06]**

1. Derive the normalization factor (N) for 3p-orbital and 3d-orbital.
2. Discuss the rotational motion of a diatomic molecules in a plane. (fixed axis.)

Q.5.A. Derive the time independent perturbation theory for non-degenerate state and calculate first order perturbation energy equations. **[06]**

B. Derive the overall wave function: $\Psi_{(1,2,\ldots n)} = \frac{1}{\sqrt{n!}} |\Phi_1(1), \Phi_1(2), \ldots \Phi_1(n)|$ for many electron Systems. **[06]**

OR

B. Answer the following: **[06]**

1. Calculate the total energy and ionization potential energy of helium atom in presence of repulsion energy and compare with experimental Value.
   [Given: 1 a.u. = 0.435x10-17 JS and 1J= 6.24x 1018 eV]
2. Explain: Hartree's self-consistent field method.

Q.6.A. Derive the energy equation $H_{AA} = 2E_H + \frac{1}{R} + J$ for Hydrogen molecule on the basis of Heitler & London theory. **[06]**

B. Answer the following: **[06]**

1. Determine the coefficient a_1 and a_2 and Explain the electron density distribution in hydrogen molecule on the basis of valence bond theory and hydrogen molecule ion on the basis of molecular orbital theory.
2. Derive the molecular term symbols for C_2^+, F_2^+ and O_2^+.

OR

B. Answer the following: **[06]**

1. Discuss the adiabatic and crude Born Oppenheimer approximation.
2. Explain LCAOMO treatment for diatomic molecule.

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