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Total No. of Questions : 09

M.Sc.(Chemistry) (2015 to 2017) (Sem.–2)

QUANTUM CHEMISTRY

Subject Code : MSCH-204

M.Code : 71665

Time : 3 Hrs. Max. Marks : 100

INSTRUCTION TO CANDIDATES :

1. Atttempt FIVE questions in all selecting ONE question from each UNIT. All questions carry equal marks.
2. Q. No. 1 is Compulsory.

1. **Answer Briefly :** **(2×10=20)**

a) Determine whether the following operator is linear or nonlinear :

$$\hat{A}\, f(x) = x^2 f(x)$$

b) Show that the functions ψ, $-\psi$ and $2i\psi$ represent same state; ψ being real.

c) Calculate the number of radial node and angular node of 4d orbital.

d) What is the complex conjugate of the wave function ($\psi = 4 + 3i$)?

e) Calculate the number of degenerate states for Hydrogen atom for $n = 4$.

f) Determine whether the given statement is true or false. Justify your choice.

The function $\exp[-\alpha x^2]$ is an acceptable wave function.

g) Write down the Hamiltonian equation of He atom.

h) A particle in one dimensional box simple harmonic oscillator in x-direction is perturbed by a potential λx. What is the 1st order correction for ground state?

i) Calculate the magnitude of the angular momentum of an electron that occupies the following atomic orbitals: 1s and 3d.

j) Calculate the number of radial node and angular node of 3p orbital.

UNIT-I

2. a) If A is a linear operator and $A\psi_1 = a\psi_1$ and $A\psi_2 = a\psi_2$ then prove that any linear combination of ψ_1 and ψ_2 say $C_1\psi_1 + C_2\psi_2$ or $C_1\psi_1 - C_2\psi_2$ is an eigen function of 'A' with the same eigen value 'a' where C_1 and C_2 are constants.

   State Heisenberg's uncertainty principle and using it show that electrons cannot reside in nucleus.

   b) Calculate the expectation value of x-component of momentum of a free particle in a box of length 1, $\psi = \sqrt{\frac{2}{l}}\sin\left(\frac{n\pi x}{l}\right)$. Show that e^{ax} is an eigen function of the operator d^n/dx^n. What is the eigen value? Prove that eigen values of Hermitian operator are real. (10, 10)

3. a) Write down the quantum mechanical postulates with proper explanation.

   b) For the ground state of a particle in 1-d box, calculate $\langle p_x \rangle$ and $\langle (p_x)^2 \rangle$. Explain the physical interpretations of your outcomes. (10, 10)

UNIT-II

4. a) Find out the probability of finding the 1s electron within the first Bohr orbit a_0. Tabulate all of the allowed microstates of p^2 electronic configuration.

   b) Sketch ψ and $|\psi|^2$ for $n = 1$, $n = 2$ states of a particle in a one dimensional box of length 1 and indicate the most likely locations of the particle in these states. (10, 10)

5. a) Plot the shapes (polar plots) of the atomic orbitals corresponding to $2p_x$, $2p_y$ and $2p_z$ for a hydrogen-like atom using the following equations :

$$\psi_{2p_x} = A\sin\theta\cos\phi,\ \psi_{2p_y} = A\sin\theta.\sin\phi \text{ and } \psi_{2p_z} = A\cos\theta$$

   Where, $A = \frac{1}{4\sqrt{2\pi}} Z^{5/2} r e^{-Zr/2}$. Denote the range of θ and ϕ used for the polar plots and label the axes properly.

   b) Find out the probability density of finding the 1s electron of hydrogen atom described by the wave function $\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)\left(2-\frac{r}{a_0}\right)^{3/2} e^{-r/2a_0}$ at the nucleus and at a distance a_0 from the nucleus. Also find out the relative probability of finding the 1s electron in Bohr's first orbit and at a distance of 1×10^{-4} a_0 from the nucleus. (10,10)

UNIT-III

6. a) Calculate the energy value of H_2 molecule ion by using LCAO-MO wave function.

   b) Write a short note on degenerate perturbation theory. (10,10)

7. a) Briefly describe the differences between perturbation method and variation method. Calculate the bond order of the following molecules : (i) He_2, (ii) H_2, (iii) H_2^{2+}, (iv) He_2^{2+} and (v) H_2^{+}

   b) State and prove the variation theorem. (10,10)

UNIT-IV

8. a) Derive the Huckel MO theory for ethylene/ethane. Draw simple schematics of the bonding and anti-bonding energy level diagrams.

   b) Draw and explain the MO diagram of H_2O. (10,10)

9. a) Derive the Huckel MO theory for 1,3-butadiene. Draw simple schematics of the bonding and anti-bonding energy level diagrams.

   b) Write a short note on Born-Openheimer approximation method. (10,10)

NOTE : Disclosure of Identity by writing Mobile No. or Making of passing request on any page of Answer Sheet will lead to UMC against the Student.