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14 (CHM-1) 104

2018

**CHEMISTRY**

Paper : CH 104

**(Quantum Chemistry)**

Full Marks : 60

Time : 2½ hours

**The figures in the margin indicate full marks for the questions.**

1. Answer **any four** of the following :

5×4=20

- (a) Determine which of the following functions are eigenfunctions of the

operator  $\frac{d^2}{dx^2}$

5

(a)  $e^{ikx}$

(b)  $\cos(kx)$

(c)  $k$

(d)  $kx$

(e)  $e^{-ax^2}$

Give the corresponding eigenvalue where appropriate.

Contd.

(b) Evaluate the following commutators :  
2½×2½

(a)  $[J_z, J_-]$

(b)  $[J^2, J_x]$

(c) Write the expression for the step-up and step-down operators. Why are they called so ? 5

(d) Prove that two observables A and B are compatible if and only if their corresponding operators,  $\hat{A}$  and  $\hat{B}$  commute. 5

(e) (i) Prove that eigenfunctions of a linear operator belonging to different eigenvalues are linearly independent. 2½

(ii) Prove that eigenfunctions of Hermitian operators belonging to different eigenvalues are orthogonal. 2½

(f) Consider the following function : 5

$$Y_{lm} = -\left(\frac{3}{8\pi}\right) \sin \theta \exp i\phi$$

Verify whether the function is an eigenfunction of  $\hat{L}^2$  and  $\hat{L}_z$  operators. Give the corresponding eigenvalues where appropriate. 5

2. Correlate the Heisenberg uncertainty principle in terms of quantum mechanical uncertainty principle. 2

3. Answer **any two** of the following :

5×2=10

(a) Write down the Schrödinger Equation in spherical polar coordinate defining the Laplacian operator. Then, derive the expression of Schrödinger equation for a particle moving in a circular motion in the  $xy$ -plane. Find out the solution of the equation.

(b) Evaluate the expectation values of  $r$  and  $r^2$  for a hydrogen atom with the wave function given by

$$\Psi = \sqrt{\frac{1}{32\pi a_0^3}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

(c) In the ground state of the harmonic oscillator, what is the probability of finding the particle outside the classically allowed region ?

4. Answer **any one** of the following:  $6 \times 1 = 6$

(a) What are the assumptions of Rayleigh-Schrödinger perturbation theory? Derive the expression for the perturbed energy levels of a two level system by employing time independent degenerate perturbation theory.  $1+5$

(b) Derive the explicit expression of  $\frac{dc_a}{dt}$  and  $\frac{dc_b}{dt}$  for a two level system employing time dependent perturbation theory.  $c_a$  and  $c_b$  represents the coefficients of unperturbed states  $\Psi_a$  and  $\Psi_b$ .  $6$

5. Why variation theorem is significant in quantum mechanics? State and prove the variational theorem.  $1+5$

6. Identify  $H^0$  and  $H^1$  for the following problems:  $1+1+1$

(a) An oscillator governed by the potential:

$$U(x) = \frac{kx^2}{2} + \frac{\gamma x^3}{6} + \frac{bx^4}{24}$$

(b) A particle constrained to move in the region  $0 < x < a$  with the potential

$$U(x) = 0 \quad 0 < x < a/2$$

$$U(x) = b \quad a/2 < x < a$$

(c) A H atom in an electric field of strength  $\epsilon$ . The Hamiltonian for the system is

$$\hat{H} = \frac{-\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} + e\epsilon r \cos\theta$$

7. The trial wave function of a system is expanded as  $\Psi_t = c_1\phi_1 + c_2\phi_2$ . The matrix elements of the Hamiltonian are

$$\langle \phi_1 | \hat{H} | \phi_1 \rangle = 0; \langle \phi_1 | \hat{H} | \phi_2 \rangle = 2 = \langle \phi_2 | \hat{H} | \phi_1 \rangle$$

and  $\langle \phi_2 | \hat{H} | \phi_2 \rangle = 3$ . Calculate the ground state energy of the system by employing linear variational principle.  $3$

8. What do you mean by product wave function? What is an STO? Write the Slater determinant for a three electron system.  $1+1+1$

9. Answer **any one** of the following:  $5 \times 1 = 5$

(a) Write the Hamiltonian of a system having  $N$  electrons and  $M$  nuclei. Discuss the Börn-Oppenheimer approximation for a system of  $N$  electrons and  $M$  nuclei.  $1+4$

(b) Derive the Spin-orbit coupling Hamiltonian ( $H_{SO}$ ) for a one electron and one nucleus system.  $5$

10. Answer **any one** of the following:  $2 \times 1 = 2$

(a) Derive the possible terms for the  $SP^3$  configuration.  $2$

(b) Construct a diagram showing the form of the Zeeman effect when a magnetic field is applied to a  ${}^3D_2 \rightarrow {}^3P_1$  transition.  $2$