2117

B.Sc. (H.S.) Third Semester

CHEMISTRY

Paper—Chem-303

(Quantum Chemistry)

Time allowed—Three Hours] [Maximum Marks—75

Note :— All parts of any question should be attempted in continuation at one place.

SECTION—A

(Compulsory)

1. (i) E = h f (f is frequency) is known as .... and this term was given by ....

(ii) Name the relation

$$\text{energy density } \alpha \frac{8 f^2 kT}{C^3}.$$

(iii) How many orbitals are there in a shell with n = 3 ?

(iv) What is the difference between a scalar matrix and unit matrix ?

(v) What is the degeneracy of the state having the energy 17 in units of $\frac{h^2}{8 ma^2}$ for a particle in two dimensional square box of each side 'a'.

(vi) What is orthogonality ?

(vii) Write the Hamiltonian for H_2^+ ion.

(viii) What is the third postulate of quantum mechanics ?

(ix) Why the wave function should be anti-symmetric ?

(x) What is Born-Oppenheimer approximation ?

1½×10=15

SECTION—B

Note :— Attempt any **EIGHT** questions out of the twelve questions each question carry 4½ marks.

1. If AB = –BA, the matrices A and B anti-commute. Show that the Pauli-Spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -1 \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$(i^2 = -1)$

Anti-commute in pairs. Show only in one case.

2. The eigenvalues i.e. energy levels of each rotational level, of rigid rotator problem is given by :

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

where I is the moment of inertia and J = 0, 1, 2, ... Calculate the energies of the first four levels and find the energy difference between each level.

3. The wave functions for a particle in a box of width 'a' is given by :

$$\psi_n = \sqrt{\frac{2}{a}} \sin\frac{n\pi}{a} x.$$

Plot this function for n = 4 and explain how many nodal points are there.

4. Show that sin 2x is not an eigen function of the operator $\frac{d}{dx}$ but of $\frac{d^2}{dx^2}$; what is the eigen value.

5. Prove that $\psi = A\cos 2\pi\left(\frac{x}{\lambda} - vt\right)$ is a solution of the equation

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi.$$

What is the physical meaning of the Schrödinger equation ?

6. Explain the significance of particle in a box.

7. The Hermite polynomial of degree 'n' is given by :

$$H_n = (-1)^n e^{\xi^2} \frac{d^n e^{-\xi^2}}{d\xi^n}.$$

Obtain the Hermite polynomial H_0, H_1 and H_2.

8. Set up Schrödinger equation for the rigid rotor and separates into two equations.
9. Show that the reduced atomic mass is close to the electronic mass.
10. Show that in atomic units

$$\hat{L}_z \hat{L}_+ = L_+ \left(\hat{L}_z H\right).$$

11. Set up the S.W.E. for hydrogen atom in polar co-ordinates.
12. What should be the characteristics of a well behaved function ?

SECTION—C

Note :— Attempt any **TWO** questions from this section. Each question carries 12 marks.

1. Using the first order-time independent perturbation theory solve the Schrödinger equation for the ground state of Helium atom. 15
2. Outline the salient features of the Hartree-Fock self consistent field theory for solving the Schrödinger wave equation for a many electron atom. 15
3. Starting from Plank's distribution law for the energy density in a cavity containing "black body radiation",

$$E(v)dv = \frac{8\pi h v^3}{C^3} \frac{dv}{e^{hv/kT} - 1}$$

derive :—

(i) the Stefan-Boltzmann fourth-power law $E = \sigma T^4$ where σ is the Stefan-Boltzmann constant,

(ii) the Wein displacement law, $\lambda_{max} = \frac{C}{T}$ where C is a constant and λ_{max} is the wavelength where energy density reaches a maximum at a given temperature.

(iii) Show that the Planck radiation law becomes identical with the Rayleigh-Jeans law if the size of the energy quantum is allowed to vanish or if the temperature is too high. 5+5+5=15

4. (a) Verify that the function $\psi(x) = x\, e^{-x^2/2}$ is an eigen function of the operator $\frac{d^2}{dx^2} - x^2$. What is the corresponding eigen value ? 6

(b) On the basis of the particle in a box model verify that the π-electron density in butadiene is maximum between carbon atoms 1 and 2 (and 3 and 4) but minimum between carbon atoms 2 and 3. (average C–C bond length is 0·140 nm). 9