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14 (CHM-1) 104

2022

CHEMISTRY

Paper : CH-104

(Quantum Chemistry)

Full Marks : 60

Time : Three hours

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

1. Prove that in the polar co-ordinate representation, the Heisenberg uncertainty is given by, $\Delta L \Delta \theta \geq h/2$, where L and θ represent angular momentum and the angle of the position vector with respect to x-axis respectively. 3
2. Justify if the following wavefunction is well-behaved or not ? 2

$$\bullet \frac{\tan x}{\sqrt{1-x^2}}, x \in -(\infty, \infty)$$

Contd.

3. Answer **any four** from the following :

2×4=8

(a) What is the physical significance of $\langle \hat{x} \rangle = L/2$, for an electron moving in straight chained conjugated polyene, where L is the length of the polyene.

(b) What is the molecular interpretation of an eigenvector ?

(c) The wavefunction for the 1s orbital in

$$H\text{-atom is given by } \psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

which is an exponentially decaying function in r . How does the 1s orbital become spherical in shape ?

(d) Evaluate the commutator $[\hat{p}_x, \hat{y}]$.

(e) Calculate the energy of 3 non-interacting electrons trapped in a box of length L .

(f) For the wavefunction of the H -atom, what is the reason behind the expression

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi) ?$$

4. The general wavefunction of a harmonic oscillator is given by $\psi_v(z) = N_v H_v(z) e^{-z^2/2}$, where N_v is a normalization constant,

$H_v(z) = (-1)^v e^{z^2} \frac{d^v}{dz^v} e^{-z^2}$ is the Hermite polynomial and v is the quantization number. Find out the expression for the ground state wavefunction. 2

5. Starting from a 2-dimensional Hamiltonian in the 1s atomic orbital basis, show that the bonding orbital of a H_2 molecule is given by $\frac{1}{\sqrt{2}}(1s_A + 1s_B)$, where A and B refer to the two H -atoms bonded together by a constant potential V . 4

OR

✓ Prove that $i \frac{d^2}{dx^2}$ is not a Hermitian operator.

6. Systematically predict the linear combinations of the contributing orbitals for the π -bonds' wavefunctions in cis-butadiene using Hückel theory. 4

7. Answer **any one** :

- (a) The wavefunctions of three molecular orbitals are given by :

$$\phi_1 = \psi_1 - \frac{1}{\sqrt{2}}\psi_2 + \sqrt{\frac{3}{2}}\psi_3$$

$$\phi_2 = \psi_1 + \sqrt{2}\psi_2$$

$$\phi_3 = \psi_1 - \frac{1}{\sqrt{2}}\psi_2 - \sqrt{\frac{3}{2}}\psi_3$$

where the atomic orbitals obey,

$$\hat{H}_i\psi_i = E_i\psi_i, \quad i = 1, 2, 3.$$

Answer the following :

- (i) Express the molecular orbitals in bracket notation using the atomic orbitals as basis. 0.5×3=1.5
- (ii) Find the normalization constant for ϕ_1 . 1.5
- (iii) Show that ϕ_2 and ϕ_3 are orthogonal to each other. 1.5
- (iv) Which orbital has the highest energy and why? 1.5

- (b) How does a diatomic molecule represent simple harmonic vibration? Starting from Schrödinger's equation of a diatomic molecule, show that the quantized vibrational energy is given by $E_v = (v + 1/2)\hbar\omega$, where v is the vibrational quantum number and ω is the angular frequency. 1+5=6

8. The wavefunction for an excited electron in F-atom is given by,

$$\psi(\rho) = \frac{1}{81\sqrt{3\pi}} \left(\frac{9}{a_0}\right)^{3/2} (27 - 18\rho + 2\rho^2) e^{-\rho/3}, \quad \rho = 9r/a_0$$

- (a) How many nodes are present? 1
- (b) Sketch and explain the radial part as a function of r . 2
- (c) What orbital can the wavefunction represent? 1

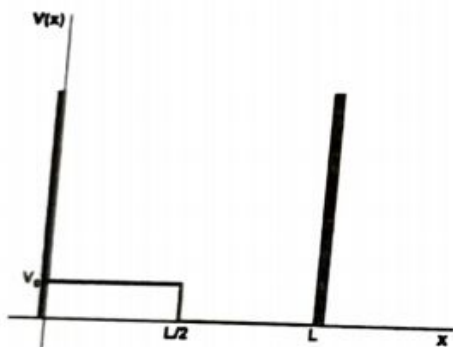
9. Answer **any three** from the following : 3×3=9

- (a) Construct the Hamiltonian for a system of M electrons and N nuclei. What are the spin orbitals that you can construct from $\psi(r)$? 1.5+1.5=3

- (b) What is a product wavefunction? What is the advantage of an STO over Hartree product? 1.5+1.5=3
- (c) The unperturbed wavefunctions for the infinite square well are

$$\psi_n^0(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right).$$

If one applies perturbation as given in the figure, find the first order correction to the energies.



- (d) Identify $H^{(0)}$ and $H^{(1)}$ for the following problems: 1.5×2=3
- (i) An oscillator governed by the potential

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

- (ii) A hydrogen atom is in an electric field of strength ϵ . The Hamiltonian operator for this system is

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

10. Answer **any four** from following: 4×4=16

- (a) What is the importance of Rabi formula? Derive the expression for the second order energy correction of a non-degenerate system having time independent potential. 1+3=4
- (b) State the variation theorem. Find the optimum form of a trial function having form $e^{-\alpha r}$. 1+3=4

Use the following Standard Integral:

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

- (c) Derive the form of the secular determinant considering a fixed set of two basis functions (linearly dependent on parameters) and hence find the expression for the optimum energy. 4

(d) What are Börn-Oppenheimer approximations? How will you solve the electronic and nuclear Schrödinger equations for a many electron system?

1+3=4

(e) What is Stark effect? Derive the expression for spin-orbit coupling Hamiltonian (H_{SO}).

1+3=4

11. Account for the form of the Zeeman effect when a magnetic field is applied to the transition ${}^3D_2 \longrightarrow {}^3P_1$.

2
