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14 (CHM-1) CH 104

2019

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) Derive the normalization condition in plane polar coordinate. Normalize the following wavefunction :

$$f(x, y) = Ne^{-(x^2 + y^2)} \quad 2+3$$

(b) (i) For the general angular momentum operator, $\hat{J}$, evaluate the following commutator : 2½

$$[\hat{J}_z, \hat{J}_-]$$

Contd.

- (ii) For the position and linear momentum operators, evaluate the following commutator relationship :

$$[\hat{x}, \hat{p}_x] \quad 2\frac{1}{2}$$

- (c) Show that the operators $\hat{x}$ and $\hat{p}_x$ are hermitian. 5
- (d) (a) Prove that hermitian operators have real eigenvalues. $2\frac{1}{2}$
- (b) Prove that eigenfunctions of hermitian operators having non-degenerate eigenvalues are orthogonal. $2\frac{1}{2}$
- (e) Determine the average value of the kinetic energy T for the one-dimensional particle in an infinite box. The wave functions of the one-dimensional particle in an infinite box have the form

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) , & 0 \leq x \leq L \\ 0 & , \quad x < 0, x > L \end{cases},$$

where n is the quantum number and L is the width of the box. 5

(f) For a system of two interacting particles of mass m_1 and m_2 , derive the expression of the total Hamiltonian of the system as a sum of Hamiltonians of two independent particles of mass $M = m_1 + m_2$ and reduced mass μ . Assume that the interacting potential is dependent only on the distance between the particles. 5

2. Explain the principles of L - S and J - J coupling. 3

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

5×2=10

(a) Consider a simultaneous eigenfunction $Y(\theta, \phi)$ of $\hat{L}^2$ and $\hat{L}_z$. Write the eigenvalue equation of $\hat{L}^2$ and apply the method of separation of variables to derive two independent equations based on θ and ϕ . Base on this find a solution of the ϕ -equation to obtain the eigenvalues of $\hat{L}_z$. 5

(b) Describe the free-electron MO theory of benzene. 5

(c) (i) What is the orbital angular momentum for electrons in 3s, 3p, and 3d orbitals (expressed in terms of $\hbar$)? How many radial and angular nodes do each of these orbitals have? 3

(ii) The radial wave function for the 2s orbital of the hydrogen atom can be written as

$$R_{n,l} = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} (2 - \rho) e^{-\rho/2}$$

$$\text{where } \rho = \frac{2Zr}{na_0}$$

Find the location of the radial nodes in this orbital in terms of a_0 . 2

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

$$5 \times 4 = 20$$

(a) What are the underlying principles of perturbation theory? For a non-degenerate system if the potential function is independent of time, derive the second order energy correction (E_n^2) .

$$1+4$$

(b) If the trial function is of following form :

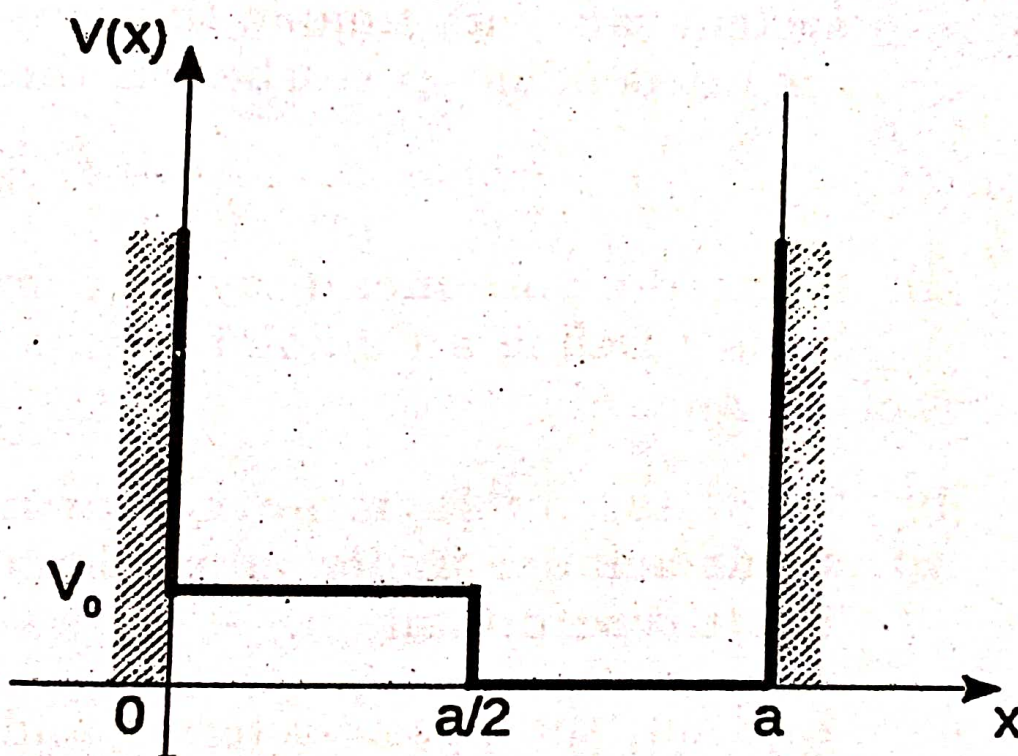
$$\varphi = c_1 f_1 + c_2 f_2$$

then find the variational approximation for the ground state energy by employing linear variational theorem.

5

(c) (i) Find the first-order correction to the energy of a particle in an infinite square well if the perturbation applies to only a half-way across the well as shown in the following figure :

3

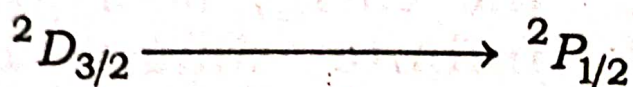


(ii) Why is the Rabi formula significant ?

2

(d) What is a product wavefunction? How one will calculate the Born-Oppenheimer approximation to the total energy? 1+4

(e) (i) Construct a diagram showing the form of the Zeeman effect when the magnetic field is applied to the transition



(ii) Describe the Stark effect. 3+2

(f) How will the coefficients of a two level system vary with time in the context of time dependent perturbation theory? 5

5. (a) What do you mean by a complete basis? Define an adjoint matrix. 1+1

(b) Why is antisymmetry principle significant? For He atom derive the Slater-type orbital. 1+2

(c) Find out the possible terms and their degeneracies for the s^1p^1 case. 2