

2019

CHEMISTRY

( Major )

Paper : 5.1

( Quantum Chemistry )

Full Marks : 60

Time : 3 hours

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

*Symbols signify their usual meanings*

1. Answer any seven of the following in brief :

1×7=7

- (a) Write the postulate of quantum mechanics regarding the expectation value of a physical quantity of a system.
- (b) Find the expression for the Hamiltonian operator for a particle of mass  $m$  with potential energy  $V$ . Consider only  $x$ -dimension.

- (c) The state function  $\Psi$  takes on only real values. State True or False.
- (d) The normalization condition is  $\int \psi^2 d\tau = 1$ . State what this condition actually means.
- (e) Write the spin orbital for ground state H-atom.
- (f) State why the molecular orbitals of a heteronuclear diatomic molecule cannot be classified as *g* or *u*.
- (g) Write the term symbol for the ground state hydrogen molecule.
- (h) The energy of a free axis rigid rotator is given by  $\frac{\hbar^2}{I}$ . State how many folds this energy level will degenerate.
- (i) Give the schematic plot of  $\psi^2$  against  $x$  of one-dimensional harmonic oscillator, if the value of the quantum number is zero.

2. Answer the following questions : 2×4=8

- (a) A function must be quadratically integrable in order to be well-behaved. State when a function is said to be quadratically integrable. Write why the function has to be quadratically integrable.
- (b) Show that  $e^{ikx}$  is an eigenfunction of the momentum operator,  $p_x$ .
- (c) Normalize the function  $\cos \frac{\pi x}{a}$  over the interval  $0 \leq x \leq a$ .

Or

Out of  $\frac{d}{dx}$  and taking square-root ( $\sqrt{\quad}$ ), explain which is linear operator and which is not.

- (d) Write the expressions for the magnitude and the  $z$ -component of angular momentum. Find the magnitude of the orbital angular momentum of an electron in  $d$ -orbital.

Or

Find the magnitude of the spin angular momentum of an electron. Write how many orientations of the spin angular momentum will be observed in presence of a magnetic field applied in a particular direction.

3. (a) Write the approximate spatial function and the spin functions for the electrons of the ground state He-atom. State Pauli's antisymmetry principle and hence find the acceptable complete wave function of He-atom. 2+3=5
- (b) Using Hückel method, find the  $\pi$ -bond energy of ethene. Hence explain how the formation of the  $\pi$ -molecular orbital stabilizes the molecule. 3+2=5
- (c) Write the time-independent Schrödinger equation for  $H_2^+$ . Indicate the kinetic energy terms and the potential energy terms present in the Hamiltonian of the equation. Using Born-Oppenheimer approximation, explain how the Schrödinger equation for  $H_2^+$  can be separated into two equations. 1+1+3=5

Or

Use the LCAO method to form the MO wave function of  $H_2^+$ . Using this wave function, deduce the energy expressions for the bonding and the antibonding MOs.

1+4=5

4. Answer either (a), (b) and (c) or (d), (e) and (f) :

(a) For a particle moving on a ring of radius  $r$ , the wave function is  $\psi = Ne^{im\phi}$ . Show that the possible values of  $m$  are  $0, \pm 1, \pm 2, \dots$  . 3

(b) For a particle in a one-dimensional box of length  $a$ , where potential energy is zero, solve the time-independent Schrödinger equation to get the value of the wave function and energy. 4

(c) The ground-state translational energy of a particle in a one-dimensional box of length 300 pm is 4 eV. Find the ground-state translational energy of the same particle, if it is moving in a cube of length 100 pm. 3

(d) Deduce Planck's radiation law in terms of wavelength in case of blackbody radiation. 4

(e) For a particle in one-dimensional box, where potential energy is zero, show that the average value of momentum is zero. 3

(f) Assume  $b \sin \frac{n\pi x}{a}$  to be the wave function for a particle in one-dimensional box of length  $a$ , where  $V=0$ . Verify whether it satisfies the eigenvalue equation,  $H\psi = E\psi$ , or not. 3

5. Answer either (a), (b) and (c) or (d), (e) and (f) :

(a) Mention the quantum numbers on which the radial function and the angular function of H-atom depend. Discuss what information can be drawn from the plots of the radial function and the square of the radial function against the radial distance. 1+3=4

(b) Write in brief about the Russell-Saunders coupling of angular momentum. Write the term symbol for  $3s^1$  electron. 2+1=3

(c) Show that the maximum probability of finding the electron of the ground state H-atom is at  $r = a_0$ . 3

- (d) Write a short note on Stern-Gerlach experiment. 4
- (e) Deduce an expression for the radial distribution function for non-s state. 3
- (f) Calculate the average value of the radial distance of the electron from the nucleus of the H-atom in ground state. 3
6. Answer either (a) and (b) or (c) and (d) :
- (a) Heitler and London used the following wave function for the bonding in  $H_2$  :
- $$\psi = C_1 1s_A(1) 1s_B(2) + C_2 1s_A(2) 1s_B(1)$$
- Explain why this wave function is preferred to the MO wave function of  $H_2$ . Write how this wave function is an improvement over the MO wave function of  $H_2$ . 3+3=6
- (b) Using the energy expression of the bonding MO of  $H_2^+$ , write how the potential energy diagram is constructed. Also write what information you can draw from this diagram. 2+2=4

- (c) Using the energy expressions, find the normalized MO wave functions of  $H_2^+$ . Give the schematic plots of the square of the wave functions against internuclear distance. State what information can be drawn from these plots. 4+2=6
- (d) The energies of the  $\pi$ -MOs of benzene, according to Hückel method, are  $\alpha + 2\beta$ ,  $\alpha + \beta$ ,  $\alpha - \beta$  and  $\alpha - 2\beta$ . Here each of the energy levels  $\alpha + \beta$  and  $\alpha - \beta$  is doubly degenerate. Using this result, explain how the formation of delocalized  $\pi$ -MOs stabilizes the molecule. 4

★ ★ ★

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