

2017

CHEMISTRY

(Major)

Paper : 5.1

(Quantum Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks
for the questions

(The symbols used signify their usual meanings)

1. Answer the following questions in brief (any seven) : 1×7=7

(a) Show whether the following operation is linear or not :

$$\hat{D}\psi = \frac{d\psi}{dx}$$

(b) What do you mean by degree of degeneracy?

(c) Define complete wave function.

(d) Why is Pauli's antisymmetry principle not applicable for bosons?

- (e) Find the number of levels for the term $2D$.
- (f) What is equivalent electron?
- (g) Find the term symbol for H_2^+ .
- (h) When is Russell-Saunders coupling valid?

2. Answer the following questions (any four) :

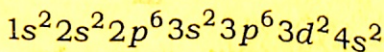
2×4=8

- (a) Normalize the following wave function :

$$\psi = e^{-ar}, \quad a > 0 \text{ for } -\infty \text{ to } +\infty$$

- (b) Show that hydrogenic wave functions are n^2 -fold degenerate.

- (c) Apply Hund's rule to predict the lowest term of the configuration



- (d) What are the magnitudes of total orbital, total spin and total angular momenta for the ground state term $4F$ of vanadium?

(e) The ψ_{2s} atomic orbital for H-like atom are given as

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{z}{a_0} \right)^{3/2} \left(2 - \frac{z_r}{a_0} \right) \exp(-z_r / 2a_0)$$

Calculate the radii of the nodal surfaces for H and He^+ . Comment.

3. Answer the following questions :

(a) Write short notes on : $2^{1/2} + 2^{1/2} = 5$

(i) Spectral selection rule

(ii) Pauli's antisymmetry principle

Or

(i) Taking $2p_z$ orbital as an example, explain why p -orbital is dumbbell in shape. 3

(ii) Compare the results of particle in a ring with particle in a box. 2

(b) (i) For linear harmonic oscillator, compare the classical and quantum mechanical results. 3

(ii) Normalize the H-like function $\psi = e^{-n}$. 2

Or

Applying Heitler-London theory, give the expression for Heitler-London wave function and corresponding energy of H_2 molecule. Draw the potential energy curve for H_2 molecule showing symmetric, antisymmetric states and experimental curve.

2+3=5

- (c) Mention the basic differences in the study of solution of Schrödinger equation for H-atom with that of Bohr's theorem.

5

Or

Explain what you mean by electron probability density. Prove that the electron probability density is maximum at the nucleus for ψ_{1s} orbital of the hydrogen atom. Write the expression for probability of finding the electron for the same orbital.

2+2+1=5

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

- (a) For a free particle, how can you show that its energy is not quantized? What is the restriction imposed on its energy? Give one example of free particle.

3+1+1=5

(b) Applying Schrödinger equation to one-dimensional harmonic oscillator, show that the energy levels of it are evenly spaced. 3

(c) Show that the probability density for a rotating particle on a ring is independent of angle θ . 2

Or

(d) A particle of mass m is confined in a one-dimensional box of length $2a$. If the origin of the coordinate system is located at the centre of the box so that the particle lies between $-a$ and $+a$, then show that the potential energy $V(x)$ of the particle under such condition becomes

$$\begin{aligned} V_x &= 0, & -a \leq x \leq +a \\ &= \infty, & |x| > a \end{aligned} \quad 5$$

(e) Show that

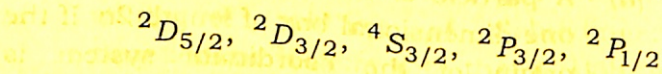
$$[\hat{x}, \hat{p}_x] = \frac{ih}{2\pi} \psi \quad 2$$

(f) An electron is accelerated by applying a potential difference of 1000 V. What is the de Broglie wavelength associated with it? Write one postulate of quantum mechanics. 2+1=3

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

(a) Describe the experiment to show that electron behaves like a spinning particle. Give the explanation for the doublet structure of electron spin. $3+2=5$

(b) Explain the selection rule of normal Zeeman effect. Arrange the following terms according to Hund's rule for ground-state nitrogen : $3+2=5$



Or

(c) Calculate the average distance of the electron from the nucleus of H-atom in the 2s-state. 3

(d) Calculate the ground-state energy of electron in (i) one-dimensional box of length 3×10^{-10} m and (ii) a cubical box of edge length 1×10^{-10} m in eV. Draw the energy-level diagrams for the 3D and 3P states. $3+2=5$

(e) Why s-type wavefunction has a maximum value at the nucleus while p-type and d-type functions have node at the nucleus? 2

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

(a) Write the approximation of the Hückel molecular orbital theory. 5

(b) Explain what is resonance using wave function concept and taking the example of H_2 . 3+2=5

Or

(c) Define radial distribution function. Deduce an expression for radial distribution function in case of non-s state. Give schematic plot of radial distribution function for $1s$, $2s$ and $2p$ -orbitals. 1+2+2=5

(d) What is the wavelength of the light absorbed when an electron in a linear molecule of 10 \AA long makes a transition from the energy level $n = 1$ to the level $n = 2$? 3

(e) For a particle in a three-dimensional box with $L_x = L_y = L_z/2$, what would be the energy when $n_x = 1$, $n_y = 2$, $n_z = 2$ and when $n_x = 1$, $n_y = 1$, $n_z = 4$? 2
