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

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$$

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

(Continued)

(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 : 2½+2½=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

$$V_x = 0 \quad , \quad -a \leq x \leq +a$$
$$= \infty \quad , \quad |x| > a$$

5

(e) Show that

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

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

$^2D_{5/2}$, $^2D_{3/2}$, $^4S_{3/2}$, $^2P_{3/2}$, $^2P_{1/2}$

Or

(c) Calculate the average distance of the electron from the nucleus of H-atom in the 2*s*-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 3*D* and 3*P* 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 2*p*-orbitals. 1+2+2=5

(d) What is the wavelength of the light absorbed when an electron in a linear molecule of 10 Å 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

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