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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 used signify their usual meanings

1. Answer in brief : 1×7=7

(a) Find the eigenvalue for the operator $\frac{d^2}{dx^2}$ if the function is $\cos 4x$.

(b) An operator $\hat{O}$ is defined as $\hat{O}\psi = \lambda\psi$, where λ is a constant. Show whether the operator is linear or not.

(c) Show whether the function $\psi = e^{-x}$ is well-behaved or not within the interval $0 \leq x \leq \infty$.

Or

One of the conditions for a function to be well-behaved is that the function must be single-valued. State why the function has to be single-valued.

(d) Draw a diagram to show the orientations of the orbital angular momentum of magnitude $\sqrt{2}\hbar$ in presence of the applied magnetic field in the z-direction.

(e) Find the term symbol for an electron in the d-orbital.

(f) Write the value of the angular function for s-orbital.

Or

Define the shape of an orbital.

(g) For the ground-state H-atom, write the wave functions for the spin-orbital.

2. Answer the following questions : $2 \times 4 = 8$

(a) Find the operator for total energy of a particle with mass m having coordinate (x, y, z).

(b) Normalize the function $\sin\frac{n\pi x}{a}$ within the interval $0 \le x \le a$. Here $n = 1, 2, 3, \cdots$.

Or

Show that the functions $\sin\frac{\pi x}{a}$ and $\cos\frac{\pi x}{a}$ are orthogonal within the interval $0 \le x \le a$.

(c) Let ψ_1 and ψ_2 be the eigenfunctions of the linear operator $\hat{O}$, having the same eigenvalue λ. Show that the linear combination of ψ_1 and ψ_2 is also an eigenfunction of $\hat{O}$ having the same eigenvalue.

(d) Consider the following sets of quantum numbers :

(i) $n = 2,\ l = 0,\ m_l = 0$

(ii) $n = 2,\ l = 1,\ m_l = 0$

(iii) $n = 2,\ l = 1,\ m_l = +1$

(iv) $n = 2,\ l = 1,\ m_l = -1$

State which of these sets yield imaginary wave functions. State how real functions are obtained from these imaginary functions.

Or

Taking $2p_z$-orbital as example, write why the p-orbital is dumbbell in shape.

3. What do you mean by complete wave function? Using Pauli's anti-symmetry principle, prove that no two electrons of an atom can have all the four quantum numbers alike. 1+4=5

Or

What do you mean by spin-orbit interaction? Write in brief about the Russell-Saunders scheme of coupling of angular momenta. Find the term symbols for the first excited state of He-atom. 1+2+2=5

4. Answer any *two* questions : 5×2=10

(a) Write the time-independent Schrödinger equation for H_2^+. State Born-Oppenheimer approximation. Discuss how this approximation can be applied to separate the Schrödinger equation for H_2^+ into two equations—one for the nuclei and the other for the electron. 1+1+3=5

(b) Applying Hückel molecular orbital method, calculate the π-bond energy of ethene. Also find the expressions for the π-molecular orbitals. 3+2=5

(c) Write how the molecular orbitals of a homonuclear diatomic molecule can be classified as σ or π. Which of these two is doubly degenerate and why? What is the basis of classifying the MOs as g or u? 2+2+1=5

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

(a) A particle of mass m is moving within a box of lengths a, b and c along x-, y- and z-axes respectively. The potential energy within the box is considered to be zero; outside the box it is considered to be infinity. Solve the time-independent Schrödinger equation for the particle to get the values of the wave function and the energy. Use these results to explain degeneracy. 4+2=6

(b) Calculate the zero-point vibrational energy of HCl if its force constant is $516 \ \mathrm{N m^{-1}}$. 4

Or

(c) State the experimental observation of the photoelectric effect. Discuss how Einstein explained the observation. 3+2=5

(d) A particle of mass m is moving in a one-dimensional box of length a, where potential energy is zero. Calculate the average kinetic energy of the particle. 3

(e) An electron is confined to a molecule of length 10^{-9} m. Considering the electron to be a particle in one-dimensional box, where $V = 0$, calculate its minimum energy. 2

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

(a) Define radial distribution function. Deduce an expression for the radial distribution function for non-*s* state. 1+3=4

(b) Explain what you mean by space quantization. 3

(c) Calculate the average value of potential energy of the electron of H-atom in the 1s state. 3

Or

(d) What do you mean by radial function? Give the plots of radial function against r for $n = 2$. State what information you can draw from these plots. 1+1+2=4

(e) State Hund's rule of maximum multiplicity. For the $2p^2$ electrons of the ground-state C-atom, the following terms are obtained :

$$^1D_2,\ ^3P_2,\ ^3P_1,\ ^3P_0,\ ^1S_0$$

Using Hund's rule, state which of these terms will be the lowest in energy. 2+1=3

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

7. Answer *either* (a) and (b) *or* (c) and (d) :

(a) Write the energy expressions for the bonding and the anti-bonding molecular orbitals of H_2^+. Hence explain how the potential energy diagram is constructed. Write what information can be drawn from this diagram. 1+3+2=6

(b) Write the approximations of the Hückel molecular orbital theory. 4

Or

(c) Write the ground-state molecular orbital wave function of H_2. Hence explain the drawback of the molecular orbital theory in case of H_2. State how Heitler and London modified the wave function. 1+3+1=5 *(d)* Using LCAO-MO method, deduce the secular equations of H_2^+. Hence deduce the expressions for the MO wave functions and their energies. 5

Standard integration :

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

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