Department

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 Ψ 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 ψ^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 $0 \le x \le a$.

Or

Out of $\frac{d}{dx}$ and taking square-root ($\sqrt{\ }$), 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 π-bond energy of ethene. Hence explain how the formation of the π-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 $0, \pm 1, \pm 2, \ldots$. 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 π-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 π-MOs stabilizes the molecule. 4

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