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OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. Degree (Chemistry) Examination (Part III)
CHM 303: Quantum Chemistry
2023/2024 Harmattan Semester Examination

Time Allowed: 2 Hrs **Date: 6th March, 2025**

Instruction: Answer ALL Questions

Useful constants: $m_p = 1.673 \times 10^{-27}$ kg, $m_e = 9.110 \times 10^{-31}$ kg, $\hbar = 1.055 \times 10^{-34}$ J s, electric charge $(e) = 1.602 \times 10^{-19}$ C, $\varepsilon_0 = 8.854 \times 10^{-12} J^{-1} C^2 m^{-1}$, $\pi = 3.143$, $h = 6.626 \times 10^{-34}$ J.s, $c = 3.0 \times 10^8$ m s^{-1}, $R_H = 1.097 \times 10^7$ m^{-1}, 1 Hartree = 4.360×10^{-18} J, 1 Hartree = 27.212 eV, $a_0 = 5.292 \times 10^{-11}$ m.

SECTION A

x^2 $= 2x$

(1.) a. The functions given below are defined in the interval $x = -a$ to $x = +a$ $\frac{1}{4}\left(\frac{15}{a^5}\right)^{1/2}$

(i) $\psi_1 = N_1(a^2 - x^2)$

(ii) $\psi_2 = N_2 x(a^2 - x^2)$

Find the value of the normalization constants, N_1 and N_2

b. Examine if ψ_1 and ψ_2 in question 1(a) above are orthogonal to each other.

c. Find the commutators:

(i.) $\left[\frac{d}{dr}, \frac{1}{r}\right]$ (ii.) $\left[\frac{d}{dx}, x^2\right]$

d. Find the results of operation of:

$L_z = -i\hbar\frac{\partial}{\partial\phi}$ on $\Phi = Ae^{im\phi}$ and $\Phi = A\sin m\phi$; and state if they are eigenfunctions. What is the eigenvalue in each case? **[20 mks]**

(2.) a. Calculate the wavenumber frequencies in cm^{-1} of an emission resulting from a transition between $N_2 = 3$ and $N_1 = 2$ for He^+, assuming that $R_{He^+} = 4R_H$. What name is given to this frequency range?

b. For a particle in a one-dimensional box for which the wavefunction is given as UV

P-Series

$$\psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin\frac{n\pi x}{a} \qquad 0 \le x \le a$$

Show that the $\sigma^2 = \langle E^2\rangle - \langle E\rangle^2 = 0$ [Use: $\int \sin^2 bx dx = \frac{x}{2} - \frac{1}{4b}\sin(2bx)$]

c. State any consequence(s) of the expression above as it relates to the energy of the particle in a one-dimensional box. **[15 mks]**

SECTION B

Square

(3.) a. The total energy of quantum harmonic oscillator can be expressed as:

$$E_n = \left(n + \frac{1}{2}\right)h\nu$$

(i) Define all the terms in the expression for the E_n and derive the expression for the energy gap (ΔE) between successive vibrational states in the oscillator.

Balmer Series

(ii) State four conclusions that could be deduced from the expressions of the total energy, E_n and energy gap, ΔE.

(iii) The H-F bond in HF molecule has a force constant of 966 Nm^{-1}. If H-F bond length is 0.917 Å and the bond behaves as a classical harmonic oscillator with classical energy, E_{cl}, calculate the vibrational frequency of a particular (different) quantum harmonic oscillator whose energy gap, ΔE has a value that is equivalent to the E_{cl} of H-F. ($h = 6.626 \times 10^{-34}$ Js, 1 Å $= 10^{-10}$ m).

(b) Given that the Hamiltonian for a particle rotating on a ring is $\hat{H} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$. If the wavefunction for the particle is $\psi = \frac{1}{\sqrt{2\pi}}e^{im\phi}$ (where $i^2 = -1$, and m = 0, ±1, ±2,...), show that the Hamiltonian and wavefunction of the particle obey the eigen value equation $\hat{H}\psi = E\psi$. Hence, write the expression for the energy of the particle in terms of m and I.

(4.) a. In an attempt to determine the ground state energy of an electron in a hydrogen atom, a theorist started with a trial function of the form $e^{-\alpha r}$ and derived that $\int_0^\infty \phi(r)\hat{\mathcal{H}}\phi(r)dr = \frac{\pi\hbar^2}{2m\alpha} - \frac{e^2}{4\varepsilon_0\alpha^2}$; and $\int_0^\infty \phi(r)\phi(r)dr = \frac{\pi}{\alpha^3}$.

(i) Write the expression for the variational integral $E = \frac{\int_0^\infty \phi(r)\hat{\mathcal{H}}\phi(r)dr}{\int_0^\infty \phi(r)\phi(r)dr}$.

(ii) Determine the value of α for which $\frac{dE}{d\alpha} = 0$, that is, the tightest bound, and hence

(iii) Show that the ground state energy (E_0) of the hydrogen atom is $-\frac{me^4}{8\varepsilon_0^2 h^2}$.

b. The normalized unperturbed (υ=0) harmonic oscillator wave function is $\psi = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha\frac{x^2}{2}}$, while a perturbed Hamiltonian for the system is $\hat{H} = \hat{H^0} + \hat{H}' = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \gamma x^3 + \frac{b}{4}x^4$.

(i) Which term(s) from the $\hat{H}$ is/are the perturbation potential term(s)?

(ii) Determine the perturbation correction to the energy.

[Hint: $\int_{-\infty}^{+\infty} x^3 e^{-zx^2}dx = 0$; $\int_{-\infty}^{+\infty} x^4 e^{-zx^2}dx = \frac{3}{4}\left(\frac{\pi}{z^5}\right)^{1/2}$] **(10 marks)**

c. Given the ground electron configurations of oxygen and chlorine atoms as $1s^2 2s^2 2p^4$ and $1s^2 2s^2 2p^6 3s^2 3p^5$, respectively. Derive the atomic term symbols for the level of the oxygen and chlorine atoms.

$E = h\nu$

$kx^2 = h\nu$

g/mol

$\frac{\hbar^2}{2m}$

$\frac{\hbar^2}{2m} - e$

$\frac{1}{\alpha^4}\left(\frac{\hbar^2}{2m} - \frac{e^2}{4\pi\varepsilon_0\alpha}\right)$