



## 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

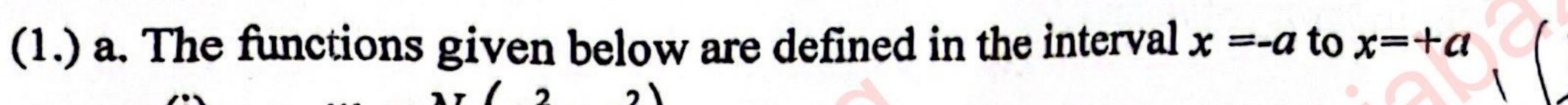
Time Allowed: 2 Hrs

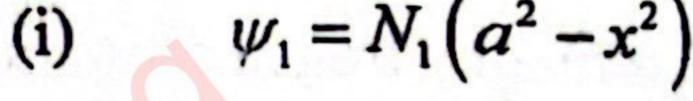
Date: 6th March, 2025

Instruction: Answer ALL Questions

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

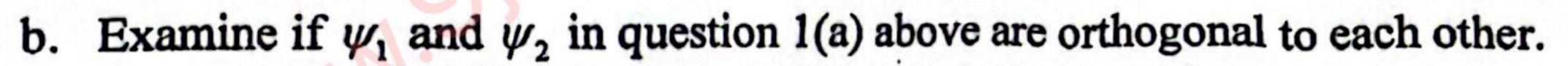
## SECTION A





(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<sub>1</sub> and N<sub>2</sub>





(i.) 
$$\left[\frac{d}{dr}, \frac{1}{r}\right]$$

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

- d. Find the results of operation of:  $L_z = -i\hbar \frac{\sigma}{\partial \phi}$  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<sup>-1</sup> of an emission resulting from a transition between  $N_2 = 3$  and  $N_1 = 2$  for He<sup>+</sup>, 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

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

Show that the 
$$\sigma^2 = \langle E^2 \rangle - \langle E \rangle^2 = 0$$

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 [Use:  $\int \sin^2 bx dx = \frac{x}{2} - \frac{1}{4b} \sin(2bx)$ ]

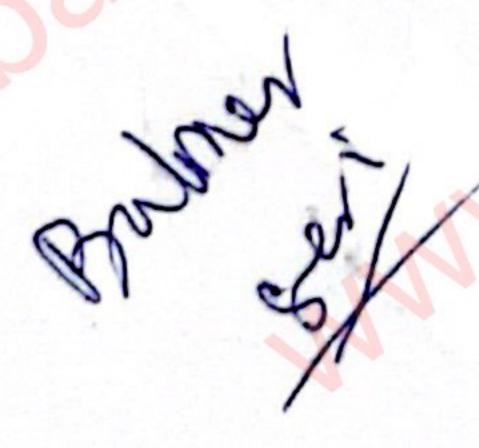
c. State any consequence(s) of the expression above as it relates to the energy of the particle in a onedimensional box. [15 mks]

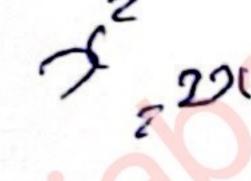
## SECTION B

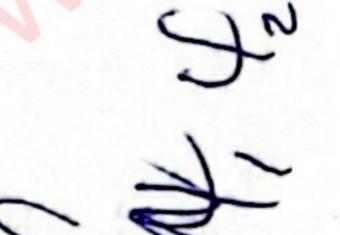
(3.) a. The total energy of quantum harmonic oscillator can be expressed as:

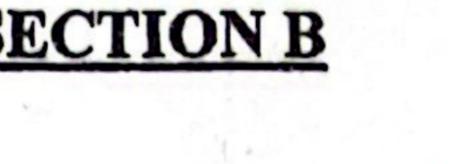
$$E_n = \left(n + \frac{1}{2}\right)h\nu$$

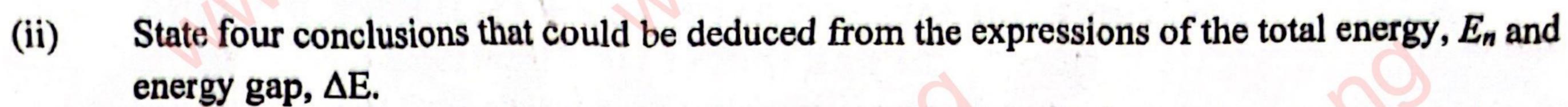
Define all the terms in the expression for the  $E_n$  and derive the expression for the energy gap (i) (ΔE) between successive vibrational states in the oscillator.











- (iii) The H-F bond in HF molecule has a force constant of 966 Nm<sup>-1</sup>. If H-F bond length is 0.917 Å and the bond behaves as a classical harmonic oscillator with classical energy, E<sub>cl</sub>, calculate the vibrational frequency of a particular (different) quantum harmonic oscillator whose energy gap, ΔE has a value that is equivalent to the E<sub>cl</sub> of H-F. (h = 6.626 x 10<sup>-34</sup> Js, 1 Å = 10<sup>-10</sup> m).
- (b) Given that the Hamiltonian for a particle rotating on a ring is  $\widehat{H} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$ . If the wavefunction for the particle is  $\psi = \frac{1}{\sqrt{2\pi}}e^{im\phi}$  (where  $i^2 = -1$ , and  $m = 0, \pm 1, \pm 2,...$ ), show that the Hamiltonian and wavefunction of the particle obey the eigen value equation  $\widehat{H}\psi = E\psi$ . 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  $\int_0^\infty \phi(r) \mathcal{H} \phi(r) dr = \frac{\pi \hbar^2}{2m\alpha} \frac{e^2}{4\epsilon_0 \alpha^2}$ ; and  $\int_0^\infty \phi(r) \phi(r) dr = \frac{\pi}{\alpha^3}$ .
  - (i) Write the expression for the variational integral  $E = \frac{\int_0^\infty \phi(r) \Re \phi(r) dr}{\int_0^\infty \phi(r) \phi(r) dr}$ .

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- (ii) Determine the value of  $\alpha$  for which  $\frac{dE}{d\alpha} = 0$ , that is, the tightest bound, and hence
- (iii) Show that the ground state energy (E<sub>0</sub>) of the hydrogen atom is  $\frac{me^4}{8\epsilon_0^2h^2}$ .
- b. The normalized unperturbed (v=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 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  $1s^22s^22p^4$  and  $1s^22s^22p^63s^23p^5$ , respectively. Derive the atomic term symbols for the level of the oxygen and chlorine atoms.

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