NAMIBIA UNIVERSITY
OF SCIENCE AND TECHNOLOGY

FACULTY OF HEALTH, NATURAL RESOURCES AND APPLIED SCIENCES

SCHOOL OF NATURAL AND APPLIED SCIENCES

DEPARTMENT OF BIOLOGY, CHEMISTRY AND PHYSICS

QUALIFICATION: BACHELOR OF SCIENCE	
QUALIFICATION CODE: 07BOSC	**LEVEL:** 7
COURSE NAME: QUANTUM CHEMISTRY AND SPECTROSCOPY	**COURSE CODE:** QCM701S
SESSION: JUNE/JULY 2023	**PAPER:** THEORY
DURATION: 3 HOURS	**MARKS:** 100

SUPPLEMENTARY/SECOND OPPORTUNITY EXAMINATION QUESTION PAPER	
EXAMINER(S)	**Prof Habauka M Kwaambwa**
MODERATOR:	**Prof Edet F Archibong**

INSTRUCTIONS
1. Answer ALL the SIX questions 2. Write clearly and neatly 3. Number the answers clearly 4. All written work must be done in blue or black ink 5. No books, notes and other additional aids are allowed 6. Mark all answers clearly with their respective question numbers

PERMISSIBLE MATERIALS

Non-programmable Calculators

ATTACHMENT

List of Useful Constants

THIS QUESTION PAPER CONSISTS OF 5 PAGES (Including this front page and list of useful constants as an attachment)

QUESTION 1 **[16]**

(a) State briefly what is meant by ***blackbody radiation***. Show graphically the effect of temperature a typical wavelength distribution curve of the emitted blackbody radiation. (5)

(b) Explain briefly ***quantisation of energy, particle-wave duality*** and **degeneracy** as used in quantum mechanics. (3)

(c) The photoelectric effect experiment demonstrates that light has particle-like properties. What is the effect of increasing (i) the frequency of incident light and (ii) intensity of the incident light. (4)

(d) Calculate the energy of photon and an electron when each has a wavelength of 1 Å and comment on the relative magnitude of your answers. (4)

QUESTION 2 **[21]**

(a) Investigate whether the function y(x) = Acosx + Bsinx (where A and B are constants) is a solution to the differential equation:

$$\frac{d^2y(x)}{dx^2} + y(x) = 0$$ (4)

(b) Explain using mathematical expressions what you understand by the following terms as used in quantum mechanics: (6)

(i) Linear operators
(ii) Normalised wavefunction
(iii) Expectation value

(c) The normalised wavefunction for a particle-in-a-box is of the form

$$\Psi = \left(\frac{2}{a}\right)^{\frac{1}{a}} \sin\left(\frac{n\pi}{a}x\right), \text{ for } 0 \le x \le a$$

Calculate the probability that a particle in a one-dimensional box of length *a* is found to be between 0 and *a*/2. (5)

Note: $\int \sin^2 kx dx = \int\left(\frac{1}{2}(1-\cos 2kx)\right)dx$

(d) Using the wavefunction in (c) above, sketch e variations of $\Psi(n=4)$ and $\Psi^2(n=4)$ in the range $0 \le x \le a$. At what values of x in terms of *a* is $\Psi(n=4)$ = 0 in the range $0 \le x < a$. (6)

QUESTION 3 **[10]**

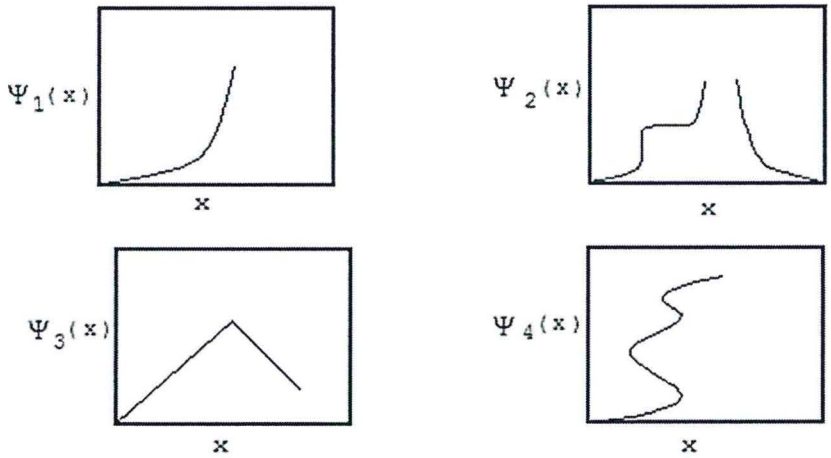
(a) If Φ_A and Φ_A are real normalised and orthogonal atomic orbitals belonging to A and B, respectively, show that the molecular orbital of their linear combination below is also normalised.

$$\Psi = \frac{1}{\sqrt{2}}(\Phi_A + \Phi_B) \quad (5)$$

(b) Using the Quantum theory rules, construct the operators $\hat{T}^2$. (5)

QUESTION 4 **[10]**

One of the postulates of quantum theory states that **"a wavefunction must be well-behaved"**. Explain what this means. The four diagrams below show some sketches that are supposed to represent wavefunctions. State, with reasons, whether each of the following is a well-behaved function or not.



QUESTION 5 **[11]**

Consider a π-electron which is part of a conjugated hydrocarbon chain. Take the length of the conjugated carbon chain as 16 Å. Use the free-electron molecular orbital (FEMO) method, which assumes that the π-electrons are trapped in a 1-D box, to answer the following questions. (Assume the electrons fill up to the n = 5 level)

(a) Calculate the zero-point energy (in eV) of the system. (3)

(b) Starting with the E_n expression for a particle-in-a-box, show that $\lambda = \frac{8mL^2c}{(2n+1)h}$ for a given transition. (5)

(c) What is the wavelength (in **nm**) of the light necessary to excite a transition from n = 5? (3)

QUESTION 6 **[15]**

(a) Which of the following molecules will possess a (i) rotational microwave spectrum, and; (ii) vibrational (infrared) spectrum: N_2, IBr, CS_2, CH_3Cl? Give brief reasons for your answers. (5)

(b) The allowed rotational energy levels of a rigid diatomic molecule are given by:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

(i) State what all the symbols in this equation represent. (2)

(ii) What is the selection rule for the rotational energy transitions and hence show that the separation between the successive spectral absorption lines is always 2B, where B is the rotational constant. (4)

(iii) The rotational constant of $^1H^{35}Cl$ (hydrogen chloride) is greater than of $^2D^{35}Cl$ (deuterium chloride). Explain, with reasons, this statement. (4)

QUESTION 7 **[17]**

After a freaky accident in the lab only a small part at the centre of the ro-vibrational spectrum of $^1H^{127}I$, with peaks at 2296.40, 2322.60 and 2335.70 cm^{-1}, was recovered. From the recovered data of the spectrum:

(a) Assign the transitions to each of the peaks. (6)

(b) Calculate the bond length. (7)

(c) Calculate the force constant. (4)

Atomic masses (amu): ^1H = 1.008 ^{127}I = 126.90

END OF EXAM QUESTIONS

USEFUL CONSTANTS:

Universal Gas constant	R	=	$8.314\ J\ K^{-1}\ mol^{-1}$
Boltzmann's constant,	k	=	$1.381 \times 10^{-23}\ J\ K^{-1}$
Planck's constant	h	=	$6.626 \times 10^{-34}\ J\ s$
Debye-Huckel's constant,	A	=	$0.509\ (mol\ dm^{-3})^{1/2}$ or $mol^{-0.5}kg^{0.5}$
Faraday's constant	F	=	$96485\ C\ mol^{-1}$
Mass of electron	m_e	=	$9.109 \times 10^{-31}\ kg$
Velocity of light	c	=	$2.998 \times 10^{8}\ m\ s^{-1}$
Avogadro's constant	N_A	=	6.022×10^{23}
1 electron volt (eV)		=	$1.602 \times 10^{-19}\ J$