NAMIBIA UNIVERSITY
OF SCIENCE AND TECHNOLOGY
FACULTY OF HEALTH, APPLIED SCIENCES AND NATURAL RESOURCES

DEPARTMENT OF NATURAL AND APPLIED SCIENCES

QUALIFICATION: BACHELOR OF SCIENCE	
QUALIFICATION CODE: 07BOSC	**LEVEL:** 7
COURSE NAME: QUANTUM CHEMISTRY AND SPECTROSCOPY	**COURSE CODE:** QCM701S
SESSION: JULY 2022	**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 bule 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 6 PAGES (Including this front page and list of useful constants as an attachment)

QUESTION 1 **[18]**

(a) Waves can be characterised by **amplitude, wavelength** and **frequency**. Define these three terms. (3)

(b) The photoelectric effect experiment demonstrates that light has particle-like properties. What is effect of increasing (i) the frequency of incident light and (ii) the intensity of the incident light? (iii) 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. (8)

(c) The work function of potassium (K) is 2.20 eV. (i) Calculate the threshold frequency of the metal. (ii) Will violet light of wavelength 4000 Å cause the photoelectric effect in K? (4)

(d) The stopping voltage for the electrons emitted from a metal due to photoelectric effect is found to be 1 V for light of 2500 Å. Calculate the work function of the metal in eV. (3)

QUESTION 2 **[17]**

(a) The normalised wave function, $\Psi_n(x)$, for an electron in the highest occupied molecular orbital of butadiene based on 1-dimensional particle-in-a-box model is given by:

$$\Psi_n(x) = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{n\pi}{L}x\right) \qquad \text{for } 0 \le x \le L \text{ and } n = 1, 2, 3, \text{etc.}$$

(i) What is the physical meaning of such a normalised wave function? (1)

(ii) Why is n = 0 not permissible for the particle-in-a-box model? (1)

(iii) Sketch the variation of $\Psi_3(x)$ versus x and $\Psi_3^2(x)^2$ versus x. (2)

(iv) For what value(s) of x in the range 0 < x < 30 nm is $\Psi_3(x) = 0$ for a box of length 30 nm? (2)

(b) On the same diagram show the variation of $\Psi(n=1)$, $\Psi(n=2)$ and the product $\Psi(n=1)\cdot\Psi(n=2)$ across the length of the box. Comment on the physical significance of the product $\Psi(n=1)\cdot\Psi(n=2)$. (5)

(c) For the five wavefunctions (n = 1 through n = 5) for a particle-in-a-box, state whether each of the following statements is **TRUE** or **FALSE** about the probability of finding the particle near $x = \frac{L}{2}$: (5)

(i) Least for n = 1

(ii) The same (and non-zero) for n = 1, 2, 3, 4 and 5

(iii) Zero for n = 1, 2, 3, 4 and 5

(iv) Least for n = 5

(v) Least for n = 2 and n = 4

QUESTION 3 **[19]**

(a) With reference to a free particle moving in the x-direction whose wave function is $\Psi = Ae^{ikx}$, derive expressions of the eigenvalue of the momentum operator, $\hat{P}_x = -i\hbar\frac{d}{dx}$ and the expectation value of the momentum of an observable. (9)

(b) The normalised wave function for a particle-in-a-box is of the form

$$\Psi(x) = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{n\pi}{L}x\right)$$

Show that the particle-in-a-box wavefunctions are not eigenfunctions of the momentum operator, $\hat{P}_x$, but they are for $\hat{P}_x^2$. (6)

(c) Show that the position operator, x, and momentum operator, $\hat{P}_x$, do not commute. What does this indicate about the measurement of position and momentum? (4)

QUESTION 4 **[13]**

(a) For the operators A and B, prove the identity $\left[A^2,B\right]=A[A,B]+[A,B]A$. (4)

(b) Show that $\Phi=Ae^{im\phi}+Be^{im\phi}$ is a solution to the differential equation (4)

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=-m^2$$

(c) The solution of the Schrödinger equation of a plane rigid rotor is of the form

$\Psi(\phi)=A\cos(\phi)$ for $0\leq\phi\leq 2\pi$.

Determine the normalisation constant, A. (5)

(Given: $\cos^2\phi=\frac{1}{2}(1+\cos 2\phi)$)

QUESTION 5 **[13]**

(a) A wavefunction of a Quantum Mechanics (QM) particle of an observable is given by

$\Psi=Ax \quad -1\leq x\leq 1$

(i) Determine the normalisation constant A. (4)

(ii) Evaluate the expectation value of x, <x>. (4)

(iii) What is the probability of observing the QM particle at x = 0? (2)

(b) The wavefunctions for a particle confined to move on a circle are

$\Psi(\phi)=\left(\frac{1}{2\pi}\right)^{\frac{1}{2}}e^{im\phi}$, where m = 0, ±1, ±2, etc. and $0\leq\phi\leq 2\pi$

What do zero, positive and negative values of the quantum number ***m*** mean? (3)

QUESTION 6 **[20]**

(a) What are the essential properties required of a molecule in order that it will show:

(i) A pure rotational (i.e. microwave) spectrum, and;

(ii) A vibrational (infrared) spectrum?

(2)

(b) Which of the following molecules will be (i) microwave active, (ii) infrared active, and (iii) neither microwave active nor infrared active: HCl, OCS, CO_2, NH_3, CH_3Cl, Cl_2? (5)

(c) Briefly define the terms **selection rule**, **zero point energy** and **degeneracy** as used in quantum chemistry of atoms and molecules. Use a plane rigid rotator as an example. (3)

(d) The rotational constant of $^{1}H^{35}Cl$ (hydrogen chloride) is greater than that of $^{2}H^{35}Cl$ (deuterium chloride) if bond length is the same. State, with reasons, whether this statement is true or false. (3)

(e) The quantum mechanical expression for the vibrational energy (in Joules) of a diatomic molecule is well approximated as:

$$E_{vib} = \left(v + \frac{1}{2}\right)h\nu - \left(v + \frac{1}{2}\right)^2 xh\nu$$

For $^{1}H^{35}Cl$, the vibrational frequency is ν = 8.97 x 10^{13} s^{-1} and anharmonicity constant x = 0.018.

(i) Calculate the energies of the v = 0 and v = 1 levels. (4)

(ii) What is the relative populations at 300 K of the levels v = 0 and v = 1, i.e. $\frac{N_{v=1}}{N_{v=0}}$? Comment on the result. (3)

END OF EXAM QUESTIONS

USEFUL CONSTANTS:

Universal Gas constant	R	=	8.314 J K^{-1} mol^{-1}
Boltzmann's constant,	k	=	1.381 x 10^{-23} J K^{-1}
Planck's constant	h	=	6.626 x 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 x 10^{-31} kg
Velocity of light	c	=	2.998 x 10^{8} m s^{-1}
Avogadro's constant	N_A	=	6.022 x 10^{23}
1 electron volt (eV)		=	1.602 x 10^{-19} J