NAMIBIA UNIVERSITY
OF SCIENCE AND TECHNOLOGY

FACULTY OF HEALTH AND APPLIED SCIENCES

DEPARTMENT OF NATURAL AND APPLIED SCIENCES

QUALIFICATION: BACHELOR OF SCIENCE	
QUALIFICATION CODE: 07BOSC	**LEVEL:** 7
COURSE CODE: QCM701S	**COURSE NAME:** QUANTUM CHEMISTRY AND MOLECULAR SPECTROSCOPY
SESSION: JUNE 2019	**PAPER:** THEORY
DURATION: 3 HOURS	**MARKS:** 100

FIRST OPPORTUNITY EXAMINATION QUESTION PAPER	
EXAMINER(S)	Prof Habauka M Kwaambwa
MODERATOR:	Prof Edet F Archibong

INSTRUCTIONS
1. Answer ALL the questions. 2. Write clearly and neatly. 3. Number the answers clearly.

PERMISSIBLE MATERIALS

Non-programmable Calculators

ATTACHMENT

List of Useful Constants

THIS QUESTION PAPER CONSISTS OF 6 PAGES (Including this front page and attachment)

QUESTION 1 **[20]**

(a) Define the terms **blackbody radiation** and **UV catastrophe.** Draw a schematic diagram of the energy density, U(ν), against ν for the blackbody radiation at temperatures T_1 and T_2 (where $T_1 < T_2$). (5)

(b) Rayleigh-Jeans law of a blackbody radiation as function of frequency is given as:

$$U(\nu) = \frac{8\pi kT\nu^3}{c^3}$$

Under what condition would this theory be in agreement with blackbody radiation experimental results. (2)

(c) The derivation by Bohr of the hydrogen atom given below.

$$\bar{\nu} = R_g\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$, where R_g = 109677.58 cm^{-1}

(i) State the **three** basic considerations this equation is based on or was derived. (3)

(ii) Calculate the wavelength, λ(in **nm**) and ionisation energy (in **eV**) for the Balmer line of the H emission. (The n_1 = 2 for the Balmer series). (3)

(d) Electromagnetic radiation of wavelength 200 nm is used to irradiate gold metal.

(i) Given that the work function of gold is 5.10 eV, determine the kinetic energy (in Joules) and velocity of the electrons ejected. (5)

(ii) State briefly the effect, if any, of increasing the intensity of incident light of wavelength 200 nm? (2)

QUESTION 2 **[18]**

(a) Consider a π-electron which is a part of a conjugated polymethine dye. Use the free-electron molecular orbital (FEMO) method, which assumes that the π electrons are trapped in a 1-D box of length 11.2 Å to answer the following questions:

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

(ii) Why is the zero point energy equal to zero not feasible? (2)

(iii) Assuming the length of the chain to be 11.2 Å, determine the transition caused by excitation using the light of wavelength of 460 nm. (6)

(iv) Determine the number of pi electrons. (1)

(v) What is the main weakness of the FEMO model? (2)

(b) The maximum in the ultraviolet absorption spectrum of butadiene, CH_2=CH-CH=CH_2, occurs at a lower wavelength (higher frequency) than that in the spectrum of hexatriene, CH_2=CH-CH=CH-CH=CH_2. Explain your answer using the "particle-in-a-box" model. (4)

QUESTION 3 **[32]**

(a) One of the requirements for useful wave functions in Quantum Mechanics is that they must be well-behaved. State briefly the meaning of **well-behaved wave function.** (2)

(b) The wave function, Ψ, for an electron in the highest occupied molecular orbital of polydiene based on 1-dimensional particle-in-a-box model is given by:

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

(i) Plot the variation of $\Psi(x)$ and $\Psi^2(x)$ for a particle-in-a-box with n = 4 for $0 \le x \le L$. (3)

(ii) If the system is in state n = 4, state for which values of **x** in terms of L is the probability of finding the particle, i.e. $\Psi^2(x)$, maximum in the range $0 < x < L$. (4)

(c) State using a mathematical expression what is meant in quantum theory for each of the following: (10)

(i) Operator $\hat{A}$ is linear to the wave functions Ψ_i and Ψ_j.

(ii) Wave functions Ψ_1 and Ψ_2 **are not** orthogonal.

(iii) Operators A and B commute of wave function Ψ.

(iv) Hermitian operator $\hat{A}$ of wave functions Ψ_i and Ψ_j.

(v) Expectation value, $\langle a \rangle$, of the observable A derived from a normalised wave function Ψ.

(d) What are the physical meanings of **commuting operators** and **orthogonal wave functions** in Quantum mechanics? (4)

(e) Show that the function $\Psi = e^{-ikx}$ of the free particle is also an eigenfunction of the linear operator, $\hat{P}_x = -i\hbar\frac{d}{dx}$. What is the expression for the eigenvalue corresponding to this eigenfunction? (4)

(f) For circular motion in a fixed plane, the operator the Schrodinger equation is of the form

$$-\frac{\hbar^2}{2mr^2}\left(\frac{d^2\Psi}{d\phi^2}\right) = E\Psi$$, where $m_l = 0, \pm1, \pm2, \pm3$, etc.

Show that $\Psi = \frac{1}{\sqrt{2\pi}}e^{im_l\phi}$ is an acceptable solution of the differential equation. What is the eigenvalue expression? (5)

QUESTION 4 **[15]**

(a) Which of the species would be: (4)

(i) microwave active?

(ii) infrared active?

NH_3, HCl, H_2, CO_2, O_2, CH_3Cl, C_2H_4

Explain briefly your choice.

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

$$E_J = BJ(J+1)$$

State the selection rule for the rotational energy transitions and derive the separation between the successive spectral absorption lines in terms of the rotation constant, B. (4)

(c) The rotational absorption lines for $^1H^{35}Cl$ gas were found at the following wavenumbers: 83.32, 104.13, 124.73, 145.37, 165.89, 186.23, 206.60 and 226.86 cm^{-1}. Calculate the moment of inertia and the bond length of the molecule (in Å). (7)

Atomic masses (amu): $^{1}H = 1.0079$ $^{35}Cl = 34.9688$

QUESTION 5 **[15]**

Two particles of masses 3.32×10^{-27} kg and 31.5×10^{-27} kg are connected by a Hooke's law spring which requires force of 13.2×10^{2} N to stretch it by 1.5 m.

(a) Calculate the force constant (in Nm^{-1}) of the system. (2)

(b) What is the fundmamental vibration frequency (s^{-1}) of the system? (4)

(c) Calculate the potential energy of the system when stretched by 1.5 m from its equilibrium position? (3)

(d) What is the zero point energy (based on quantum theory of simple harmonic oscillator) of the system? (3)

LIST OF 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)		=	$1.602 \times 10^{-19}\ J$