



**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 MOLECULAR SPECTROSCOPY	COURSE CODE: QCM701S
SESSION: JUNE 2023	PAPER: THEORY
DURATION: 3 HOURS	MARKS: 100

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

INSTRUCTIONS
<ol style="list-style-type: none">1. Answer ALL the SIX questions2. Write clearly and neatly3. Number the answers clearly4. All written work must be done in blue or black ink5. No books, notes and other additional aids are allowed6. Mark all answers clearly with their respective question numbers

PERMISSIBLE MATERIALS

Non-programmable Calculators

ATTACHMENT

List of Useful Constants

THIS QUESTION PAPER CONSISTS OF 7 PAGES (Including this front page and List of Useful Constants)

QUESTION 1**[23]**

(a) Define the term **blackbody radiation**. (2)

(b) Explain how classical mechanics failed to explain the phenomenon of blackbody radiation and how this phenomenon contributed to the development of quantum mechanics. (3)

(c) The Rayleigh-Jeans law of a blackbody radiation as function of wavelength is given as:

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

Deduce the corresponding expression and SI units of the energy density, $U(\nu)$, as function of frequency, ν . (3)

(d) Under what condition does the Rayleigh-Jeans law of a blackbody radiation as function of frequency agree with blackbody radiation experimental results. (1)

(e) Sodium metal with a work function of 2.28 eV gives off photoelectrons when it is bombarded with ultraviolet radiation of 200 nm.

(i) Calculate the maximum possible kinetic energy and velocity of photoelectrons emitted from Na exposed to 200 nm of light. (6)

(ii) Calculate the wavelength required to cause photoelectron emission from Na. (3)

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

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

Calculate the wavelength, λ (in nm) and ionisation energy (in eV) for the Lyman line of the H emission. (The $n_1 = 2$ for the Balmer series). (5)

QUESTION 2**[21]**

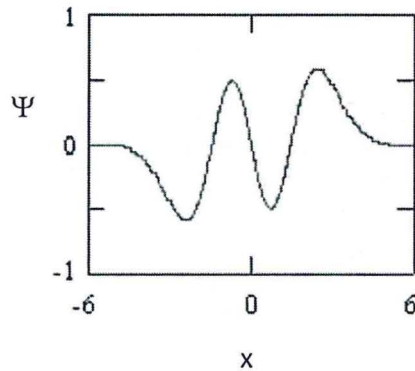
The free-electron molecular orbital (FEMO) method, which assumes that the π electrons are trapped in a 1-D box of length assumed to be 9.8 \AA and if the λ_{max} was measured to be 352 nm, answer the following questions:

- (a) Calculate the zero-point energy (in eV) of the system. (3)
- (b) Why is the zero-point energy equal to zero not feasible? (2)
- (c) Determine the transition for the wavelength ($\lambda_{\text{max}} = 352 \text{ nm}$) measured. (6)
- (d) Determine the number of π electrons and identify the HOMO and LUMO. (3)
- (e) What is the main source of error of the model in predicating the maximum wavelength of absorption of conjugated diene molecules? (2)
- (f) For 3-dimension cubic particle-in-a-box of length 9.8 \AA , calculate the ground state energy (in eV)? (3)
- (g) From the above information and calculations, the most likely conjugated diene(s) to fit the model is/are: (2)
- (i) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH}_2$
- (ii) $(\text{CH}_3)_2\text{N}^+ = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{N}(\text{CH}_3)_2$
- (iii) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH}_2$

QUESTION 3

[34]

- (a) Is the wave function shown in the diagram **well-behaved** or **not well-behaved**? State the reason(s) for your answer. (3)



- (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:

$$\Psi(x) = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{5\pi x}{L}\right) \text{ for } 0 \leq x \leq 40 \text{ nm}$$

- (i) Plot the variation of $\Psi(x)$ and $\Psi^2(x)$ for a particle-in-a-box for $0 \leq x \leq 40 \text{ nm}$. (3)
- (ii) At what values of x is $\Psi(x)$ equal to **zero**, **minimum** and **maximum**, and the probability of finding the particle (probability density function) **maximum** in the range $0 < x < 40 \text{ nm}$? (7)
- (iii) What is the probability of finding the particle in the range $L/10 \leq x \leq L/2$? (2)
- (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 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? (3)
- (e) Give the Schrödinger equation for a plane rigid rotor (circular motion in a fixed plane) and show that $\Psi = \frac{1}{\sqrt{2\pi}} e^{im\phi}$ is an acceptable solution of the operator form of the plane rigid rotor Schrödinger equation. What is the eigenvalue expression? (6)

QUESTION 5

[22]

- (a) Which of the species would possess (2)
- (i) Rotational microwave spectrum?
- (ii) Vibrational (infrared) spectrum?
- N_2 , IBr, CO_2 ,
- (b) Define the term **selection rule** using the following as examples: (6)
- (i) Particle-in-box (ii) Plane rigid rotor (iii) Simple harmonic oscillator
- (iv) Anharmonic oscillator (v) Rigid rotor – Harmonic Oscillator
- (c) If the degeneracy in pure rotational energy states is 7, what is the value of the quantum number J and the possible values of the quantum number m_J ? (2)
- (d) The ro-vibrational spectrum is divided into three branches, namely, P , Q and R . What is the approximate separation in terms B between the innermost line of the P and second innermost line of the R branch? (1)

(e) From the ro-vibrational spectrum of $^1\text{H}^{127}\text{I}$, the spacing between the peaks was approximated to be 13.1 cm^{-1} . Answer the following questions:

(i) Deduce the moment inertia, I , of $^1\text{H}^{127}\text{I}$. (3)

(ii) Calculate the reduced mass of $^1\text{H}^{127}\text{I}$. (2)

(iii) Evaluate the internuclear distance (in \AA) of $^1\text{H}^{127}\text{I}$. (2)

Atomic masses (amu): $^1\text{H} = 1.0079$ $^{127}\text{I} = 126.90447$

(f) The force constant of $^{79}\text{Br}^{79}\text{Br}$ is 240 Nm^{-1} . Calculate the fundamental vibrational wavenumber of Br_2 . Given: RAM for Br = 78.92 amu (4)

END OF EXAM QUESTIONS

LIST OF 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
