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 SPECTROSCOPY
SESSION: JULY 2019	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 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 list of useful constants as an attachment)

QUESTION 1   **[17]**

(a) Waves can be characterised by **amplitude** and **frequency**. Define these two terms. (2)

(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   **[15]**

(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? (2)

   (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 $0 < x \le 30$ 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 $\Psi(n=1)\cdot\Psi(n=2)$. (6)

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, $\hat{P}_x=-i\hbar\dfrac{d}{dx}$ and the expectation value of the momentum of an observable. (8)

(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? (5)

QUESTION 4 [14]

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

$$\Psi(\phi)=A\cos(\phi) \text{ for } 0\le\phi\le2\pi.$$

Determine the normalisation constant, A. (6)

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

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QUESTION 5 [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 $^1H^{35}Cl$ (hydrogen chloride) is greater than that of $^2H^{35}Cl$ (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 $^1H^{35}Cl$, the vibrational frequency is $\nu = 8.97 \times 10^{13}$ 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.

        $\dfrac{N_{v=1}}{N_{v=0}}$? Comment on the result. (3)

QUESTION 6 [17]

(a) State briefly the selection rules (both gross selection rules and otherwise) operating for a rotational Raman spectra and vibration Raman spectra. (4)

(b) Which of the following molecules may show a pure rotational Raman spectrum?

    N_2, SF_6, CH_3CH_3, CH_3Cl (2)

(c) The rotational Raman spectrum of $^{35}Cl_2$ shows a series of Stokes lines separated by 0.9852 cm^{-1} and similar series of anti-Stokes lines. Calculate the bond length of the molecule. [Given: Relative atomic mass of ^{35}Cl = 34.9688 amu] (8)

(d) The Anti-stokes spectral lines are usually very much weaker that the Stokes lines. Explain why this so. (3)

END OF EXAM QUESTIONS

USEFUL CONSTANTS:

Universal Gas constant	R	=	8.314 J K^{-1} mol^{-1}
Boltzmann's constant,	k	=	1.381×10^{-23} J K^{-1}
Planck's constant	h	=	6.626×10^{-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	=	9.109×10^{-31} kg
Velocity of light	c	=	2.998×10^8 m s^{-1}
Avogadro's constant	N_A	=	6.022×10^{23}
1 electron volt (eV)		=	1.602×10^{-19} J