

Name: _____

Student Number: _____

CHEMISTRY 3PA3 - QUANTUM MECHANICS AND SPECTROSCOPY

DURATION OF EXAMINATION: 3 Hours

Instructor: Dr. Peter Kruse

McMASTER UNIVERSITY **PRACTICE** EXAMINATION

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THIS EXAMINATION PAPER INCLUDES 2 PAGES AND 4 SETS OF QUESTIONS. YOU ARE RESPONSIBLE FOR ENSURING THAT YOUR COPY OF THE PAPER IS COMPLETE. BRING ANY DISCREPANCY TO THE ATTENTION OF YOUR INVIGILATOR.

Special Instructions:

Use of Casio FX-991 only is allowed.

No notes, books or personal paper are allowed!

Attempt all questions.

In answering the questions, show all steps of your reasoning and calculation!

Use the exam booklets to record your workings and answers for all questions.

This paper must be returned with your answers.

Potentially Useful Numbers and Formulas: (Note the difference between h and \hbar !)

$h = 6.6261 \times 10^{-34}$ Js; $m_e = 9.1094 \times 10^{-31}$ kg; $e = 1.6022 \times 10^{-19}$ C; $c = 2.9979 \times 10^8$ m/s;
 $N_A = 6.022 \times 10^{23}$ mol $^{-1}$; $k_B = 1.38066 \times 10^{-23}$ J/K; $a_0 = 5.291772 \times 10^{-9}$ cm; $l_{C=C, \text{Benzene}} = 0.14$ nm;
 $1 \text{ nm} = 10^{-9}$ m; $1 \text{ J} = 6.242 \times 10^{18} \text{ eV} = 5.034 \times 10^{22} \text{ cm}^{-1}$

Rigid Rotor: $B = \frac{h}{8\pi^2 c \mu r^2}$ Harmonic Oscillator: $\psi_0(x) = \sqrt{\frac{\beta^2}{\pi}} e^{-\frac{(\beta x)^2}{2}}$; $\beta^2 = \frac{\sqrt{km}}{\hbar}$

$\psi_1(x) = \sqrt{\frac{4\beta^2}{\pi}} (2\beta x) e^{-\frac{(\beta x)^2}{2}}$; $\beta^2 = \frac{\sqrt{km}}{\hbar}$ $\psi_2(x) = \sqrt{\frac{4\beta^2}{8\pi}} (4(\beta x)^2 - 2) e^{-\frac{(\beta x)^2}{2}}$; $\beta^2 = \frac{\sqrt{km}}{\hbar}$

Potentially Useful Integrals:

$$\int_0^\infty e^{-cx^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{c}} \quad ; \quad \int_0^\infty x^2 e^{-cx^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{c^3}} \quad ; \quad \int_0^\infty x e^{-cx^2} dx = \frac{1}{2c} \quad ; \quad \int_0^\infty x^{2n+1} e^{-cx^2} dx = \frac{n!}{2c^{n+1}}$$

$$\int_0^\infty x^{2n} e^{-cx^2} dx = \frac{(2n-1)(2n-3)\dots(3)(1)}{2^{n+1}} \sqrt{\frac{\pi}{c^{2n+1}}} \quad ; \quad \int_{-\infty}^0 x^n e^{-cx^2} dx = (-1)^n \int_0^\infty x^n e^{-cx^2} dx$$

$$\int \sin^2(cx) dx = \frac{x}{2} - \frac{\sin(2cx)}{4c} \quad ; \quad \int x \sin^2(cx) dx = \frac{x^2}{4} - \frac{x \sin(2cx)}{4c} - \frac{\cos(2cx)}{8c^2}$$

$$\int x^2 \sin^2(cx) dx = \frac{x^3}{6} - \left(\frac{x^2}{4c} - \frac{1}{8c^3} \right) \sin(2cx) - \frac{x \cos(2cx)}{4c^2}$$

Question	1	2	3	4	Total
Max.	13.0	5.0	4.0	8.0	30.0
Score	_____	_____	_____	_____	_____

(Numbers in brackets after each question number are the points achievable for that question.)

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1) (13) Particle in a box.

- (a) (2) Derive expressions for the constants a , b and k in the equation for the wavefunction of a one-dimensional particle in a box with infinitely tall sidewalls given as $\psi(x) = a \sin(kx) + b \cos(kx)$. You may find it useful to refer to the length of the box as l . [Note: l refers to the letter l , not to 'one'!]
- (b) (2) Qualitatively sketch the appearance of the wavefunctions corresponding to the lowest 3 states for the two cases of a particle in a box with infinitely tall sidewalls and with finite height sidewalls. Is the shape of any of the wavefunctions you have just drawn unphysical and why?
- (c) (2) What are the degeneracies of the first 8 energy levels of a three-dimensional ($l_x=l_y=l_z$) particle in a box system?
- (d) (3) What is the right size for a cubic box for an electron (i.e. a "quantum dot") in order for the lowest transition to be the same as $k_B \cdot T$ (meaning Boltzmann's constant times temperature) at room temperature? Assume infinitely tall sidewalls and a flat potential bottom.
- (e) (4) If the quantum dot from question (1d) was exposed to an electric field, the potential inside it would be more accurately described by a sloped bottom in one direction (e. g. x-axis). How would the transition energy change in that direction, given the size of the quantum dot that you calculated in (1d)? Show the derivation of your answer from first order perturbation theory.

2) (5) Vibrational-rotational spectroscopy.

Assume $r_{eq} = 113.1 \text{ pm}$, $k = 1902 \text{ N/m}$ for all isotopes of CO.

- (a) (2) What is ΔH^0 (in Joules) of the reaction $^{13}\text{C}^{17}\text{O} + ^{12}\text{C}^{16}\text{O} \rightarrow ^{12}\text{C}^{17}\text{O} + ^{13}\text{C}^{16}\text{O}$? Assume that all molecules are harmonic oscillators in their vibrational ground states. You only need to consider the differences in vibrational energy between the different isotopes.
- (b) (3) The selection rules in Raman vibrational-rotational spectroscopy are $\Delta n = \pm 1$, $\Delta J = 0, \pm 2$. Assuming that the harmonic oscillator and rigid rotor models hold, derive a formula for the locations of the vibrational-rotational transitions in the O branch in terms of B_e . For $^{13}\text{C}^{17}\text{O}$, predict the positions (in cm^{-1}) of the first line each of the O and the S branch.

3) (4) Angular momentum coupling.

For the electron configuration $1s^2 2s^2 2p^2 3d^2$, determine all terms and find the ground state. Explain all steps.

4) (8) Molecular orbital theory.

- (a) (3) Discuss the important features of Hückel theory! Include a definition of commonly used symbols such as α , β , ϵ !
- (b) (3) Using Hückel theory, write out the secular determinants for propene, the allyl radical, benzene and naphthalene!
- (c) (2) Calculate the molecular orbital energies for the π -system of ethylene in terms of α and β !

THE END