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MAIN EXAMINATION

AUGUST - DECEMBER 2016 TRIMESTER

FACULTY OF SCIENCE

DEPARTMENT OF CHEMISTRY

REGULAR PROGRAMME

CHEM 406: QUANTUM CHEMISTRY

Date: DECEMBER 2016	**Duration: 2 Hours**
INSTRUCTIONS: Answer Question ONE and ANY OTHER TWO Questions	

Useful Information

$h = 6.626\times10^{-34}\ Js$; $c = 2.998\times10^{8} m/s$; $1\,eV = 1.602\times10^{-19}$ J $m_e = 9.10\times10^{-31} kg$;

$$\varepsilon_0 = 8.85418\times10^{-18} C^2 J^{-1} m^{-1};\ r_n = \frac{\varepsilon_0 n_n^2 h^2}{\pi m_e e^2}$$

$$1\ amu == 1.66054\times10^{-27} kg;\ \int_o^a \sin^2\left(\frac{n\pi x}{a}\right)dx = \frac{a}{2},\ \int_0^a x\sin^2\left(\frac{n\pi x}{a}\right)dx = \frac{a^2}{4},$$

$$\int \sin^2 bx\ dx = \left[\frac{x}{2} - \frac{\sin(2bx)}{4b}\right];\ \int_0^\infty e^{-\beta x^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{\beta}};$$ Momentum operator, $P_x = i\eta\frac{d}{dx}$;

$$\int_0^a \sin\left(\frac{n\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right)dx = \int_0^a \cos\left(\frac{n\pi x}{a}\right)\cos\left(\frac{m\pi x}{a}\right)dx = \frac{a}{2}\delta_{mn}$$ (m and n are integers)

$$\sin\alpha\sin\beta = \frac{1}{2}\cos(\alpha-\beta) - \frac{1}{2}\cos(\alpha+\beta);\ \int\cos(bx)dx = \frac{1}{b}\sin(bx)$$

$$\int_0^a x^2\sin^2\left(\frac{n\pi x}{a}\right) = \frac{a^3}{6} - \frac{a^3}{4n\pi^2} \qquad i = \sqrt{-1}$$

QUESTION ONE [30 marks]

(a) Sodium lamp emits light of 589.0 nm. Calculate :

(i) The frequency of the light **[2 marks]**

(ii) The wave number of the light **[2 marks]**

(iii) The energy of the photons in J and eV **[2 marks]**

(iv) The momentum of the photons **[2 marks]**

(b) Write down the time dependent Schrödinger Equation for a 1-dimensional quantum problem (depends upon time, t, and position, x). State clearly the meaning of any constants or functions in your equation. **[5 marks]**

(c) A particle is constrained to move in a one-dimensional box between $x = a$ and $x = b$. The potential energy is such that the particle cannot be outside these limits and the wave function is given by $\Psi = \frac{A}{x^2}$ where A is a real normalization constant. Determine the value of the normalization constant A. **(5 marks)**

(d) The harmonic vibrational transition of CO from $v = 0 \longrightarrow v = 1$ 2170 cm^{-1}

Wave numbers. Determine the harmonic force constant k in g/s^2.

(C = 12, O = 16) **[4 marks]**

(e) Calculate the uncertainty in the velocity of a cricket ball of mass 150 g if the uncertainty in its position is of order of 1Å. **[4 marks]**

(f) Calculate the wavelength of electrons that have been accelerated from rest through a potential difference of 45 kV. **[4 marks]**

QUESTION TWO [20 marks]

(a) A particle in a one dimensional infinite potential well is in the n = 1 state.

Calculate the probability that the particle will be located in the range $0.5a \le x \le 0.75a$ where a is the width of the well. Recall the particle in a box wavefunction is $\Psi_n = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right)$ [Hint use: $b = \frac{\pi}{a}$] **[8 marks]**

(b) A particle travelling in the negative x direction has a wavefunction given by $\psi(x) = e^{-ikx}$

(i) Show that this wavefunction is an eigenfunction of the momentum operator and thus that the momentum is known exactly.

(ii) What is the uncertainty in the momentum of the particle?

(iii) Given the uncertainty in the momentum from (ii), use Heinsenberg Uncertainty Principle to determine the uncertainty in the position.

[9 marks]

(c) Write down the time independent Schrödinger equation for a 1-D and define all your constants. **[3 marks]**

QUESTION THREE [20 marks]

(a) State the stringent conditions a wavefunction must satisfy to be acceptable.

[6 marks]

(i) Define zero point energy **[2 marks]**

(ii) The force constant for $H^{18}F$ molecule is 966 Nm^{-1}. Calculate the zero-point vibrational energy for this molecule for a harmonic potential.

[5 marks]

(iii) Assume that you prepare a more general state that is a superposition of the first and the third stationary state so that $\psi(x,0) = A[u_1(x) - iu_3(x)]$. Assuming that the stationary states are normalized already, calculate the normalization constant A. **[7 marks]**

QUESTION FOUR [20 marks]

(a) The energy levels of a particular 3-dimensional particle in a box (non-cubical) are given by $E_{n,n_y,n_z} = \frac{h^2}{8mL}\left(4n_x^2 + 4n_y^2 + n_z^2\right)$, where L is the height of the box in the z direction. What are the energies and degeneracies of the 4 lowest energy levels? Label each state by its quantum numbers. **[4 marks]**

(b) Describe the major features of Born-Oppenheimer approximation and its impact on solutions to the molecular Schrödinger equation. **[3 marks]**

(c) State the limitations of Bohr's theory. **[3 marks]**

(d) A diatomic molecule HX (X is an unknown atom) has a harmonic vibrational force constant $k = 9.680 \times 10^5$ g/s^2. The harmonic vibrational frequency in wavenumbers is 4143.3 cm^{-1}.

(i) What is the reduced mass of the molecule? **[3 marks]**

(ii) Identify atom X **[3 marks]**

(e) Prove that the particle in a box with wavefunctions $\Psi_1 = \left(\frac{2}{a}\right)^{\frac{1}{2}} \sin\left(\frac{\pi x}{a}\right)$ and $\Psi_2 = \left(\frac{2}{a}\right)^{\frac{1}{2}} \sin\left(\frac{2\pi x}{a}\right)$ are orthogonal and prove that ψ_2 is normalizable.

[4 marks]

QUESTION FIVE [20 marks]

(a) Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral lines of lowest energy in the visible region of its atomic spectra. **[5 marks]**

(b) Give the number of orbitals in each of the *s, p, d, f* and *g* subshells of the shell with $n = 5$. **[4 marks]**

(c) (i) Differentiate between lattice energy and ionization energy. **[2 marks]**

(ii) The ionization energy of O_2 is lower than the ionization energy of atomic O. Explain this in terms of the where the electrons are in atomic and MO's of O_2. (Use MO diagram to explain). **[4 marks]**

(d) Calculate the de Broglie wavelength of an electron in the first Bohr orbit in the hydrogen atom. **[5 marks]**

END