

Issue: Thursday 2nd February 2012 **Hand-in:** 16:00 Thursday 9th February 2012

Hand-In questions 1, 2 and 3.

Please post your solutions in the box outside the 1st floor departmental offices

QUESTION 1.

a) Carbon monoxide (CO) is a diatomic molecule. The masses of the carbon and Oxygen atoms are $m_C = 12u$ and $m_O = 16u$ ($u = 1.66 \times 10^{-27} \text{kg}$). Given that the force constant for the C-O bond is 1860 Nm^{-1} :

i) Calculate the vibrational transition energy, $\hbar\omega_0$, in eV, of this molecule.

ii) What wavelength of light does this correspond to?

iii) How does $\hbar\omega_0$ compare to $k_B T$ at room temperature? Comment on your result.

iv) Calculate the classical turning points associated with the *ground state* and *first excited* state oscillations of this molecule. How do these compare to the C-O bond length of 1.2 \AA ?

b) Another diatomic molecule is NO; given that the mass of the nitrogen atom is $m_N = 14u$, and that this molecule shows a broad, low resolution absorption peak centred around $5.33 \mu\text{m}$, what is the force constant of the N-O bond?

c) Hydrochloric acid (HCl) has a Hydrogen – Chlorine bond of effective spring constant $= 480 \text{ Nm}^{-1}$. Given that the mass of the Chlorine atom is $35u$ and that for ordinary Hydrogen the mass is $1u$:

i) Calculate the vibrational transition energy $\hbar\omega_0$, and its corresponding wavelength for HCl.

ii) Repeat the calculation in c)i) for an HCl molecule formed using deuterium.

QUESTION 2.

The harmonic approximation is used to describe certain features of the molecular energy spectrum of diatomic molecules.

a) Draw a diagram describing what is meant by “harmonic approximation” in the context of a diatomic molecule.

b) Draw an energy-internuclear separation diagram, corresponding to the ground and first excited electronic states, for a diatomic molecule. Include any additional energy levels present (vibrational, rotational), and label any transitions with the part of the electromagnetic spectrum they correspond to.

QUESTION 3.

Last week you calculated the allowed η_n values for an electron in a 8 \AA wide, 8 eV deep, one-dimensional potential well. You should have obtained $\eta_1 \approx 1.337$ as your first solution.

Given that the ground state solutions are:

$$\Psi_1(x, t) = B e^{+\kappa x} e^{\frac{-iE_1 t}{\hbar}} \quad \text{for } x \leq -\frac{L}{2}$$

$$\Psi_1(x, t) = A \cos(kx) e^{\frac{-iE_1 t}{\hbar}} \quad \text{for } -\frac{L}{2} \leq x \leq +\frac{L}{2}$$

$$\Psi_1(x, t) = B e^{-\kappa x} e^{\frac{-iE_1 t}{\hbar}} \quad \text{for } x \geq +\frac{L}{2}$$

where κ and k have their usual meanings

- What can you conclude about the ratio, $C = \frac{B}{A}$, for this state?
- How would you go about calculating the probability of detecting the electron in the classically forbidden region?

Note: in b) I'm not actually asking for the probability, just the outline method you would use. If you calculate the actual probability, so much the better.

Exercise Class Questions.

Consider a quantum mechanical simple harmonic oscillator (SHO).

- Write down an expression for the potential, $V(x)$.
- Calculate the classical turning points, $\pm x_0$, for a particle with total energy, E .
- Sketch the ground state and first two excited state wavefunctions and probability densities. Indicate the position of the classical turning points on your probability density diagrams.
- Write down a general expression for the eigenfunction of the SHO, $\psi_n(x)$, in terms of the Hermite polynomial, $H_n(\xi)$, and other quantities, given that:

$$a = \frac{m\omega_0}{\hbar} \quad \text{and} \quad \xi = \sqrt{a}x$$

- Write down a general expression for the allowed energy eigenvalues, E_n , of the SHO.
- Prove that the solutions, ψ_0 and ψ_1 , given below, satisfy the Time-Independent Schrödinger Equation for a SHO, obtaining E_0 and E_1 .

$$\psi_0 = N_0 e^{-\frac{ax^2}{2}} \quad \psi_1 = N_1 x e^{-\frac{ax^2}{2}}$$

- The first excited state wavefunction of a quantum mechanical harmonic oscillator can be written as:

$$\Psi(x, t) = A_1 2\sqrt{a} x e^{-\frac{ax^2}{2}} e^{-\frac{3}{2}i\omega_0 t} \quad \text{where} \quad a = \frac{m\omega_0}{\hbar}$$

- Prove that the normalisation constant, A_1 , is given by: $A_1 = \frac{1}{\sqrt{2}} \left(\frac{a}{\pi} \right)^{\frac{1}{4}}$

- Prove that the positional uncertainty, Δx , is given by: $\Delta x = \sqrt{\frac{3}{2a}}$

- Prove that the momentum uncertainty, ΔP , is given by: $\Delta P = \hbar \sqrt{\frac{3a}{2}}$

Useful Stuff:

$$\int_{-\infty}^{\infty} x e^{-Cx^2} dx = 0 \quad \int_{-\infty}^{\infty} x^2 e^{-Cx^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{C^3}} \quad \int_{-\infty}^{\infty} x^3 e^{-Cx^2} dx = 0 \quad \int_{-\infty}^{\infty} x^4 e^{-Cx^2} dx = \frac{3}{4} \sqrt{\frac{\pi}{C^5}}$$