

## QMS Problem set 2 (due 28.1.2021)

**Warm-up:** (Each warm-up is connected to one of the problems (first warm-up to first problem etc.))

**W1:** Answer problem E7E.5(a) (2 points)

**E7E.5(a)** Assuming that the vibrations of a  $^{35}\text{Cl}_2$  molecule are equivalent to those of a harmonic oscillator with a force constant  $k_f = 329 \text{ N m}^{-1}$ , what is the zero-point energy of vibration of this molecule? Use  $m(^{35}\text{Cl}) = 34.9688 m_u$ .

**W2:** Answer problem E7E.4(a) (2 points)

**E7E.4(a)** Sketch the form of the wavefunctions for the harmonic oscillator with quantum numbers  $v = 0$  and 1. Use a symmetry argument to explain why these two wavefunctions are orthogonal (do not evaluate any integrals).

**W3:** Answer problem P7E.5 (4 points)

**P7E.5** In infrared spectroscopy it is common to observe a transition from the  $v = 0$  to  $v = 1$  vibrational level. If this transition is modelled as a harmonic oscillator, the energy of the photon involved is  $\hbar\omega$ , where  $\omega$  is the vibrational frequency. (a) Show that the wavenumber of the radiation corresponding to photons of this energy,  $\bar{\nu}$ , is given by  $\bar{\nu} = \omega / 2\pi c$ , where  $c$  is the speed of light. (b) The vibrational frequency of  $^1\text{H}^{35}\text{Cl}$  is  $\omega = 5.63 \times 10^{14} \text{ s}^{-1}$ ; calculate  $\bar{\nu}$ . (c) Derive an expression for the force constant  $k_f$  in terms of  $\bar{\nu}$ . (d) For  $^{12}\text{C}^{16}\text{O}$  the  $v = 0 \rightarrow 1$  transition is observed at  $2170 \text{ cm}^{-1}$ . Calculate the force constant and estimate the wavenumber at which the corresponding absorption occurs for  $^{14}\text{C}^{16}\text{O}$ . Use integer relative atomic masses for this estimate.

## Problems:

**P1:** Answer P7E.1 (4 points)

**P7E.1** If the vibration of a diatomic A–B is modelled using a harmonic oscillator, the vibrational frequency is given by  $\omega = (k_f / \mu)^{1/2}$ , where  $\mu$  is the effective mass,  $\mu = m_A m_B / (m_A + m_B)$ . If atom A is substituted by an isotope (for example  $^2\text{H}$  substituted for  $^1\text{H}$ ), then to a good approximation the force constant remains the same. Why? (*Hint:* Is there any change in the number of charged species?) (a) Show that when an isotopic substitution is made for atom A, such that its mass changes from  $m_A$  to  $m_{A'}$ , the vibrational frequency of A'–B,  $\omega_{A'B}$ , can be expressed in terms of the vibrational frequency of A–B,  $\omega_{AB}$  as  $\omega_{A'B} = \omega_{AB} (\mu_{AB} / \mu_{A'B})^{1/2}$ , where  $\mu_{AB}$  and  $\mu_{A'B}$  are the effective masses of A–B and A'–B, respectively. (b) The vibrational frequency of  $^1\text{H}^{35}\text{Cl}$  is  $5.63 \times 10^{14} \text{ s}^{-1}$ . Calculate the vibrational frequency of (i)  $^2\text{H}^{35}\text{Cl}$  and (ii)  $^1\text{H}^{37}\text{Cl}$ . Use integer relative atomic masses.

**P2:** Answer P7E.17 (6 points)

**P7E.17** (a) Without evaluating any integrals, explain why you expect  $\langle x \rangle_v = 0$  for all states of a harmonic oscillator. (b) Use a physical argument to explain why  $\langle p_x \rangle_v = 0$ . (c) Equation 7E.13c gives  $\langle E_k \rangle_v = \frac{1}{2} E_v$ . Recall that the kinetic energy is given by  $p^2/2m$  and hence find an expression for  $\langle p_x^2 \rangle_v$ . (d) Note from Topic 7C that the uncertainty in the position,  $\Delta x$ , is given by  $\Delta x = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2}$  and likewise for the momentum  $\Delta p_x = (\langle p_x^2 \rangle - \langle p_x \rangle^2)^{1/2}$ . Find expressions for  $\Delta x$  and  $\Delta p_x$  (the expression for  $\langle x^2 \rangle_v$  is given in the text). (e) Hence find an expression for the product  $\Delta x \Delta p_x$  and show that the Heisenberg uncertainty principle is satisfied. (f) For which state is the product  $\Delta x \Delta p_x$  a minimum?

**P3:** Answer P7E.7 (3 points)

**P7E.7** Carbon monoxide binds strongly to the  $\text{Fe}^{2+}$  ion of the haem (heme) group of the protein myoglobin. Estimate the vibrational frequency of CO bound to myoglobin by using the data in Problem P7E.6 and by making the following assumptions: the atom that binds to the haem group is immobilized, the protein is infinitely more massive than either the C or O atom, the C atom binds to the  $\text{Fe}^{2+}$  ion, and binding of CO to the protein does not alter the force constant of the CO bond.

**P4:** Answer P7D.11 (3 points)

**P7D.11** Many biological electron transfer reactions, such as those associated with biological energy conversion, may be visualized as arising from electron tunnelling between protein-bound co-factors, such as cytochromes, quinones, flavins, and chlorophylls. This tunnelling occurs over distances that are often greater than 1.0 nm, with sections of protein separating electron donor from acceptor. For a specific combination of donor and acceptor, the rate of electron tunnelling is proportional to the transmission probability, with  $\kappa \approx 7 \text{ nm}^{-1}$  (eqn 7D.17). By what factor does the rate of electron tunnelling between two co-factors increase as the distance between them changes from 2.0 nm to 1.0 nm? You may assume that the barrier is such that eqn 7D.20b is appropriate.