

## 6.S: Vibrational States (Exercises)

### Q6.1

Demonstrate for one or two cases that the harmonic oscillator wavefunctions form an orthonormal set.

### Q6.2

Show that the behavior of the harmonic oscillator for the  $v = 0$  state is consistent with the Heisenberg Uncertainty Principle by computing the product of the standard deviations for displacement and momentum, i.e.  $\sigma_Q \sigma_P$ . You can express  $\sigma_Q \sigma_P$  in terms of  $\langle Q \rangle$ ,

,  $\langle Q^2 \rangle$ , and  $\langle p^2 \rangle$ .

### Q6.3

Complete the following:

- For  $v = 0$  vibrations of HF, HCl, and HBr compute the standard deviations for the displacements from equilibrium. The vibrational frequencies are given by 4139, 2886, and 2559  $\text{cm}^{-1}$ .
- Use the standard deviation in the displacement as well as the classical maximum possible displacement ( $Q_0$ ) to characterize the ground state vibrational amplitude and compare these quantities to an estimate of the bond lengths in these molecules obtained from the atomic covalent radii for H (37 pm), F (72 pm), Cl (99 pm), and Br (114 pm).
- What percent of the original bond length are these characteristic displacements? Is this bond length changing significantly during a vibration?
- What molecular properties determine the vibrational amplitude? How does the vibrational amplitude depend on these properties?
- Explain the differences in the vibrational amplitudes for these three molecules.

### Q6.4

Complete the following:

- Use the harmonic oscillator model to describe the vibration of nitrogen, and prepare a Mathcad graph showing the potential energy function. The vibrational frequency is given by 2360  $\text{cm}^{-1}$ .
- Mark the energy of the  $v = 8$  state on your graph of the potential energy with a horizontal line. Prepare another graph showing the  $v = 8$  harmonic oscillator wavefunction and probability density function.
- On both graphs, mark the classical limit to the displacement of the oscillator with the energy in (b) from its equilibrium position.
- Describe the probability of finding the oscillator at various distances away from the equilibrium position. How does the quantum mechanical oscillator differ from the classical oscillator in this regard?

### Q6.5

Complete the following

- Do unwanted bands due to oxygen, nitrogen, water, and carbon dioxide in the air appear in infrared spectra of chemical samples?
- How many normal modes are there for  $\text{H}_2\text{O}$ ? How many of these are infrared active?
- How many normal modes and infrared active modes are there for  $\text{CO}_2$ ?
- Look up the vibrational frequencies of water and carbon dioxide in library books on spectroscopy and make sketches of the low-resolution IR spectra that you would expect. Include overtone, combination, and hot bands. Key references on molecular vibrations are Molecular Vibrations by Wilson, Decius, and Cross and Infrared and Raman Spectra by Herzberg.

### Q6.6

1. Complete the following:

- Compare the potentials and the wavefunctions for the harmonic oscillator and the particle in a box. Summarize the similarities and the differences.

2. Is the harmonic oscillator selection rule  $\Delta v = \pm 1$  almost or approximately true also for the particle in a box?
3. Why would you expect this selection rule to be approximately valid or to fail completely for the particle in a box?

### Q6.7

Another model that often is applied to molecules is the Morse oscillator. The potential energy for the Morse oscillator has the following form:

$$V(x) = D_e(1 - e^{-\beta x})^2, \quad (6.S.1)$$

where  $x$  is the displacement of the oscillator from its equilibrium position, and  $D_e$  and  $\beta$  are constants or parameters.

- a. At what value of  $x$  is  $V(x)$  a minimum?
- b. What is  $V(x)$  when  $x$  becomes very large?
- c. What happens to  $V(x)$  as  $x$  becomes a large negative number?
- d. Based on your answers to a, b, and c, sketch a graph of  $V(x)$  vs  $x$ .
- e. From your graph, identify the parameter in the Morse potential that you would call the equilibrium dissociation energy.
- f. How does the equilibrium dissociation energy in the Morse potential differ from the actual bond dissociation energy at 0 K?
- g. Mark, using arrows and labels, the equilibrium dissociation energy and the bond dissociation energy on your graph.
- h. Expand  $V(x)$  in a power series and show that the force constant for a corresponding harmonic potential is given by  $k = 2D_e\beta^2$ .
- i. The parameters  $D_e$  and  $\beta$  generally are evaluated for specific molecules from observed vibrational frequencies. Using values obtained for HCl ( $D_e = 7.31 \times 10^{-19}$  J,  $\beta = 1.82 \times 10^{10} \text{ m}^{-1}$ ), plot on the same graph both the Morse potential and the harmonic potential for HCl. In making your plot, use  $x = R - R_e$ , where  $R$  is the internuclear separation, and  $R_e$  is the equilibrium bond length, 127.5 pm.
- j. What insights, especially regarding the idea of anharmonicity, do you gain by comparing the plots that you constructed in the previous part (above) of the Morse potential and the harmonic potential?

### Q6.8

1. Sketch a double well potential for the hydrogen bond found between oxygen and nitrogen in a G-C base pair of DNA. On which side of the diagram is the nitrogen? Sketch the wavefunction with  $v = 0$  for the N-proton bond. Draw a continuation of the wavefunction into the forbidden region and beyond into the oxygen side of the bond. How do you think the wavefunction on the oxygen side of the bond will look? Use the relative amplitudes as predicted by the probability distribution for the wavefunction to predict the likelihood for finding the proton on the oxygen side of the hydrogen bond. If the DNA double strand separated at just the moment when the proton was on the oxygen side of the molecule, and this situation were stable for a period of time that is longer than required for most biochemical reactions, what might be the consequences for replication or transcription using this mutated strand of DNA? You may need to review some biochemistry, especially the structures of hydrogen-bonded base pairs to complete this problem.

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