

## 6.S: Vibrational States (Summary)

In this chapter we developed the quantum mechanical description of the harmonic oscillator for a diatomic molecule and applied it to the normal modes of molecular vibrations. We examined the functional form of the wavefunctions and the associated energy level structure. We can calculate expectation values (average values) and standard deviations for the displacement, the momentum, the square of the displacement, and the square of the momentum. The wavefunctions, which form an orthonormal set, were used to determine electric dipole selection rules for spectroscopic transitions, and in the problems at the end of the chapter, they are used to calculate several properties of the harmonic oscillator. The phenomenon of quantum mechanical tunneling through a potential-energy barrier was introduced and its relationship to real chemical phenomena was illustrated by consideration of hydrogen bonding in DNA. We finally looked at the nature of low-resolution IR spectra and introduced the anharmonicity concept to account for forbidden overtone transitions in spectra. The presence of combination bands in spectra was attributed to second derivative terms in the expansion of the dipole moment operator in terms of the normal coordinates. The simple harmonic oscillator model works well for molecules at room temperature because the molecules are in the lower vibrational levels where the effects of anharmonicity are small.

### Self-Assessment Quiz

1. Write a definition of a normal vibrational mode.
2. Write a definition of a normal vibrational coordinate.
3. List the steps in a methodology for finding the normal vibrational coordinates and frequencies.
4. What is a harmonic oscillator?
5. How is the harmonic oscillator relevant to molecular properties?
6. Write the Hamiltonian operator for a one-dimensional harmonic oscillator.
7. What are the major steps in the procedure to solve the Schrödinger equation for the harmonic oscillator?
8. What are the three parts of a harmonic oscillator wavefunction?
9. How is the quantum number  $v$  produced in solving the Schrödinger equation for the harmonic oscillator?
10. What are the allowed energies for a quantum harmonic oscillator?
11. What determines the frequency of a quantum harmonic oscillator?
12. What information about a molecular vibration is provided by the harmonic oscillator wavefunction for a normal coordinate?
13. Sketch graphs of the harmonic oscillator potential energy and a few wavefunctions.
14. Draw the harmonic oscillator energy level diagram.
15. Why is the lowest possible energy of the quantum oscillator not zero?
16. Compute the approximate energy for the first overtone transition in HBr given that the fundamental is 2564  $\text{cm}^{-1}$ .
17. If a transition from vibrational energy level  $v = 3$  to  $v = 4$  were observed in an infrared spectrum, where would that spectral line appear relative to the one for the transition from  $v = 0$  to  $v = 1$ ?
18. What is the harmonic oscillator selection rule for vibrational excitation by infrared radiation?
19. Explain why the infrared absorption coefficient is larger for some normal modes than for others.
20. Why is it possible for quantum particles to tunnel through potential barriers?
21. What are the values of integrals like  $\int_{-\infty}^{\infty} \psi_n^*(Q) \psi_m(Q) dQ$  using harmonic oscillator wavefunctions?

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