

## 6.4: Harmonic Oscillator Properties

In this section we contrast the classical and quantum mechanical treatments of the harmonic oscillator, and we describe some of the properties that can be calculated using the quantum mechanical harmonic oscillator model. The problems at the end of the chapter require that you do some of these calculations, which involve the evaluation of non-trivial integrals. Methods for evaluating such integrals are provided in a detailed math supplement. These integrals are important. They also will appear in later chapters on electronic structure. Working through the problems with the support of the link will give you the opportunity to engage the mathematics on your own terms and deepen your understanding of the material in this section.

For a classical oscillator as described in Section 6.2 we know exactly the position, velocity, and momentum as a function of time. The frequency of the oscillator (or normal mode) is determined by the effective mass  $M$  and the effective force constant  $K$  of the oscillating system and does not change unless one of these quantities is changed. There are no restrictions on the energy of the oscillator, and changes in the energy of the oscillator produce changes in the amplitude of the vibrations experienced by the oscillator.

For the quantum mechanical oscillator, the oscillation frequency of a given normal mode is still controlled by the mass and the force constant (or, equivalently, by the associated potential energy function). However, the energy of the oscillator is limited to certain values. The allowed quantized energy levels are equally spaced and are related to the oscillator frequencies as given by Equation 6.4.1.

$$E_v = \left( v + \frac{1}{2} \right) \hbar \omega \quad (6.4.1)$$

with

$$v = 0, 1, 2, 3, \dots \quad (6.4.2)$$

In a quantum mechanical oscillator, we cannot specify the position of the oscillator (the exact displacement from the equilibrium position) or its velocity as a function of time; we can only talk about the probability of the oscillator being displaced from equilibrium by a certain amount. This probability is given by

$$Pr[Q \text{ to } Q + dQ] = \psi_v^*(Q) \psi_v(Q) dQ \quad (6.4.3)$$

We can, however, calculate the average displacement and the mean square displacement of the atoms relative to their equilibrium positions. This average is just  $\langle Q \rangle$ , the expectation value for  $Q$ , and the mean square displacement is  $\langle Q^2 \rangle$ , the expectation value for  $Q^2$ . Similarly we can calculate the average momentum  $\langle P_Q \rangle$ , and the mean square momentum  $\langle P_Q^2 \rangle$ , but we cannot specify the momentum as a function of time.

Physically what do we expect to find for the average displacement and the average momentum? Since the potential energy function is symmetric around  $Q = 0$ , we expect values of  $Q > 0$  to be equally as likely as  $Q < 0$ . The average value of  $Q$  therefore should be zero.

These results for the average displacement and average momentum do not mean that the harmonic oscillator is sitting still. As for the particle-in-a-box case, we can imagine the quantum mechanical harmonic oscillator as moving back and forth and therefore having an average momentum of zero. Since the lowest allowed harmonic oscillator energy,  $E_0$ , is  $\frac{\hbar \omega}{2}$  and not 0, the atoms in a molecule must be moving even in the lowest vibrational energy state. This phenomenon is called the zero-point energy or the zero-point motion, and it stands in direct contrast to the classical picture of a vibrating molecule. Classically, the lowest energy available to an oscillator is zero, which means the momentum also is zero, and the oscillator is not moving.

### Exercise 6.4.23b

Compare the quantum mechanical harmonic oscillator to the classical harmonic oscillator at  $v=1$  and  $v=50$ .

Since the average values of the displacement and momentum are all zero and do not facilitate comparisons among the various normal modes and energy levels, we need to find other quantities that can be used for this purpose. We can use the root mean square deviation (see also root-mean-square displacement) (also known as the standard deviation of the displacement) and the root-mean-square momentum as measures of the uncertainty in the oscillator's position and momentum. These uncertainties are

calculated in Problem 3 at the end of this chapter. For a molecular vibration, these quantities represent the standard deviation in the bond length and the standard deviation in the momentum of the atoms from the average values of zero, so they provide us with a measure of the relative displacement and the momentum associated with each normal mode in all its allowed energy levels. These are important quantities to determine because vibrational excitation changes the size and symmetry (or shape) of molecules. Such changes affect chemical reactivity, the absorption and emission of radiation, and the dissipation of energy in radiationless transitions.

In Problem 2, we show that the product of the standard deviations for the displacement and the momentum,  $\sigma_Q$  and  $\sigma_p$ , satisfies the **Heisenberg Uncertainty Principle**.

$$\sigma_Q \sigma_p \geq \frac{\hbar}{2} \quad (6.4.4)$$

The harmonic oscillator wavefunctions form an **orthonormal set**, which means that all functions in the set are normalized individually

$$\int_{-\infty}^{\infty} \psi_v^*(x) \psi_v(x) dx = 1 \quad (6.4.5)$$

and are orthogonal to each other.

$$\int_{-\infty}^{\infty} \psi_{v'}^*(x) \psi_v(x) dx = 0 \quad (6.4.6)$$

for  $v' \neq v$ .

The fact that a family of wavefunctions forms an orthonormal set is often helpful in simplifying complicated integrals. We will use these properties in Section 6.6, for example, when we determine the harmonic oscillator selection rules for vibrational transitions in a molecule and calculate the absorption coefficients for the absorption of infrared radiation.

Finally, we can calculate the probability that a harmonic oscillator is in the classically forbidden region. What does this tantalizing statement mean? Classically, the maximum extension of an oscillator is obtained by equating the total energy of the oscillator to the potential energy, because at the maximum extension all the energy is in the form of potential energy. If all the energy weren't in the form of potential energy at this point, the oscillator would have kinetic energy and momentum and could continue to extend further away from its rest position. Interestingly, as we show below, the wavefunctions of the quantum mechanical oscillator extend beyond the classical limit, i.e. beyond where the particle can be according to classical mechanics.

The lowest allowed energy for the quantum mechanical oscillator is called the zero-point energy,  $E_0 = \frac{\hbar\omega}{2}$ . Using the classical picture described in the preceding paragraph, this total energy must equal the potential energy of the oscillator at its maximum extension. We define this classical limit of the amplitude of the oscillator displacement as  $Q_0$ . When we equate the zero-point energy for a particular normal mode to the potential energy of the oscillator in that normal mode, we obtain

$$\frac{\hbar\omega}{2} = \frac{KQ_0^2}{2} \quad (6.4.7)$$

Recall that  $K$  is the effective force constant of the oscillator in a particular normal mode and that the frequency of the normal mode is given by Equation 6.4.8 which is

$$\omega = \sqrt{\frac{K}{M}} \quad (6.4.8)$$

Solving for  $Q_0$  in Equation 6.4.7 by substituting for  $\omega$  and rearranging, we obtain the very interesting result

$$Q_0^2 = \frac{\hbar\omega}{K} = \frac{\hbar}{M\omega} = \frac{\hbar}{\sqrt{KM}} = \beta^2 \quad (6.4.9)$$

Here we see that  $\beta$ , the parameter we introduced in Equation 6-20, is more than just a way to collect variables;  $\beta$  has physical significance. It is the classical limit to the amplitude (maximum extension) of an oscillator with energy  $E_0 = \frac{\hbar\omega}{2}$ . Because  $\beta$  has

this meaning, the variable  $x$  gives the displacement of the oscillator from its equilibrium position in units of the maximum classically allowed displacement for the  $v = 0$  state (lowest energy state). In other words,  $x = 1$  means the oscillator is at this classical limit, and  $x = 0.5$  means it is halfway there.

#### Exercise 6.4.24

The HCl equilibrium bond length is 0.127 nm and the  $v = 0$  to  $v = 1$  transition is observed in the infrared at 2886  $\text{cm}^{-1}$ . Compute the vibrational energy of HCl in its lowest state. Compute the classical limit for the stretching of the HCl bond from its equilibrium length in this state. What percent of the equilibrium bond length is this extension?

The classical limit,  $Q_0$ , for the lowest-energy state is given by Equation 6.4.9; i.e.,  $Q_0 = \pm\beta$  or  $x = \frac{Q_0}{\beta} = \pm 1$ . Examination of the quantum mechanical wavefunction for the lowest-energy state reveals that the wavefunction  $\Psi_0(x)$  extends beyond these points. Higher energy states have higher total energies, so the classical limits to the amplitude of the displacement will be larger for these states.

#### Exercise 6.4.25

Mark  $x = +1$  and  $x = -1$  on the graph for  $|\psi_0(x)|^2$  in Figure 6.4.7 and note whether the wavefunction is zero at these points.

The observation that the wavefunctions are not zero at the classical limit means that the quantum mechanical oscillator has a finite probability of having a displacement that is larger than what is classically possible. The oscillator can be in a region of space where the potential energy is greater than the total energy. Classically, when the potential energy equals the total energy, the kinetic energy and the velocity are zero, and the oscillator cannot pass this point. A quantum mechanical oscillator, however, has a finite probability of passing this point. For a molecular vibration, this property means that the amplitude of the vibration is larger than what it would be in a classical picture. In some situations, a larger amplitude vibration could enhance the chemical reactivity of a molecule.

#### Exercise 6.4.26

Plot the probability density for  $v = 0$  and  $v = 1$  states. Mark the classical limits on each of the plots, since the limits are different because the total energy is different for  $v = 0$  and  $v = 1$ . Shade in the regions of the probability densities that extend beyond the classical limit.

The fact that a quantum mechanical oscillator has a finite probability to enter the classically forbidden region of space is a consequence of the wave property of matter and the Heisenberg Uncertainty Principle. A wave changes gradually, and the wavefunction approaches zero gradually as the potential energy approaches infinity.

We should be able to calculate the probability that the quantum mechanical harmonic oscillator is in the classically forbidden region for the lowest energy state, the state with  $v = 0$ . The classically forbidden region is shown by the shading of the regions beyond  $Q_0$  in the graph you constructed for Exercise 6.4.26. The area of this shaded region gives the probability that the bond oscillation will extend into the forbidden region. To calculate this probability, we use

$$Pr[\text{forbidden}] = 1 - Pr[\text{allowed}] \quad (6.4.10)$$

because the integral from 0 to  $Q_0$  for the allowed region can be found in integral tables and the integral from  $Q_0$  to  $\infty$  cannot. The form of the integral,  $Pr[\text{allowed}]$ , to evaluate is

$$Pr[\text{allowed}] = 2 \int_0^{Q_0} \psi_0^*(Q) \psi_0(Q) dQ \quad (6.4.11)$$

The factor 2 appears in Equation 6.4.11 from the symmetry of the wavefunction, which extends from  $-Q_0$  to  $+Q_0$ . To evaluate the integral in Equation 6.4.11, use the wavefunction and do the integration in terms of  $x$ , Equation (6-29). Recall that for  $v = 0$ ,  $Q = Q_0$  corresponds to  $x = 1$ . Including the normalization constant, Equation ??? produces

$$Pr[\text{allowed}] = \frac{2}{\sqrt{\pi}} \int_0^1 \exp(-x^2) dx \quad (6.4.12)$$

The integral in Equation 6.4.12 is called an error function (ERF), and can only be evaluated numerically. Values can be found in books of mathematical tables or obtained with Mathcad. When the limit of integration is 1,  $\text{ERF}(1) = 0.843$  and  $\text{Pr}[\text{forbidden}] = 0.157$ . This result means that the quantum mechanical oscillator can be found in the forbidden region 16% of the time. This effect is substantial and leads to the phenomenon called quantum mechanical tunneling.

#### Exercise 6.4.27

Numerically Verify that  $\text{Pr}[\text{allowed}]$  in Equation (6-39) equals 0.843. To obtain a value for the integral do not use symbolic integration or symbolic equals.

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