

# The Quantum Harmonic Oscillator

C. David Sherrill

School of Chemistry and Biochemistry

Georgia Institute of Technology

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## 1 Introduction

The harmonic oscillator is extremely useful in chemistry as a model for the vibrational motion in a diatomic molecule. Polyatomic molecules can be modeled by coupled harmonic oscillators. The atoms are viewed as point masses which are connected by bonds which act (approximately) like springs obeying Hooke's law. In these notes we will review the classical harmonic oscillator problem and then discuss the quantum harmonic oscillator.

## 2 Classical Harmonic Oscillator

Consider two masses  $m_1$  and  $m_2$  at positions  $x_1$  and  $x_2$ , connected by a spring with spring constant  $k$ . If the rest length of the spring is  $l_0$ , then the two equations governing the motion of the masses are

$$m_1\ddot{x}_1 = k(x_2 - x_1 - l_0) \quad (1)$$

$$m_2\ddot{x}_2 = -k(x_2 - x_1 - l_0). \quad (2)$$

It will be more convenient to work in terms of  $(x_2 - x_1 - l_0)$ , which is the amount by which the spring is stretched or compressed from its natural length. Denoting this quantity simply as  $x$ , the equations reduce to

$$m_1\ddot{x}_1 = kx \quad (3)$$

$$m_2\ddot{x}_2 = -kx. \quad (4)$$

Subtracting the second equation from the first gives

$$m_1\ddot{x}_1 + m_2\ddot{x}_2 = 0. \quad (5)$$

It will be convenient to introduce the total mass and center of mass coordinates, defined as

$$M = m_1 + m_2 \quad (6)$$

$$x_{cm} = \frac{m_1x_1 + m_2x_2}{m_1 + m_2}, \quad (7)$$

so that we now have

$$M\ddot{x}_{cm} = 0. \quad (8)$$

This means that the center of mass is not accelerating or decelerating, but is either at rest or moves with constant velocity; of course this simply reflects the fact that there is no external force acting on the two masses.

Now dividing (3) by  $m_1$  and (4) by  $m_2$  and subtracting the second equation from the first, we can obtain

$$\ddot{x}_1 - \ddot{x}_2 = kx \left( \frac{1}{m_1} + \frac{1}{m_2} \right). \quad (9)$$

Since  $x = x_2 - x_1 - l_0$ , we have  $\ddot{x} = \ddot{x}_2 - \ddot{x}_1$ . If we also introduce the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}, \quad (10)$$

we obtain

$$\ddot{x} = -\frac{k}{\mu}x, \quad (11)$$

which is a second-order differential equation describing the displacement  $x$  from the rest length  $l_0$  as a function of time. This can be solved to yield

$$x(t) = A\cos(\omega t) + B\sin(\omega t), \quad (12)$$

where  $\omega$  is defined as

$$\omega = \sqrt{\frac{k}{\mu}} \quad (13)$$

and represents the frequency of oscillation (in  $\text{rad s}^{-1}$ ) of the oscillator. One could also define a frequency  $\nu$  in Hertz ( $\text{s}^{-1}$ ) through  $\omega = 2\pi\nu$ .

### 3 Quantum Harmonic Oscillator

The quantum mechanical version of this harmonic oscillator problem may be written as

$$\left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 \right) \Psi(x) = E\Psi(x). \quad (14)$$

By considering the limiting behavior as  $x \rightarrow \infty$  and as  $x \rightarrow 0$ , one finds that only certain energies  $E_n$  yield reasonable solutions  $\Psi(x)$ . The eigenvalues and associated eigenvectors are

$$E_n = \hbar\omega \left( n + \frac{1}{2} \right) = h\nu \left( n + \frac{1}{2} \right), \quad (15)$$

$$\Psi_n(x) = \left( \frac{\mu\omega}{\pi\hbar 2^{2n}(n!)^2} \right)^{1/4} \exp\left(-\frac{\mu\omega x^2}{2\hbar}\right) H_n \left[ \left( \frac{\mu\omega}{\hbar} \right)^{1/2} x \right], \quad (16)$$

where  $H_n$  are the Hermite polynomials of order  $n$ . The Hermite polynomials have a number of useful properties such as

$$\frac{d}{dx} H_n(x) = 2n H_{n-1}(x) \quad (17)$$

$$H_{n+1}(x) = 2x H_n(x) - 2n H_{n-1}(x) \quad (18)$$

$$\int_{-\infty}^{\infty} H_n(x) H_m(x) e^{-x^2} dx = \delta_{nm} \sqrt{\pi} 2^n n!. \quad (19)$$

### 3.1 Units

Absorption or emission of infrared light can cause transitions between energy levels in the harmonic oscillator. Usually, only transitions between adjacent energy levels ( $\Delta n = 1$ ) occurs with a large intensity. The frequency of the photon  $\nu_{photon}$  thus needs to match

$$h\nu_{photon} = \Delta E = h\nu. \quad (20)$$

In this particular case, the frequency of the photon  $\nu_{photon}$  must be the same as the frequency  $\nu$  of the oscillator. Often,  $\nu_{photon}$  is measured in wavenumbers ( $\text{cm}^{-1}$ ) instead of Hertz. Since the photon obeys  $c = \lambda\nu$ , the reciprocal wavelength of the photon  $1/\lambda$  can be written as

$$\frac{1}{\lambda} = \frac{\nu}{c} = \frac{\omega}{2\pi c} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}. \quad (21)$$

Note that units of  $\text{cm}^{-1}$  will result for  $1/\lambda$  if, for example,  $c$  is in  $\text{cm s}^{-1}$ ,  $k$  is in  $\text{J m}^{-2}$ , and  $\mu$  is in  $\text{kg}$ . Because of the numerical equivalence between  $\nu_{photon}$  and  $\nu$ , one also frequently reports  $\nu$  in units of  $\text{cm}^{-1}$  using the above conversion. Unfortunately, spectroscopists frequently denote this  $\nu$  as  $\omega$ , which as we have seen is defined differently above ( $\nu$  and  $\omega$  differ by a factor of  $2\pi$ ). When  $\omega$  is reported in  $\text{cm}^{-1}$ , this is actually  $\nu$  in  $\text{cm}^{-1}$ , not the  $\omega$  defined above. One reason for this unfortunate discrepancy in notation is that spectroscopists prefer to use  $\nu$  to refer to *fundamental* (actually observed) frequencies, which differ from the *harmonic* (model) frequencies because the potential wells in diatomic molecules are not strictly harmonic but contain an anharmonic contribution.

What are the units of  $k$ ? The SI units would be  $\text{J m}^{-2}$ , but these are not really natural units for the very small energies and distances involved in a quantum oscillator. Frequently, these are reported in  $\text{mdyn \AA}^{-1}$ . The conversion is

$$\frac{\text{mdyn}}{\text{\AA}} = \frac{10^{-8}\text{N}}{10^{-10}\text{m}} \times \frac{\text{m}}{\text{m}} = 10^2 \frac{\text{J}}{\text{m}^2}. \quad (22)$$