The harmonic oscillator

Figure 1 shows a typical interatomic potential for a vibrating diatomic molecule (solid, black line). The position of the minimum of the curve, l_0, represents the equilibrium bond length. The force between the two atoms given by the first order derivative of the potential with respect to the interatomic separation l is zero at this point. The potential rises steeply to the left of l_0, for small separations (hard inner wall), while to the right of l_0, for large separations, the potential is smoother and levels off at a value representing the dissociation energy, where bond breaking occurs.

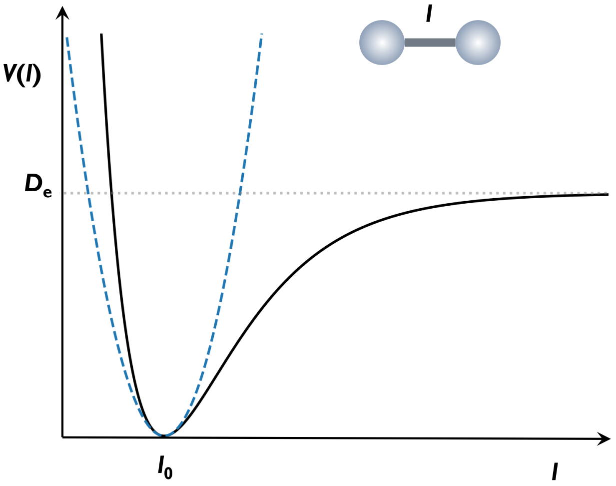

Figure 1: Interatomic potential of a diatomic molecule modelled as a Morse potential (solid, black line) and as a harmonic potential (dashed, blue line).

The *Morse potential* provides a good analytic approximation of the interatomic potential over a large range of interatomic separations:

$$V(x) = D_\mathrm{e}(1 - \mathrm{e}^{-ax})^2 \tag{1}$$

where $x = l - l_0$ is the displacement from the equilibrium bond length, D_e is the dissociation energy (value of the potential for $x \to \infty$), and a controls the curvature of the potential at the equilibrium bond length.

Consider a Taylor expansion of the potential around the equilibrium bond length ($x = 0$):

$$V(x) = V(0) + \left(\frac{\mathrm{d}V}{\mathrm{d}x}\right)_{x=0} x + \frac{1}{2!}\left(\frac{\mathrm{d}^2V}{\mathrm{d}x^2}\right)_{x=0} x^2 + \frac{1}{3!}\left(\frac{\mathrm{d}^3V}{\mathrm{d}x^3}\right)_{x=0} x^3 + \dots \tag{2}$$

If we only consider small displacements around the equilibrium bond length, we can neglect the third and higher order terms in the expansion. For the Morse potential, $V(0) = 0$ and the first two derivatives are:

$$\left(\frac{\mathrm{d}V}{\mathrm{d}x}\right)_{x=0} = 0 \quad \left(\frac{\mathrm{d}^2V}{\mathrm{d}x^2}\right)_{x=0} = \left[2D_\mathrm{e}a\left(-a\mathrm{e}^{-ax} + 2a\mathrm{e}^{-2ax}\right)\right]_{x=0} = 2D_\mathrm{e}a^2$$

Therefore, for small displacements from equilibrium, the potential can be approximated as:

$$V(x) = D_\mathrm{e}a^2x^2 = \frac{1}{2}kx^2 \tag{3}$$

where we have defined $k = 2D_e a^2$. This is the equation of a *harmonic oscillator* potential. Figure 1 shows a harmonic potential (dashed, blue curve) in comparison to the interatomic potential of a diatomic molecule modelled as a Morse potential. As expected, the harmonic oscillator is a reasonable approximation for the potential of a chemical bond for small displacements around the equilibrium bond length l_0.

Classical harmonic oscillator

Here, we review the description of the vibrations of a diatomic molecule described as a harmonic oscillator according to classical mechanics.

Consider two masses m_1 and m_2 connected by a spring (see Figure 2) as a model of a vibrating diatomic molecule. If the vibrational motion of this two-body system depends only on the relative separation $l = x_1 - x_2$ between the two masses, the two-body problem can be treated as the one body-problem of the vibration of a mass μ connected to a wall by a spring (see Figure 2), where μ is the reduced mass:

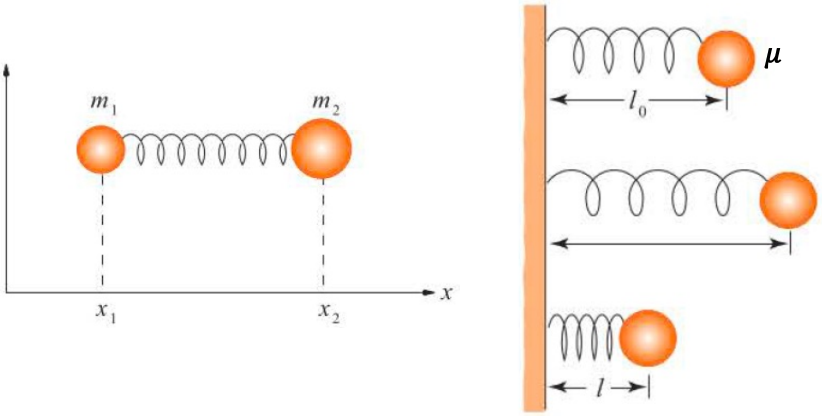

Figure 2: The motion of two masses connected by a spring can be conveniently represented as the motion of one mass corresponding to the reduced mass of the two-body system connected to a wall by a spring. Adapted from McQuarrie, Quantum Chemistry, University Science Books, ed. 2.

$$\mu = \frac{m_1 + m_2}{m_1 m_2} \tag{4}$$

The general form of the potential energy of a harmonic oscillator is:

$$V(x) = \frac{1}{2}kx^2 + \text{constant} \tag{5}$$

where $x = l - l_0$ is the displacement from the equilibrium length of the spring. For simplicity, we can choose the potential to be zero at equilibrium, giving (compare to equation 3 in the previous section):

$$V(x) = \frac{1}{2}kx^2 \tag{6}$$

The force acting on the mass is given by the first order derivative of the potential energy:

$$F(x) = -\frac{\mathrm{d}V}{\mathrm{d}x} = -kx \tag{7}$$

which shows that the harmonic oscillator follows *Hooke's law*: The restoring force on the mass for compression ($l < l_0$) or stretching ($l > l_0$) of the spring is linearly proportional to the displacement. k represents the curvature of the potential and is called *force constant*. A big value of k gives a narrow potential (stiff spring), a small k gives a wide potential (loose spring).

From Newton's second law ($\mu a = F$):

$$\mu \frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = -kx \tag{8}$$

This equation has the general solution:

$$x(t) = A \sin\left(\sqrt{\frac{k}{\mu}}t\right) + B \cos\left(\sqrt{\frac{k}{\mu}}t\right) \tag{9}$$

If we assume that $x = 0$ at $t = 0$, then $B = 0$ and:

$$x(t) = A \sin\left(\sqrt{\frac{k}{\mu}}t\right) \tag{10}$$

$x(t)$ is the trajectory describing how the displacement of a mass μ experiencing a Hooke's law restoring force varies with time. According to equation 10, in the classical harmonic oscillator model, the distance between two particles oscillates in a sinusoidal way between $-A$ and A (thus, A represents the maximum displacement from equilibrium).

The period τ of the harmonic oscillations is obtained by considering the periodicity of the sine function:

$$\sqrt{\frac{k}{\mu}}\tau = 2\pi \quad \Rightarrow \quad \tau = 2\pi\sqrt{\frac{\mu}{k}} \tag{11}$$

Therefore, the frequency ν and angular frequency ω are:

$$\nu = \frac{1}{\tau} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \omega = 2\pi\nu = \sqrt{\frac{k}{\mu}} \tag{12}$$

The frequency of the oscillations increases with the force constant, and hence the curvature of the potential, and decreases with the mass.

The time variation of the velocity of a classical harmonic oscillator is given by the time derivative of equation 10:

$$v(t) = \frac{\mathrm{d}x}{\mathrm{d}t} = \sqrt{\frac{k}{\mu}} A \cos\left(\sqrt{\frac{k}{\mu}}t\right) \tag{13}$$

By comparing equations 10 and 13, we can deduce that when $x(t) = 0$ (the spring is at the equilibrium length), for $t = 0, \frac{\tau}{2}, \tau, \ldots$, then the velocity has maximum amplitude ($v(t) = \pm\sqrt{k/\mu}A$). Conversely, when the displacement from equilibrium is largest ($x(t) = \pm A$), for $t = \frac{\tau}{4}, \frac{3\tau}{4}, \frac{5\tau}{4}, \ldots$, then $v(t) = 0$. The trajectory of a harmonic oscillator and variation of the velocity along it are shown in Figure 3.

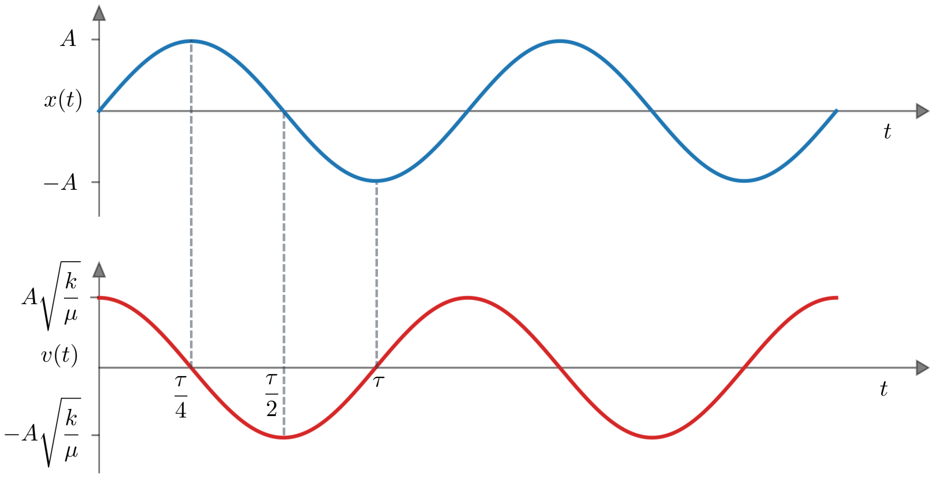

Figure 3: Displacement from equilibrium and velocity of a classical harmonic oscillator as a function of time.

Energy of a classical harmonic oscillator

Using equations 10 and 13, we can find the expressions for the potential and kinetic energy of a classical harmonic oscillator:

$$V = \frac{1}{2}kx^2 = \frac{1}{2}kA^2\sin^2\left(\sqrt{\frac{k}{\mu}}t\right) \tag{14}$$

$$T = \frac{1}{2}\mu v^2 = \frac{1}{2}kA^2\cos^2\left(\sqrt{\frac{k}{\mu}}t\right) \tag{15}$$

Thus, the total energy is:

$$\begin{aligned} E = V + T &= \frac{1}{2}kA^2\sin^2\left(\sqrt{\frac{k}{\mu}}t\right) + \frac{1}{2}kA^2\cos^2\left(\sqrt{\frac{k}{\mu}}t\right) \\ &= \frac{1}{2}kA^2\left[\sin^2\left(\sqrt{\frac{k}{\mu}}t\right) + \cos^2\left(\sqrt{\frac{k}{\mu}}t\right)\right] \\ &= \frac{1}{2}kA^2 \end{aligned} \tag{16}$$

Since k and A do not depend on time, the total energy of a harmonic oscillator is constant. When the spring has the equilibrium length ($x(t) = 0$), the potential energy is zero and therefore, the total energy is equal to the kinetic energy. For the largest displacement ($x(t) = \pm A$), the kinetic energy is zero and the total energy corresponds to the potential energy. Figure 4 illustrates how the potential, kinetic and total energy of a harmonic oscillator vary during one oscillation.
The largest displacements from equilibrium are called inner ($x(t) = -A$) and outer ($x(t) = A$) *turning points* and are related to the total energy of the oscillator (see equation 16):

$$x_{\text{tp}} = \pm A = \pm\sqrt{\frac{2E}{k}} \tag{17}$$

The probability of finding the particles is greatest close to the classical turning points, because the velocity there is zero.

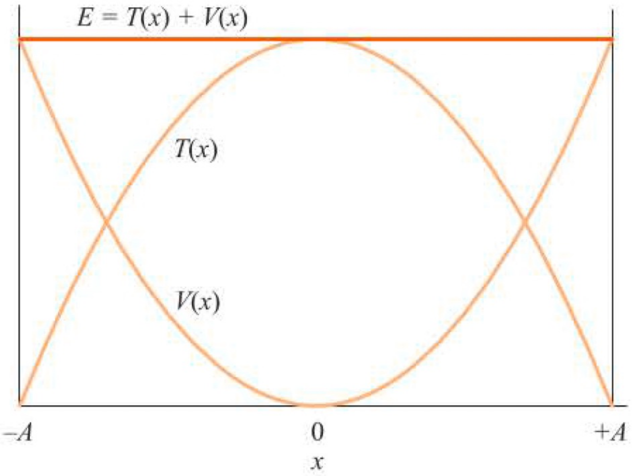

Figure 4: Energy of a classical harmonic oscillator. From McQuarrie, Quantum Chemistry, University Science Books, ed. 2.