

TOPIC 7E Vibrational motion

7E.1 The harmonic oscillator

In classical mechanics a **harmonic oscillator** is a particle of mass m that experiences a restoring force proportional to its displacement, x , from the equilibrium position. As is shown in *The chemist's toolkit 18*, the particle oscillates about the equilibrium position at a characteristic frequency, ν . The potential energy of the particle is

$$V(x) = \frac{1}{2} k_f x^2 \quad \text{Parabolic potential energy} \quad (7E.1)$$

where k_f is the **force constant**, which characterizes the strength of the restoring force (Fig. 7E.1) and is expressed in newtons per metre (N m^{-1}). This form of potential energy is called a 'harmonic potential energy' or a 'parabolic potential energy'. The Schrödinger equation for the oscillator is therefore

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + \frac{1}{2} k_f x^2 \psi(x) = E\psi(x) \quad \text{Schrödinger equation} \quad (7E.2)$$

Atoms in molecules and solids vibrate around their equilibrium positions as bonds stretch, compress, and bend. The simplest model for this kind of motion is the 'harmonic oscillator', which is considered in detail in this Topic.

The chemist's toolkit 18 The classical harmonic oscillator

A harmonic oscillator consists of a particle of mass m that experiences a 'Hooke's law' restoring force, one that is proportional to the displacement of the particle from equilibrium. For a one-dimensional system,

$$F_x = -k_f x$$

From Newton's second law of motion ($F = ma = m(d^2x/dt^2)$; see *The chemist's toolkit 3* in Topic 1B),

$$m \frac{d^2x}{dt^2} = -k_f x$$

If $x = 0$ at $t = 0$, a solution (as may be verified by substitution) is

$$x(t) = A \sin 2\pi\nu t \quad \nu = \frac{1}{2\pi} \left(\frac{k_f}{m} \right)^{1/2}$$

This solution shows that the position of the particle oscillates *harmonically* (i.e. as a sine function) with frequency ν (units: Hz). The *angular frequency* of the oscillator is $\omega = 2\pi\nu$ (units: radians per second). It follows that the angular frequency of a classical harmonic oscillator is $\omega = (k_f/m)^{1/2}$.

The potential energy becomes infinite at $x = \pm\infty$, and so the wavefunction is zero at these limits. However, as the potential energy rises smoothly rather than abruptly to infinity, as it does for a particle in a box, the wavefunction decreases

The potential energy V is related to force by $F = -dV/dx$ (*The chemist's toolkit 6* in Topic 2A), so the potential energy corresponding to a Hooke's law restoring force is

$$V(x) = \frac{1}{2} k_f x^2$$

As the particle moves away from the equilibrium position its potential energy increases and so its kinetic energy, and hence its speed, decreases. At some point all the energy is potential and the particle comes to rest at a turning point. The particle then accelerates back towards and through the equilibrium position. The greatest probability of finding the particle is where it is moving most slowly, which is close to the turning points.

The turning point, x_{tp} , of a classical oscillator occurs when its potential energy $\frac{1}{2} k_f x^2$ is equal to its total energy, so

$$x_{tp} = \pm \left(\frac{2E}{k_f} \right)^{1/2}$$

The turning point increases with the total energy: in classical terms, the amplitude of the swing of a pendulum or the displacement of a mass on a spring increases.

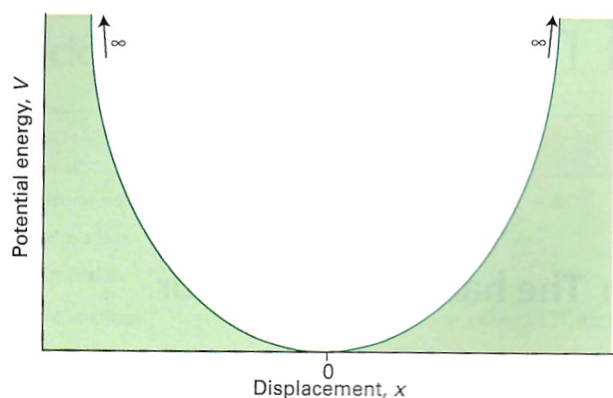


Figure 7E.1 The potential energy for a harmonic oscillator is the parabolic function $V_{\text{HO}}(x) = \frac{1}{2}k_f x^2$, where x is the displacement from equilibrium. The larger the force constant k_f , the steeper the curve and narrower the curve becomes.

smoothly towards zero rather than becoming zero abruptly. The boundary conditions $\psi(\pm\infty) = 0$ imply that only some solutions of the Schrödinger equation are acceptable, and therefore that the energy of the oscillator is quantized.

(a) The energy levels

Equation 7E.2 is a standard form of differential equation and its solutions are well known to mathematicians.¹ The energies permitted by the boundary conditions are

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega \quad \omega = (k_f/m)^{1/2} \quad \text{Energy levels} \quad (7E.3)$$

$$v = 0, 1, 2, \dots$$

where v is the **vibrational quantum number**. Note that the energies depend on ω , which has the same dependence on the mass and the force constant as the angular frequency of a classical oscillator (see *The chemist's toolkit* 18) and is high when the force constant is large and the mass small. The separation of adjacent levels is

$$E_{v+1} - E_v = \hbar\omega \quad (7E.4)$$

for all v . The energy levels therefore form a uniform ladder with spacing $\hbar\omega$ (Fig. 7E.2). The energy separation $\hbar\omega$ is negligibly small for macroscopic objects (with large mass) but significant for objects with mass similar to that of an atom.

The energy of the lowest level, with $v = 0$, is not zero:

$$E_0 = \frac{1}{2}\hbar\omega \quad \text{Zero-point energy} \quad (7E.5)$$

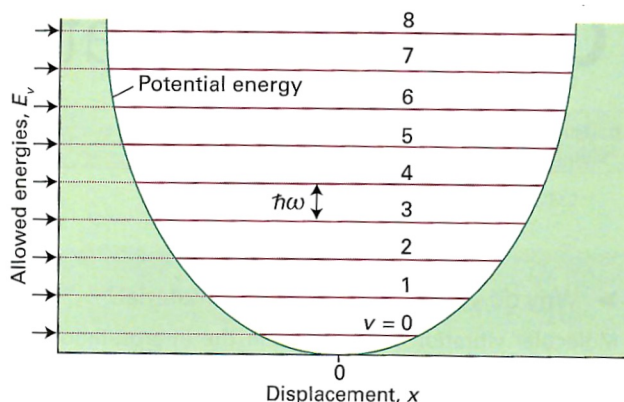


Figure 7E.2 The energy levels of a harmonic oscillator are evenly spaced with separation $\hbar\omega$, where $\omega = (k_f/m)^{1/2}$. Even in its lowest energy state, an oscillator has an energy greater than zero.

The physical reason for the existence of this zero-point energy is the same as for the particle in a box (Topic 7D). The particle is confined, so its position is not completely uncertain. It follows that its momentum, and hence its kinetic energy, cannot be zero. A classical interpretation of the zero-point energy is that the quantum oscillator is never completely at rest and therefore has kinetic energy; moreover, because its motion samples the potential energy away from the equilibrium position, it also has non-zero potential energy.

The model of a particle oscillating in a parabolic potential is used to describe the vibrational motion of a diatomic molecule A–B (and, with elaboration, Topic 11D, polyatomic molecules). In this case both atoms move as the bond between them is stretched and compressed and the mass m is replaced by the **effective mass**, μ , given by

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad \text{Effective mass [diatomic molecule]} \quad (7E.6)$$

When A is much heavier than B, m_B can be neglected in the denominator and the effective mass is $\mu \approx m_B$, the mass of the lighter atom. In this case, only the light atom moves and the heavy atom acts as a stationary anchor.

Brief illustration 7E.1

The effective mass of $^1\text{H}^{35}\text{Cl}$ is

$$\mu = \frac{m_{\text{H}} m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} = \frac{(1.0078 m_{\text{u}}) \times (34.9688 m_{\text{u}})}{(1.0078 m_{\text{u}}) + (34.9688 m_{\text{u}})} = 0.9796 m_{\text{u}}$$

which is close to the mass of the hydrogen atom. The force constant of the bond is $k_f = 516.3 \text{ N m}^{-1}$. It follows from eqn 7E.3 and $1 \text{ N} = 1 \text{ kg m s}^{-2}$, with μ in place of m , that

$$\omega = \left(\frac{k_f}{\mu}\right)^{1/2} = \left(\frac{516.3 \text{ N m}^{-1}}{0.9796 \times (1.66054 \times 10^{-27} \text{ kg})}\right)^{1/2} = 5.634 \times 10^{14} \text{ s}^{-1}$$

¹ For details, see our *Molecular quantum mechanics*, Oxford University Press, Oxford (2011).

or (after division by 2π) 89.67 THz. Therefore, the separation of adjacent levels is (eqn 7E.4)

$$E_{\nu+1} - E_{\nu} = (1.05457 \times 10^{-34} \text{ Js}) \times (5.634 \times 10^{14} \text{ s}^{-1}) \\ = 5.941 \times 10^{-20} \text{ J}$$

or 59.41 zJ, about 0.37 eV. This energy separation corresponds to 36 kJ mol^{-1} , which is chemically significant. The zero-point energy (eqn 7E.5) of this molecular oscillator is 29.71 zJ, which corresponds to 0.19 eV, or 18 kJ mol^{-1} .

(b) The wavefunctions

The acceptable solutions of eqn 7E.2, all have the form

$$\psi(x) = N \times (\text{polynomial in } x) \times (\text{bell-shaped Gaussian function})$$

where N is a normalization constant. A Gaussian function is a bell-shaped function of the form e^{-x^2} (Fig. 7E.3). The precise form of the wavefunctions is

$$\psi_{\nu}(x) = N_{\nu} H_{\nu}(y) e^{-y^2/2} \quad \text{Wavefunctions} \quad (7E.7)$$

$$y = \frac{x}{\alpha} \quad \alpha = \left(\frac{\hbar^2}{mk_f} \right)^{1/4}$$

The factor $H_{\nu}(y)$ is a **Hermite polynomial**; the form of these polynomials and some of their properties are listed in Table 7E.1. Note that the first few Hermite polynomials are rather simple: for instance, $H_0(y) = 1$ and $H_1(y) = 2y$. Hermite polynomials, which are members of a class of functions called 'orthogonal polynomials', have a wide range of important properties which allow a number of quantum mechanical calculations to be done with relative ease.

The wavefunction for the ground state, which has $\nu = 0$, is

$$\psi_0(x) = N_0 e^{-y^2/2} = N_0 e^{-x^2/2\alpha^2} \quad \text{Ground-state wavefunction} \quad (7E.8a)$$

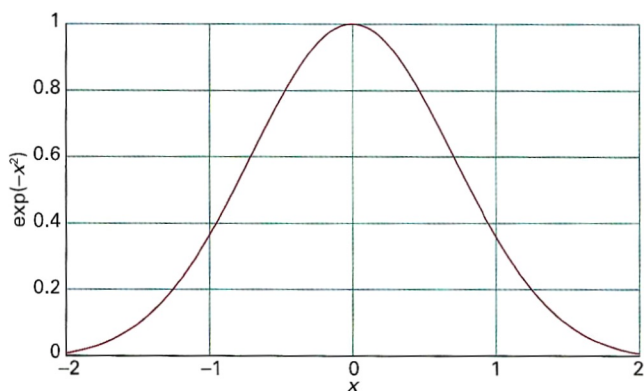


Figure 7E.3 The graph of the Gaussian function, $f(x) = e^{-x^2}$.

Table 7E.1 The Hermite polynomials

ν	$H_{\nu}(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
6	$64y^6 - 480y^4 + 720y^2 - 120$

The Hermite polynomials are solutions of the differential equation

$$H''_{\nu} - 2yH'_{\nu} + 2\nu H_{\nu} = 0$$

where primes denote differentiation. They satisfy the recursion relation

$$H_{\nu+1} - 2yH_{\nu} + 2\nu H_{\nu-1} = 0$$

An important integral is

$$\int_{-\infty}^{\infty} H_{\nu'} H_{\nu} e^{-y^2} dy = \begin{cases} 0 & \text{if } \nu' \neq \nu \\ \pi^{1/2} 2^{\nu} \nu! & \text{if } \nu' = \nu \end{cases}$$

and the corresponding probability density is

$$\psi_0^2(x) = N_0^2 e^{-y^2} = N_0^2 e^{-x^2/\alpha^2} \quad \text{Ground-state probability density} \quad (7E.8b)$$

The wavefunction and the probability density are shown in Fig. 7E.4. The probability density has its maximum value at $x = 0$, the equilibrium position, but is spread about this position. The curvature is consistent with the kinetic energy being non-zero and the spread is consistent with the potential energy also being non-zero, so resulting in a zero-point energy.

The wavefunction for the first excited state, $\nu = 1$, is

$$\psi_1(x) = N_1 2ye^{-y^2/2} = N_1 \left(\frac{2}{\alpha} \right) xe^{-x^2/2\alpha^2} \quad \text{First excited-state wavefunction} \quad (7E.9)$$

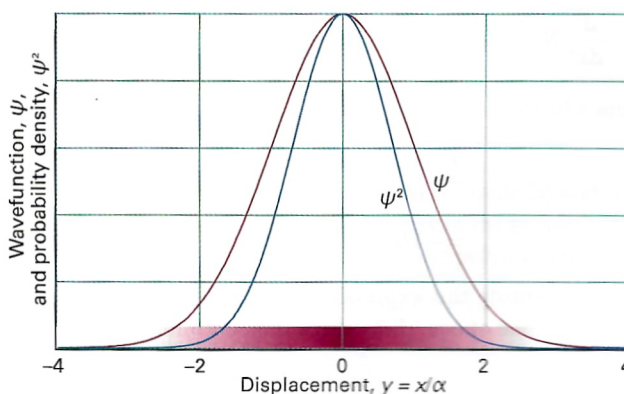


Figure 7E.4 The normalized wavefunction and probability density (shown also by shading) for the lowest energy state of a harmonic oscillator.

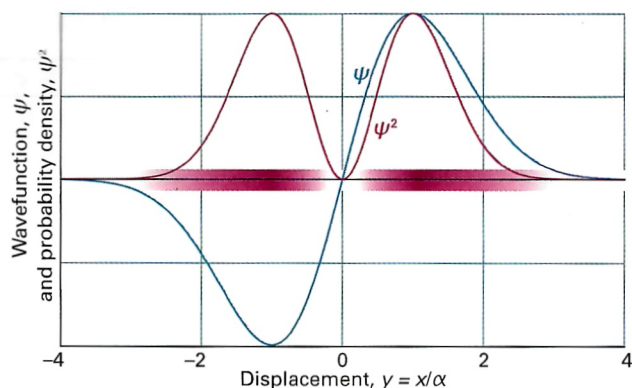


Figure 7E.5 The normalized wavefunction and probability density (shown also by shading) for the first excited state of a harmonic oscillator.

This function has a node at zero displacement ($x = 0$), and the probability density has maxima at $x = \pm 1$ (Fig. 7E.5).

Example 7E.1 Confirming that a wavefunction is a solution of the Schrödinger equation

Confirm that the ground-state wavefunction (eqn 7E.8a) is a solution of the Schrödinger equation (eqn 7E.2).

Collect your thoughts You need to substitute the wavefunction given in eqn 7E.8a into eqn 7E.2 and see that the left-hand side generates the right-hand side of the equation; use the definition of α in eqn 7E.7. Confirm that the factor that multiplies the wavefunction on the right-hand side agrees with eqn 7E.5.

The solution First, evaluate the second derivative of the ground-state wavefunction by differentiating it twice in succession:

$$\begin{aligned} \frac{d}{dx} N_0 e^{-x^2/2\alpha^2} &= -N_0 \left(\frac{x}{\alpha^2} \right) e^{-x^2/2\alpha^2} \\ \frac{d^2}{dx^2} N_0 e^{-x^2/2\alpha^2} &= \frac{d}{dx} \left\{ \overbrace{-N_0 \left(\frac{x}{\alpha^2} \right)}^f \overbrace{e^{-x^2/2\alpha^2}}^g \right\} \\ &\quad \downarrow \text{d(fg)/dx = fdg/dx + gdf/dx} \\ &= -\frac{N_0}{\alpha^2} e^{-x^2/2\alpha^2} + N_0 \left(\frac{x}{\alpha^2} \right)^2 e^{-x^2/2\alpha^2} \\ &= -(1/\alpha^2) \psi_0 + (x^2/\alpha^4) \psi_0 \end{aligned}$$

Now substitute this expression and $\alpha^2 = (\hbar^2/mk_f)^{1/2}$ into the left-hand side of eqn 7E.2, which then becomes

$$\frac{(\hbar/2)(k_f/m)^{1/2}}{2m} \psi_0 - \frac{k_f/2}{2m} \left(\frac{\hbar^2}{k_f} \right) x^2 \psi_0 + \frac{1}{2} k_f x^2 \psi_0 = E \psi_0$$

and therefore (keeping track of the blue terms)

$$\frac{\hbar}{2} \left(\frac{k_f}{m} \right)^{1/2} \psi_0 - \frac{1}{2} k_f x^2 \psi_0 + \frac{1}{2} k_f x^2 \psi_0 = E \psi_0$$

The blue terms cancel, leaving

$$\frac{\hbar}{2} \left(\frac{k_f}{m} \right)^{1/2} \psi_0 = E \psi_0$$

It follows that ψ_0 is a solution to the Schrödinger equation for the harmonic oscillator with energy $E = \frac{1}{2} \hbar (k_f/m)^{1/2}$, in accord with eqn 7E.5 for the zero-point energy.

Self-test 7E.1 Confirm that the wavefunction in eqn 7E.9 is a solution of eqn 7E.2 and evaluate its energy.

Answer: Yes, with $E_1 = \frac{3}{2} \hbar \omega$

The shapes of several of the wavefunctions are shown in Fig. 7E.6 and the corresponding probability densities are shown in Fig. 7E.7. These probability densities show that, as the quantum number increases, the positions of highest probability migrate towards the classical turning points (see *The chemist's toolkit* 18). This behaviour is another example of the correspondence principle (Topic 7D) in which at high quantum numbers the classical behaviour emerges from the quantum behaviour.

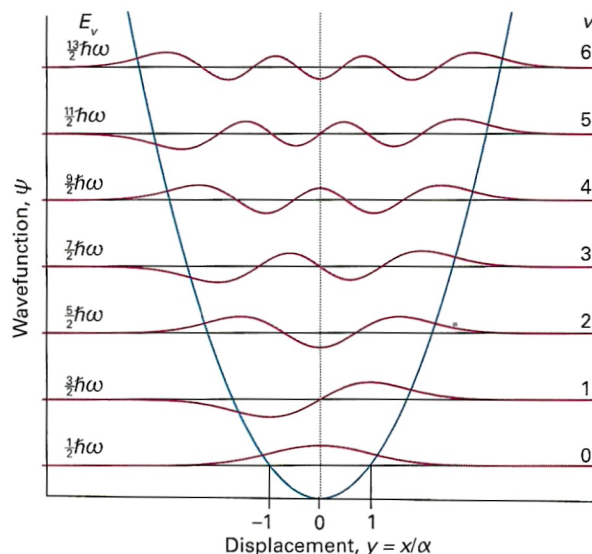


Figure 7E.6 The normalized wavefunctions for the first seven states of a harmonic oscillator. Note that the number of nodes is equal to v . The wavefunctions with even v are symmetric about $y = 0$, and those with odd v are anti-symmetric. The wavefunctions are shown superimposed on the potential energy function, and the horizontal axis for each wavefunction is set at the corresponding energy.

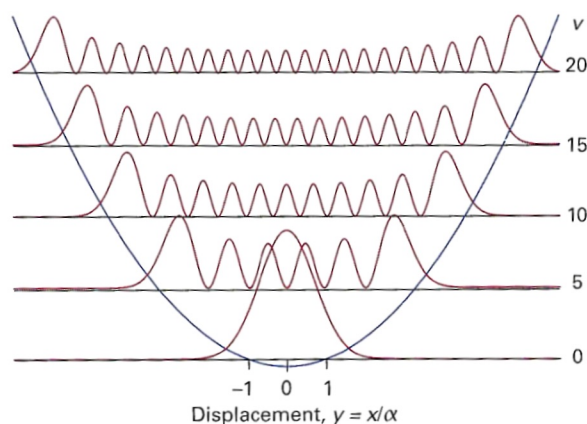


Figure 7E.7 The probability densities for the states of a harmonic oscillator with $\nu = 0, 5, 10, 15$, and 20 . Note how the regions of highest probability density move towards the turning points of the classical motion as ν increases.

The wavefunctions have the following features:

- The Gaussian function decays quickly to zero as the displacement in either direction increases, so all the wavefunctions approach zero at large displacements: the particle is unlikely to be found at large displacements.
- The wavefunction oscillates between the classical turning points but decays without oscillating outside them.
- The exponent y^2 is proportional to $x^2 \times (mk_f)^{1/2}$, so the wavefunctions decay more rapidly for large masses and strong restoring forces (stiff springs).
- As ν increases, the Hermite polynomials become larger at large displacements (as x^ν), so the wavefunctions grow large before the Gaussian function damps them down to zero: as a result, the wavefunctions spread over a wider range as ν increases (Fig. 7E.6).

Physical interpretation

Example 7E.2 Normalizing a harmonic oscillator wavefunction

Find the normalization constant for the harmonic oscillator wavefunctions.

Collect your thoughts A wavefunction is normalized (to 1) by evaluating the integral of $|\psi|^2$ over all space and then finding the normalization factor from eqn 7B.3 ($N = 1/(\int \psi^* \psi d\tau)^{1/2}$). The normalized wavefunction is then equal to $N\psi$. In this one-dimensional problem, the volume element is dx and the integration is from $-\infty$ to $+\infty$. The wavefunctions are expressed in terms of the dimensionless variable $y = x/\alpha$, so begin by expressing the integral in terms of y by using $dx = \alpha dy$. The integrals required are given in Table 7E.1.

The solution The unnormalized wavefunction is

$$\psi_\nu(x) = H_\nu(y) e^{-y^2/2}$$

It follows from the integrals given in Table 7E.1 that

$$\int_{-\infty}^{\infty} \psi_\nu^* \psi_\nu dx = \alpha \int_{-\infty}^{\infty} \psi_\nu^* \psi_\nu dy = \alpha \int_{-\infty}^{\infty} H_\nu^2(y) e^{-y^2} dy = \alpha \pi^{1/2} 2^\nu \nu!$$

where $\nu! = \nu(\nu-1)(\nu-2) \dots 1$ and $0! \equiv 1$. Therefore,

$$N_\nu = \left(\frac{1}{\alpha \pi^{1/2} 2^\nu \nu!} \right)^{1/2} \quad \text{Normalization constant} \quad (7E.10)$$

Note that N_ν is different for each value of ν .

Self-test 7E.2 Confirm, by explicit evaluation of the integral, that ψ_0 and ψ_1 are orthogonal.

Answer: Show that $\int_{-\infty}^{\infty} \psi_0^* \psi_1 dx = 0$ by using the information in Table 7E.1.

7E.2 Properties of the harmonic oscillator

The average value of a property is calculated by evaluating the expectation value of the corresponding operator (eqn 7C.11, $\langle \Omega \rangle = \int \psi^* \hat{\Omega} \psi d\tau$ for a normalized wavefunction). For a harmonic oscillator,

$$\langle \Omega \rangle_\nu = \int_{-\infty}^{\infty} \psi_\nu^* \hat{\Omega} \psi_\nu dx \quad (7E.11)$$

When the explicit wavefunctions are substituted, the integrals might look fearsome, but the Hermite polynomials have many features that simplify the calculation.