Quantum theory: techniques and applications

There exist three basic modes of motion: translation, vibration, and rotation. All three play an important role in chemistry because they are ways in which molecules can store energy. For example, gas molecules undergo translational motion, and their kinetic energy contributes to the total internal energy of a sample. Molecules can also store energy as rotational kinetic energy, and transitions between their rotational energy levels are responsible for rotational spectra. Molecules can also store energy in their vibrations, and transitions between their vibrational energy levels give rise to vibrational spectra.

We will see how the concepts of quantum mechanics can be developed into a powerful set of techniques for dealing with the three types of motion. Later, we shall also see how these calculations can be applied to account for atomic structure and atomic spectra, molecular structure, and spectroscopy.

Translational motion

The Schrödinger equation for free motion \((V = 0)\) is

\[
\frac{-\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = E \psi
\]

and the general solutions are the following:

\[
\psi = Ae^{ikx} + Be^{-ikx}
\]
Indeed, \(\frac{d\psi}{dx} = Aie^{ikx} - Bie^{-ikx}\)

\[
\frac{d^2\psi}{dx^2} = -Ak^2 e^{ikx} - Bk^2 e^{-ikx} = -k^2 \psi
\]

\[-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = \frac{\hbar^2 k^2}{2m} \psi, E = \frac{k^2 \hbar^2}{2m}\]

In this case, all values of \(k\), and therefore all values of the energy \(E\), are permitted – the energy of a free particle is not quantized. For \(B = 0\) the wavefunction describes a particle with linear momentum \(p = k\hbar\) towards positive \(x\). For \(A = 0\) the wavefunction describes a particle with the same momentum traveling towards negative \(x\). In either state the position of the particle is completely uncertain because the momentum is completely certain.

**The particle in a box**

Let us consider the problem of a particle in a box, in which a particle of a mass \(m\) is confined between two walls at \(x = 0\) and \(x = L\). In the infinite square well, the potential energy of the particle is zero inside the box but rises abruptly to infinity at the walls. This is an idealization of a gas molecule moving in a one-dimensional container.
The Schrödinger equation for the region between the walls (where $V = 0$) is
\[
-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi
\]
It is convenient to write the solution as
\[
\psi = A \sin kx + B \cos kx
\]
We can do that because $e^{i\theta} = \cos \theta + i \sin \theta$
and $e^{-i\theta} = \cos \theta - i \sin \theta$
Therefore, $\cos \theta = \frac{1}{2} e^{i\theta} + \frac{1}{2} e^{-i\theta}$
And $\sin \theta = \frac{1}{2i} e^{i\theta} - \frac{1}{2i} e^{-i\theta}$
Let’s suppose that on the walls the potential $V$ but not infinite and we will allow $V$ to become infinite later.
\[
-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi,
\]
\[
\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2} (V - E)\psi
\]
Suppose that $\psi > 0$ just within the material of the walls. Then since the right-hand side of the above equation is positive (because $V$ is very large), the curvature of $\psi$ is positive. Therefore, $\psi$ curls off rapidly towards infinite values within the walls. This makes this wavefunction unacceptable. If $\psi < 0$ just inside the material of the wall, the second derivative is negative, and so $\psi$ falls very rapidly to negatively infinite values, which also makes it unacceptable. When $V$ is actually infinite, the only acceptable wavefunctions are those with $\psi = 0$ inside the material of the walls.

Since the wavefunction must be continuous everywhere, it follows that $\psi$ must be zero at the walls themselves (at $x = 0$ and $x = L$). This is called **boundary conditions** on the wavefunction: $\psi = 0$ at $x = 0$ and $x = L$.

**The acceptable solutions**

Now we know that the wavefunction has the general form

$$\psi(x) = A \sin kx + B \cos kx$$

but with the additional requirement that it must satisfy the two boundary conditions.

Consider the wall at $x = 0$. Since $\psi(0) = B$, $B$ should be equal zero.

$$\psi = A \sin kx$$

The amplitude at the other wall (at $x = L$) is $\psi = A \sin kL$ and also must be zero. Therefore, $kL$ must be chosen so that $\sin kL = 0$, which is satisfied by

$$kL = n \pi \\
\ \ \ \ \ n = 1, 2, ...$$
\( n = 0 \) is ruled out because it implies \( k = 0 \) and \( \psi = 0 \) everywhere, which is unacceptable, and negative values of \( n \) merely change the sign of \( \sin n\pi \).

Now we can calculate the energy of the particle:

\[
E = \frac{n^2 \hbar^2 \pi^2}{2mL^2} = \frac{n^2 \hbar^2}{8mL^2} \quad n = 1, 2, \ldots
\]

The energy of the particle is quantized and the quantization arises from the boundary conditions.

**Normalization**

\[
1 = \int_{-\infty}^{\infty} \psi^* \psi \, dx = A^2 \int_{0}^{L} \sin^2 kx \, dx = \frac{1}{2} A^2 L \quad A = \left( \frac{2}{L} \right)^{1/2}
\]

(We used here \( \int \sin^2 ax \, dx = \frac{1}{2} x - \frac{1}{4a} \sin 2ax + \text{constant} \))

The complete solution of the problem is:

**Energies:** \( E_n = \frac{n^2 \hbar^2 \pi^2}{2mL^2} = \frac{n^2 \hbar^2}{8mL^2} \quad n = 1, 2, \ldots \)

**Wavefunctions:** \( \psi_n = \left( \frac{2}{L} \right)^{1/2} \sin \frac{n\pi x}{L} \)
We label the energies and wavefunctions with the quantum number $n$. A quantum number is an integer (sometimes a half-integer) that labels the state of the system. For a particle in a box there are an infinite number of acceptable solutions and $n$ specifies one of them. A quantum number is used to calculate the energy corresponding to that state and to write down the wavefunction explicitly.

It is easy to see the origin of the quantization: each wavefunction is a standing wave and, in order to fit into the cavity, successive functions must possess one more half-wavelength. Shortening the wavelength in order to fit another half-wavelength into the container implies sharpening the curvature of the wavefunction, and therefore increasing the kinetic energy of the particles it describes.

Let’s derive the energy levels of a particle in the box from the de Broglie relation. Successive wavefunctions possess one more half-length:

$$L = n \times \frac{1}{2} \lambda, \quad \lambda = \frac{2L}{n}, \quad p = \frac{h}{\lambda} = \frac{nh}{2L}$$

$$E = \frac{p^2}{2m} = \frac{n^2 h^2}{8mL^2} \quad n = 1, 2, ...$$
The linear momentum of a particle in a box is not well defined because the wavefunction sin $kx$ is a standing wave and not an eigenfunction of the linear momentum operator. However, each wavefunction is a superposition of momentum eigenfunctions:

$$\sin kx = (e^{ikx} - e^{-ikx})/2i$$

So, measurement of the linear momentum would give the value $k\hbar = nh/2L$ half the time and $-k\hbar = -nh/2L$ the other half. This is the quantum mechanical version of the classical picture that a particle in a box rattles from wall to wall, and travels to the right for half the time and to the left for the other half.

Because $n$ cannot be zero, the lowest energy that the particle may possess is not zero (as would be allowed by classical mechanics) but: $E_1 = \hbar^2/8mL^2$. This is the lowest irremovable energy, which is called **zero-point energy**. The physical origin of the zero-point energy can be explained in two ways. First, the uncertainty principle requires a particle to possess kinetic energy if it is confined to a finite region. This is because the particle’s location is not completely indefinite, and so its momentum cannot be precisely zero. Second, if the wavefunction has to be zero at the walls, but smooth, continuous, and not zero everywhere, then it must be curved, and curvature in a wavefunction implies the possession of kinetic energy.

The separation between adjacent energy levels:

$$\Delta E = E_{n+1} - E_n = (2n+1)\frac{\hbar^2}{8mL^2}$$
This separation decreases as the length of the container increases and is extremely small when the contained is large; $\Delta E$ becomes zero when the walls are infinitely far apart. Atoms and molecules free to move in laboratory-sized vessels may therefore be treated as though their translational energy is not quantized.

The distribution of the particle in a box is not uniform: the probability density at $x$ is:

$$\psi^2 = \frac{2}{L} \sin^2 \frac{n \pi x}{L}$$

The nonuniformity is pronounced when $n$ is small but $\psi^2$ becomes more uniform as $n$ increases. The distribution at high quantum numbers reflects the classical result that a particle bouncing between the walls spends, on the average, equal times at all points. That the quantum result corresponds to the classical prediction at high quantum numbers is an aspect of the **correspondence principle**, which states that classical mechanics emerges from quantum mechanics as high quantum numbers are reached.

**Example 1. Using the particle in a box solutions**

The wavefunctions of an electron in a conjugated polyene (a molecule with alternating single and double bonds) can be approximated by particle-in-a-box wavefunctions. What is the probability $P$, of locating the electron between $x = 0$ (the left-hand end of a molecule) and $x = 0.2$ nm in its lowest energy state in a conjugated molecule of length 1.0 nm?

$$P = \int_0^l \psi_n^2 dx = \frac{2}{L} \int_0^l \sin^2 \frac{n \pi x}{L} dx = \frac{l}{L} - \frac{1}{2n \pi} \sin \frac{2 \pi n l}{L}$$

For $n = 1$ and $l = 0.2$ nm, we get $P = 0.05$. 

$\psi$
Orthogonality and the bracket notation
Two wavefunctions are orthogonal if the integral of their product vanishes:

\[ \int \psi_n^* \psi_n \, d\tau = 0 \]

A general feature of quantum mechanics – *wavefunctions corresponding to different energies are orthogonal*. We can therefore be confident that all wavefunctions of a particle in a box are mutually orthogonal.

For \( n = 1 \) and \( n = 3 \):

\[ \int_0^L \psi_1^* \psi_3 \, dx = \frac{2}{L} \int_0^L \sin \frac{\pi x}{L} \sin \frac{3\pi x}{L} \, dx = 0 \]

(we use \( \int \sin ax \sin bx \, dx = \frac{\sin (a-b)x}{2(a-b)} - \frac{\sin (a+b)x}{2(a+b)} + \text{const} \))

The integral is often written as

\[ \langle n | n' \rangle = 0 \quad (n' \neq n) \]

**Dirac bracket notation:**
- **bra** \( \langle n | \) corresponds to \( \psi_n^* \)
- **ket** \( \langle n'| \) corresponds to \( \psi_{n'} \)

Integration over all space is understood

\[ \langle n | n \rangle = 1 \quad \langle n | n' \rangle = \delta_{nn'} \quad \delta_{nn'} - \text{Kronecker delta} \]

Orthogonality plays a central role in the theory of chemical bonding and spectroscopy. Sets of functions that are normalized and mutually orthogonal are called **orthonormal**.
Motion in two dimensions

Let’s consider now the two-dimensional analogue of the particle in a box. The particle is confined to a rectangular surface of length $L_1$ in the $x$-direction and $L_2$ in the $y$-direction and the potential is zero everywhere except at the walls, where it is infinite. The Schrödinger equation is

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} \right) = E \psi$$

and $\psi$ is a function of both $x$ and $y$: $\psi = \psi(x, y)$.

Separation of variables: $\psi(x, y) = X(x)Y(y)$

$$\frac{\partial^2 \psi}{\partial x^2} = Y \frac{d^2 X}{dx^2} \quad \frac{\partial^2 \psi}{\partial y^2} = X \frac{d^2 Y}{dy^2}$$

$$-\frac{\hbar^2}{2m} \left( \frac{d^2 X}{dx^2} + \frac{d^2 Y}{dy^2} \right) = E X Y$$

Let $X'' = d^2X/dx^2$, $Y'' = d^2Y/dy^2$ and divide by $X Y$: 

$$-\frac{\hbar^2}{2m} \left( \frac{X''}{X} + \frac{Y''}{Y} \right) = E$$

Since $X''/X$ is independent of $y$, if $y$ is varied only the term $Y''/Y$ can change. But the sum of these two terms is a constant; therefore, even the $Y''/Y$ term cannot change. In other words, $Y''/Y$ is a constant, which we denote $E_Y$. Similarly, $X''/X$ is a constant, $E_X$. 

10
\[- \frac{\hbar^2 X''}{2mX} = E^X, \text{ or } - \frac{\hbar^2 \frac{d^2X}{dx^2}}{2m} = E^X X \]
\[- \frac{\hbar^2 Y''}{2mY} = E^Y, \text{ or } - \frac{\hbar^2 \frac{d^2Y}{dy^2}}{2m} = E^Y Y \]

We obtained two one-dimensional particle-in-a-box Schrödinger equations.

\[X_n^1 = \left( \frac{2}{L_1} \right)^{1/2} \sin \frac{n_1 \pi x}{L_1} \quad Y_n^2 = \left( \frac{2}{L_2} \right)^{1/2} \sin \frac{n_2 \pi y}{L_2} \]

Since \( \psi = XY \) and \( E = E^x + E^y \), we obtain

\[\psi_{n_1,n_2} = \left( \frac{4}{L_1 L_2} \right)^{1/2} \sin \frac{n_1 \pi x}{L_1} \sin \frac{n_2 \pi y}{L_2} \]
\[E_{n_1,n_2} = \left\{ \left( \frac{n_1}{L_1} \right)^2 + \left( \frac{n_2}{L_2} \right)^2 \right\} \frac{\hbar^2}{8m} \]

The quantum numbers take the values \( n_1 = 1, 2, \ldots \) and \( n_2 = 1, 2, \ldots \) independently.
The particle in an actual three-dimensional box can be treated in the same way. The wavefunctions have another, $z$-dependence factor, and the energy has an additional term, $n_3^2/L_3^2$.

![Wavefunction Diagrams](image)

**Degeneracy**

An interesting feature of the solutions is obtained when the plane box has a square shape, $L_1 = L$ and $L_2 = L$. Then

$$\psi_{n_1,n_2} = \frac{2}{L} \sin \frac{n_1 \pi x}{L} \sin \frac{n_2 \pi y}{L} \quad E_{n_1,n_2} = (n_1^2 + n_2^2) \frac{\hbar^2}{8mL^2}$$

Consider the cases $n_1 = 1, n_2 = 2$, and $n_1 = 2, n_2 = 1$:

$$\psi_{1,2} = \frac{2}{L} \sin \frac{\pi x}{L} \sin \frac{2\pi y}{L}, \quad E_{1,2} = \frac{5\hbar^2}{8mL^2} \quad \psi_{2,1} = \frac{2}{L} \sin \frac{2\pi x}{L} \sin \frac{\pi y}{L}, \quad E_{2,1} = \frac{5\hbar^2}{8mL^2}$$
Thus, different wavefunctions correspond to the same energy, the condition called **degeneracy**. In this case, in which there are two degenerate wavefunctions, we say that the level with energy $\frac{5\hbar^2}{8mL^2}$ is doubly degenerate.

The occurrence of degeneracy is related to the symmetry of the system. The examples of degeneracy are numerous in atomic and molecular spectroscopy, and all of them can be traced to the symmetry properties of the system.

**Tunneling**

If the potential energy of the particle does not rise to infinity when it is in the walls of the container, the wavefunction does not decay abruptly to zero. If the walls are thin (so the potential energy falls to zero again after a finite distance), the exponential decay of the wavefunction stops, and it begins to oscillate again like the wavefunction inside the box. Hence the particle might be found on the outside the container even though according to classical mechanics it has insufficient energy to escape. Such leakage through classically forbidden zones is called **tunneling**.

**The decay of wavefunctions within barriers**

Inside a barrier (a region where $V > 0$), the Schrödinger equation is

$$\frac{d^2\psi}{dx^2} = \frac{2m(V - E)\psi}{\hbar^2}$$
The general solutions are $\psi = Ae^{kx} + Be^{-kx}$

$$k = \left\{ \frac{2m(V-E)}{\hbar^2} \right\}^{1/2}$$

Note that the exponentials are now real functions because $V > E$. If $V$ never fell back to zero, the first term would increase without limit as $x$ increased, and in due course would approach infinity. The only way to ensure that the wavefunction does not become infinite is to set $A = 0$. Therefore, inside a long barrier the wavefunction is $\psi = Be^{-kx}$ which decays exponentially towards zero as $x$ increases.

Since the wavefunction decreases exponentially inside the wall with the rate depending on $m^{1/2}$, particle of low mass are more able to tunnel through barriers than heavy ones. Tunneling is very important for electrons, and moderately important for protons; for heavier particles it is less important. A number of effects in chemistry (the isotope-dependence of some reaction rates – kinetic isotope effect) depend on the ability of the proton to tunnel more readily than the deuteron.

**Penetration probabilities**

If a particle (an electron or a proton) is fired at a barrier, its potential energy increases sharply from zero to a finite value $V$ when it enters the barrier, remains at that value for a distance $L$, and then falls to zero again. This is a model of what happens when particles are fired at an idealized metal foil of sheet of paper. What is the proportion of incident particles that penetrate the barrier when their kinetic energy is less than $V$, when classically none can penetrate?
(1) Write down the Schrödinger equation for each zone of constant potential.
(2) Write down the general solution for each zone.
(3) Find the coefficients by ensuring that (a) the wavefunction is continuous at each zone boundary, and (b) the first derivatives of the wavefunctions are also continuous at each zone boundary.

Let’s take the particle to attack the barrier from the left. There are no further barriers to the right to reflect back particles. And so no particles have momentum to the left in that zone.

Zone A: \( \psi_A = A e^{ikx} + A' e^{-ikx} \)
\[
k = \left( \frac{2mE}{\hbar^2} \right)
\]

Zone B: \( \psi_B = B e^{\kappa x} + B' e^{-\kappa x} \)
\[
\kappa = \left( \frac{2m(V - E)}{\hbar^2} \right)
\]

Zone C: \( \psi_C = C e^{ikx} + C' e^{-ikx} \)
\[
k = \left( \frac{2mE}{\hbar^2} \right)
\]

Since there are no particles articles with negative momentum in zone C, \( C' = 0 \). The probability of penetration is proportional to \( |C|^2 \), the probability of penetration relative to the incident probability, which is proportional to \( |A|^2 \), is \( P = \frac{|C|^2}{|A|^2} \)

\[
P = \frac{|C|^2}{|A|^2}
\]
The boundary conditions are the continuity of the wavefunction and its derivative at the zone boundaries:

\[ \psi_A(0) = \psi_B(0) \quad \psi_B(L) = \psi_C(L) \]
\[ \psi_A'(0) = \psi_B'(0) \quad \psi_B'(L) = \psi_C'(L) \]

\[ A + A' = B + B' \quad Be^{\kappa L} + B' e^{-\kappa L} = Ce^{ikL} \]
\[ ikA - ikA' = \kappa B - \kappa B' \quad \kappa Be^{\kappa L} - \kappa B' e^{-\kappa L} = ikCe^{ikL} \]

The probability of penetration of the barrier is:

\[ P = \frac{1}{1 + G} \quad G = \frac{\left(e^{L/D} - e^{-L/D}\right)}{16\varepsilon(1 - \varepsilon)} \]

\[ D = \left\{ \frac{\hbar^2}{2m(V - E)} \right\}^{1/2} \]
\[ \varepsilon = \frac{E}{V} \]

When the barrier is high and long \((L/D >> 1)\), the first exponential dominates the second, and since then \(G >> 1\),
\[ P \sim 1/G, \quad P = 4\varepsilon(1 - \varepsilon)e^{-2L/D} \]

\( P \) depends exponentially on the square-root of the mass and on the barrier length.
A related problem: a particle in a square well potential of finite depth. In this kind of potential, the wavefunction penetrates into the walls, where it decays exponentially towards zero, and oscillates within the well. The wavefunctions are found by ensuring (as in the discussion of tunneling) that they and their slopes are continuous at the edges of the potential. There is only a finite number of bound states, states with \( E < V \). Regardless of the depth and length of the well, there is always at least one bound state. In general, the number of levels is equal to \( N \):

\[
N - 1 < \left( \frac{8mVL}{\hbar} \right)^{1/2} < N
\]

\( V \) – the depth, \( L \) – the length of the well. The deeper and wider the well, the greater the number of bound states. As the depth becomes infinite, the number of bound states becomes infinite.
**Vibrational motion**

A particle undergoes harmonic motion if it experiences a restoring force that is proportional to its displacement: \( \mathbf{F} = -k \mathbf{x} \) is the force constant.

A force of this form corresponds to a potential energy \( V = \frac{1}{2} k \mathbf{x}^2 \)

The Schrödinger equation for the particle is:

\[
\frac{-\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + \frac{1}{2} k \mathbf{x}^2 \psi = E \psi
\]

If we introduce the following dimensionless quantities, \( y = \frac{x}{\alpha} \),

\[
\epsilon = \frac{E}{(1/2)\hbar \omega}, \quad \alpha = \left( \frac{\hbar^2}{mk} \right)^{1/4}, \quad \omega = \left( \frac{k}{m} \right)^{1/2}
\]

the appearance of this equation is simplified:

\[
\frac{d^2 \psi}{dy^2} + (\epsilon - y^2) \psi = 0
\]
The exact wavefunction has the form $\psi = fe^{-y^2/2}$, where $f$ is a function that does not increase more rapidly than $e^{-y^2/2}$ decays: then $fe^{-y^2/2}$ remains acceptable at large displacements. $f'' - 2yf' + (\varepsilon - 1)f = 0$ \hspace{1cm} \textbf{Hermite’s equation}

This differential equation has been thoroughly studied by mathematicians, and its solutions are known. Acceptable solutions of Hermite’s equation (those not going to infinity more quickly than the factor $e^{-y^2/2}$ falls to zero, so that the product is never infinite) exist only for $\varepsilon$ equal to a positive odd integer: $\varepsilon = 2\nu + 1$, with $\nu = 1, 2, ...$

$$E_\nu = (2\nu + 1) \times \frac{1}{2} \hbar \omega$$

The shapes of the wavefunction can be obtained from the solutions of Hermite’s equation. The solutions for $\nu$ as a positive integer are the Hermite polynomials $H_\nu$, which are polynomials generated by differentiating $e^{-y^2/2}$ $\nu$ times: $H_\nu(y) = (-1)^\nu e^{y^2} \left( \frac{d}{dy} \right)^\nu e^{-y^2}$

\textbf{The energy levels}

The permitted energy levels of a harmonic oscillator are

$$E_\nu = (\nu + \frac{1}{2}) \hbar \omega \hspace{1cm} \nu = 1, 2, ... \hspace{1cm} \omega = \left( \frac{k}{m} \right)^{1/2}$$
The separation between adjacent levels is \( \Delta E = E_{\nu+1} - E_{\nu} = \hbar \omega \)

which is the same for all \( \nu \). Therefore, the energy levels form a uniform ladder of spacing \( \hbar \omega \). The energy separation \( \hbar \omega \) is negligibly small for microscopic objects, but is of great importance for objects with mass similar to that of atoms. For instance, the force constant of a typical chemical bond is around 500 \( N \text{ m}^{-1} \), and since the mass of a proton is 1.7x10\(^{-27} \) kg, the frequency is 5x10\(^{14} \) s\(^{-1} \) and the separation of adjacent levels is 6x10\(^{-20} \) J, which corresponds to 30 \( kJ \text{ mol}^{-1} \) – chemically significant.

\[
\Delta E = 6 \times 10^{-20} \text{ J (0.4 eV)} \nu = \Delta E / \hbar = 9 \times 10^{13} \text{ Hz} \lambda = c / \nu \sim 3000 \text{ nm} = 3333 \text{ cm}^{-1}
\]

Therefore, transitions between the vibrational energy levels of molecules require **infrared radiation**.

Since the smallest value of \( \nu \) is zero, an oscillator has a zero-point energy \( E_0 = \frac{1}{2} \hbar \omega \)

For the typical molecular oscillator, the zero-point energy is \( \sim 3 \times 10^{-20} \) J or 0.2 eV, or 15 \( kJ \text{ mol}^{-1} \). The mathematical reason of zero-point energy is that \( \nu \) cannot take the value \(-1/2\), for if it did the wavefunction would be ill-behaved. The physical reason is the same as for the particle in a square well: the particle is confined, its position is not completely uncertain, and therefore its momentum, and hence its kinetic energy, cannot be exactly zero. We can picture this zero-point state as one in which the particle fluctuates continually around its equilibrium position; the classical mechanics would allow the particle to be perfectly still.
Quantum chemistry: *Ab initio* (from the first principles of quantum mechanics) calculations of infrared molecular spectra – the Schrödinger equation is solved for electrons moving in the electric field created by nuclei and themselves at certain positions of atoms. This gives a potential energy surface for the motion of nuclei. Near the equilibrium position, the harmonic approximation is applied:

\[ V = \frac{1}{2} k x^2 \quad \quad k = \frac{d^2 V}{dx^2} \quad \quad \omega = \left( \frac{k}{m} \right)^{1/2} \]

This procedure gives vibrational frequencies of a molecule and describes its IR spectra.

The wavefunctions

\[ \psi = f e^{-y^2/2} f(y) = H_v(y) = (-1)^v e^{y^2} \left( \frac{d}{dy} \right)^v e^{-y^2} \]

The Hermite polynomials:

\[ v = 0 \quad H_0(y) = 1 \]
\[ v = 1 \quad H_1(y) = 2y \]
\[ v = 2 \quad H_2(y) = 4y^2 - 2 \]
\[ v = 3 \quad H_3(y) = 8y^3 - 12y \]
\[ v = 4 \quad H_4(y) = 16y^4 - 48y^2 + 12 \]
\[ v = 5 \quad H_5(y) = 32y^5 - 160y^3 + 120y \]
\[ v = 6 \quad H_6(y) = 64y^6 - 480y^4 + 720y^2 - 120 \]
Example. Show that the wavefunction $e^{-\beta x^2}$ satisfies the Schrödinger equation for the quantum harmonic oscillator. What conditions does this place on $\beta$? What is $E$?

\[
-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + \frac{1}{2} kx^2 \psi = E \psi
\]

\[
-\frac{\hbar^2}{2m} \frac{d^2 (e^{-\beta x^2})}{dx^2} + \frac{1}{2} kx^2 (e^{-\beta x^2}) = -\frac{\hbar^2}{2m} \frac{d(-2\beta xe^{-\beta x^2})}{dx} + \frac{1}{2} kx^2 (e^{-\beta x^2})
\]

\[
= -\frac{\hbar^2}{2m} (-2\beta e^{-\beta x^2}) + \frac{\hbar^2}{2m} (-4\beta^2 x^2 e^{-\beta x^2}) + \frac{1}{2} kx^2 (e^{-\beta x^2})
\]

The function is an eigenfunction only if the last two terms cancel:

\[
\hat{H} e^{-\beta x^2} = \frac{\hbar^2 \beta}{m} e^{-\beta x^2} \text{ if } \frac{\hbar^2}{2m} (-4\beta^2 x^2 e^{-\beta x^2}) = -\frac{1}{2} kx^2 (e^{-\beta x^2})
\]

\[
E = \frac{\hbar^2 \beta}{m} = \frac{\hbar^2}{m} \sqrt{\frac{1}{4 \frac{\hbar^2}{2 \sqrt{m}}} = \frac{\hbar}{\sqrt{\frac{1}{2 \sqrt{m}}} = \frac{\hbar}{2 \omega}
\]

We can expect the wavefunctions of a harmonic oscillator to resemble the particle in a box wavefunctions, but with two differences. First, their amplitudes fall towards zero more slowly at large displacements, because the potential energy climbs towards zero only as $x^2$ and not abruptly. Second, as the kinetic energy of the particle depends on the displacement in a more complex way, the curvature of the wavefunction also varies in a more complex way.
\[ \psi_\nu = N_\nu H_\nu e^{-\nu^2/2} \]

\( H_\nu \) is a Hermite polynomial, \( N_\nu \) is a normalization factor.

\[ \psi_0 = N_0 e^{-y^2/2} \quad \psi_0^2 = N_0^2 e^{-y^2} \]

The probability density for \( \nu = 0 \) is the bell-shaped **gaussian function** with its maximum amplitude at zero displacement, and so it captures the classical picture of the zero-point motion as arising from the fluctuation of the particle about its equilibrium position.

Normalization factor: \( N_\nu = \left( \frac{1}{\alpha \pi^{1/2} 2^\nu \nu!} \right)^{1/2} \)
The properties of the oscillator

Once we know the wavefunctions, we can calculate the properties of the harmonic oscillator. We can calculate the expectation values of an observable $\Omega$ by evaluating integrals of the type

$$\Omega = \int \psi^* \hat{\Omega} \psi \, dx$$

Let’s for example calculate the mean displacement $\langle x \rangle$ and the mean square displacement $\langle x^2 \rangle$. The operator for position along $x$ is multiplication by the value of $x$.

$$\langle x \rangle = \int \psi_v^2 x \, dx = N_v^2 \int_{-\infty}^{\infty} \left( H_v e^{-y^2/2} \right)^2 \, dx = \alpha^2 N_v^2 \int_{-\infty}^{\infty} H_v y H_v e^{-y^2} \, dy$$

For Hermite’s polynomials, $H_{v+1} = 2yH_v - 2vH_{v-1}$ - recursion relation. Therefore, $yH_v = vH_{v-1} + (1/2)H_{v+1}$. Then

$$\int_{-\infty}^{\infty} H_v y H_v e^{-y^2} \, dy = v \int_{-\infty}^{\infty} H_v H_{v-1} e^{-y^2} \, dy + \frac{1}{2} \int_{-\infty}^{\infty} H_v H_{v+1} e^{-y^2} \, dy$$

Since

$$\int_{-\infty}^{\infty} H_v H_v e^{-y^2} \, dy = \begin{cases} 0, & v' \neq v \\ \pi^{1/2} 2^v v! & v = v' \end{cases}$$

both integrals are zero and $\langle x \rangle = 0$. This result is in fact obvious from the probability densities: they are symmetrical about $x = 0$, and so displacements to the right are as probable as displacements to the left.
\[ \langle x^2 \rangle = \int \psi_v^2 x^2 dx = N_v^2 = \int (H_v e^{-y^2/2})^2 x^2 dx = \alpha^3 N_v^2 \int (H_v y)^2 e^{-y^2} dy \]

\[ \alpha = \left( \frac{\hbar^2}{mk} \right)^{1/4} \quad N_v = \left( \frac{1}{\alpha \pi^{1/2} 2^v v!} \right)^{1/2} \]

\[ (yH_v)^2 = \left( \nu H_{v-1} + \frac{1}{2} H_{v+1} \right)^2 = \nu^2 H_{v-1}^2 + \nu H_{v-1} H_{v+1} + (1/4) H_{v+1}^2 \]

\[ \int \nu^2 H_{v-1}^2 e^{-y^2} dy = \nu^2 \pi^{1/2} 2^{v-1} (v-1)! = \frac{\nu}{2} \pi^{1/2} 2^v v! \]

\[ \int \frac{1}{4} H_{v+1}^2 e^{-y^2} dy = \frac{1}{4} \pi^{1/2} 2^{v+1} (v+1)! = \frac{\nu+1}{2} \pi^{1/2} 2^v v! \]

Finally, \[ \langle x^2 \rangle = \left( \nu + \frac{1}{2} \right) \left( \frac{\hbar^2}{mk} \right)^{1/2} \]
We can now calculate the mean potential energy of the oscillator very simply:

\[
\langle V \rangle = \frac{1}{2} k \langle x^2 \rangle = \frac{1}{2} \left( \nu + \frac{1}{2} \right) \hbar \left( \frac{k}{m} \right)^{1/2} = \frac{1}{2} \left( \nu + \frac{1}{2} \right) \hbar \omega
\]

Since the total energy in the state \( \nu \) is \( \left( \nu + \frac{1}{2} \right) \hbar \omega \), \( \langle V \rangle = \frac{1}{2} E_v \).

Since the total energy is the sum of the potential and kinetic energies, the mean kinetic energy of the oscillator is the same: \( \langle E_K \rangle = \frac{1}{2} E_v \).

The result that the mean potential and kinetic energies are equal (and therefore both equal to half the total energy) is a special result of the **virial theorem**: If the potential energy of a particle has the form \( V = ax^b \), then its mean potential and kinetic energies are related by \( 2\langle E_K \rangle = b\langle V \rangle \).

In the case of a harmonic oscillator, \( b = 2 \), and so \( \langle E_K \rangle = \langle V \rangle \).

Let’s now calculate the probability that a harmonic oscillator will be found extended into a classically forbidden region (the probability of non-classical extensions). According to classical mechanics, the turning point \( x_{tp} \) of an oscillating particle occurs when its kinetic energy is zero, which is when its potential energy \( (1/2)kx^2 \) is equal to its total energy \( E \). This occurs when

\[
x_{tp} = \pm \left( \frac{2E}{k} \right)^{1/2}
\]
The probability of finding the particle beyond a displacement \( x_{tp} \) is the sum of probabilities \( \psi^2 dx \) of finding it in any of the intervals \( dx \) lying between \( x_{tp} \) and infinity:

\[
P = \int_{x_{tp}}^{\infty} \psi^2 dx
\]

Since \( x = \alpha y \), \( y_{tp} = x_{tp} / \alpha = (2\nu + 1)^{1/2} \)

For the ground state, \( y_{tp} = 1 \) and the probability is:

\[
P = \int_{x_{tp}}^{\infty} \psi_0^2 dx = \alpha N_0^2 \int_{y_{tp}}^{\infty} e^{-y^2} dy = \frac{1}{\pi^{1/2}} \int_{1}^{\infty} e^{-y^2} dy
\]

The integral is a special case of the so-called error function, \( \text{erf} z \):

\[
\text{erf}(z) = 1 - \frac{2}{\pi^{1/2}} \int_{-\infty}^{\infty} e^{-y^2} dy \quad \text{Here, } P = (1/2)(1 - \text{erf} 1) = (1/2)(1 - 0.843) = 0.079
\]

The example shows that the oscillator may be found in classically forbidden regions, and that when \( \nu = 0 \) there is about 8% chance of finding it with a classically forbidden extension. The probability of its being found with a non-classical extension decreases quickly with increasing \( \nu \), and vanishes entirely as \( \nu \) approaches infinity, as we would expect from the \textbf{correspondence principle}. Since macroscopic oscillators (such as pendulums) are in states with very high quantum numbers, the probability that they will be found at a classically forbidden displacement is wholly negligible. Molecules, however, are normally in their vibrational ground states, and for them the probability is very significant.
Harmonic oscillator summary

1) The energy is quantized with $E_\nu = (\nu + \frac{1}{2})\hbar \omega$ where $\nu$ is an integer from 0 upwards.

2) There is a zero-point energy $E_0 = \frac{1}{2} \hbar \omega$, which is a quantum phenomenon, $E_0$ would vanish in a world in which $\hbar$ were zero.

3) The oscillating particle penetrates into classically forbidden regions.

4) The distribution of the particle approaches the classically predicted distribution as the quantum number becomes large.

5) As the force constant increases, the zero-point energy and the level separations increase. In the opposite limit where the force constant decreases and the potential becomes shallower, one finally regains continuum.