

THE HARMONIC OSCILLATOR

Features

Example of a problem in which V depends on coordinates

Power series solution

Energy is quantized because of the boundary conditions

Model for vibrational motion of a diatomic molecule

To solve the Schrödinger Eq. for molecules, make the *Born-Oppenheimer Approximation*:

Since the electrons are moving much faster than the nuclei, assume that the motions are separable & that the wavefunction can be written as a product of nuclear & electronic wavefunctions

$$\Psi = \Psi_{\text{elec}} \Psi_{\text{nucl}}$$

This leads to two separate Eq. to solve--

one for electronic energy (assuming fixed nuclei)

one for nuclear energy (in the effective potential field of the electrons)

Assume that the nuclear energy can be divided up into contributions from

translation, rotation, vibration

Or,

$$\Psi_{\text{nucl}} = \Psi_{\text{trans}} \Psi_{\text{rot}} \Psi_{\text{vib}}$$

with $E_{\text{nucl}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}}$

$$E_{\text{total}} = E_{\text{nucl}} + E_{\text{elec}}$$

We will see later that the vibrational part of the Schrödinger Eq. for a diatomic molecule is similar to the Eq. for the harmonic oscillator.

The One-Dimensional Harmonic Oscillator:

Classical Treatment:

A single particle of mass m is attracted to the origin by a linear (i.e. first power of x) restoring force F_x

$$F_x = -k x, \quad k = \text{force constant}$$

Since $F = m a$ $a = \text{acceleration}$

then $-k x = m a = m (d^2x/dt^2)$

or $(d^2x/dt^2) + (k/m) x = 0$

This is a 2nd order linear differential eq. with constant coefficients $p = 0$, $q = k/m$

Then $s = \pm i\sqrt{q}$

and $x(t) = c_1 e^{it\sqrt{(k/m)}} + c_2 e^{-it\sqrt{(k/m)}}$

$$= (c_1 + c_2) \cos (t \sqrt{(k/m)}) + i (c_1 - c_2) \sin (t \sqrt{(k/m)})$$

$$x(t) = A \cos (t \sqrt{(k/m)}) + B \sin (t \sqrt{(k/m)})$$

$$= A' \sin (t \sqrt{k/m} + b)$$

$$= A' \sin (t 2 \pi \nu + b), \quad \text{SQRT}(k/m) = 2 \pi \nu$$

NOTE: $A = A' \sin b$; $B = B' \cos b$

$$\sin(x+y) = \sin x \cos y + \cos x \sin y$$

$$\text{So } A' \sin (t \sqrt{k/m} + b)$$

$$= A' \{ \sin (t \sqrt{k/m}) \cos b + \cos (t \sqrt{k/m}) \sin b \}$$

$$= (A' \cos b) \sin (t \sqrt{k/m}) + (A' \sin b) \cos (t \sqrt{k/m})$$

$$= B \sin (t \sqrt{k/m}) + A \cos (t \sqrt{k/m})$$

Since force by definition is the negative first derivative of the potential energy, one can derive an expression for V:

$$F_x = -dV/dx = -k x$$

Integrating both sides gives

$$V(x) = (k/2) x^2 + C \quad \text{parabolic function}$$

Choosing $C = 0$, sets the minimum of V at $x=0$

$$\text{Kinetic energy: } T = (m/2) v^2, \quad v = \text{velocity} = dx/dt$$

$$T = (m/2) (dx/dt)^2$$

$$\text{If } x(t) = A \sin (t 2\pi\nu + b),$$

then $dx/dt = A 2\pi\nu \cos (t 2\pi\nu + b),$

and $T = (m/2) A^2 (2\pi\nu)^2 \cos^2 (t 2\pi\nu + b)$
 $= (k/2) A^2 \cos^2 (t 2\pi\nu + b)$

Also $V = (k/2) x^2$
 $= (k/2) A^2 \sin^2 (t 2\pi\nu + b)$

Since $E = T + V$

$$E = (k/2) A^2 \{ \sin^2 (t 2\pi\nu + b) + \cos^2 (t 2\pi\nu + b) \}$$

$$= (k/2) A^2$$

Quantum Mechanical Treatment:

$$H = T + V$$

$$= (-\hbar^2/2m) d^2/dx^2 + V(x)$$

$$= (-\hbar^2/2m) d^2/dx^2 + (k/2) x^2, \quad k = m (2\pi\nu)^2$$

$$= (-\hbar^2/2m) d^2/dx^2 + 2\pi^2\nu^2 m x^2$$

$$= (-\hbar^2/2m) (d^2/dx^2 - \alpha x^2), \quad \alpha = 2\pi\nu m / \hbar$$

$$H \psi = E \psi$$

$$(-\hbar^2/2m) (d^2/dx^2 - \alpha x^2) \psi = E \psi$$

$$d^2\psi / dx^2 + (2mE / \hbar^2 - \alpha^2 x^2) \psi = 0$$

This is a 2nd order homogeneous linear differential eq. with

$$P(x) = 0 \quad \text{and} \quad Q(x) = (2mE/\hbar^2 - \alpha^2 x^2)$$

Since we don't have constant coefficients, must try a different method of solution- *power series*

Let $\psi(x) = e^{-\alpha x^{**2}/2} f(x)$, where $f(x)$ is a power series & x^{**2} is x squared.

Prove to yourself that

$$d^2\psi / dx^2 = e^{-\alpha x^{**2}/2} (d^2f/ dx^2 - 2\alpha x df/dx - \alpha f + \alpha^2 x^2 f)$$

Then $d^2\psi / dx^2 + (2mE/\hbar^2 - \alpha^2 x^2) \psi = 0$ gives

$$d^2f/ dx^2 - 2\alpha x df/dx + (2mE/\hbar^2 - \alpha) f = 0$$

Assume f can be expanded in a Taylor Series around $x=0$:

$$f(x) = \sum_{n=0}^{\infty} c_n x^n$$

Solve for a recursion relation for the c_n from

$$d^2f/ dx^2 - 2\alpha x df/dx + (2mE/\hbar^2 - \alpha) f = 0$$

First write df/dx & d^2f/ dx^2 in terms of power series:

$$f = c_0 1 + c_1 x + c_2 x^2 + c_3 x^3 + \dots$$

$$df/dx = c_1 + c_2 2x + c_3 3x^2 + \dots = \sum_{n=1}^{\infty} c_n n x^{n-1} = \sum_{n=0}^{\infty} c_{n+1} (n+1) x^n$$

$$d^2f/ dx^2 = c_2 2 + c_3 6x + \dots = \sum_{n=2}^{\infty} c_n n(n-1) x^{n-2}$$

n=2

Convert to a sum from 0 to ∞ :

Let $n = k+2$, then when $n=2$, $k=0$ and

$$d^2f/ dx^2 = \sum_{k=0}^{\infty} c_{k+2} (k+1)(k+2)x^k$$

Since n & k are dummy indices,

$$d^2f/ dx^2 = \sum_{n=0}^{\infty} c_{n+2} (n+1)(n+2)x^n$$

Plug these series into

$$d^2f/ dx^2 - 2\alpha x df/dx + (2mE/\underline{h}^2 - \alpha) f = 0$$

and collect terms in x^n :

$$\begin{aligned} \sum c_{n+2} (n+1)(n+2)x^n - 2\alpha x \sum c_n n x^{n-1} \\ + (2mE/\underline{h}^2 - \alpha) \sum c_n x^n = 0 \end{aligned}$$

$$\sum \{ c_{n+2} (n+1)(n+2) - 2\alpha c_n n + (2mE/\underline{h}^2 - \alpha) c_n \} x^n = 0$$

Setting $\{ \dots \} = 0$ leads to a recursion relationship for the c_n 's:

$$c_{n+2} = \{ [\alpha + 2\alpha n - 2mE/\underline{h}^2]/(n+1)(n+2) \} c_n$$

Define c_0 & c_1 , then calculate all the other c_n 's

If $c_0 = 0$ & $c_1 = 1$, have a power series in odd powers of x

If $c_0 = 1$ & $c_1 = 0$, have a power series in even powers of x

The most general solution is a combination of the series

Rewrite $\sum_{n=1,3,5,\dots}^{\infty} c_n x^n$ as $\sum_{n=0}^{\infty} c_{2n+1} x^{2n+1}$

$\sum_{n=0,2,4,\dots}^{\infty} c_n x^n$ as $\sum_{n=0}^{\infty} c_{2n} x^{2n}$

Then
$$\psi = A e^{-\alpha x^{**}2/2} \sum_{n=0}^{\infty} c_{2n+1} x^{2n+1} + B e^{-\alpha x^{**}2/2} \sum_{n=0}^{\infty} c_{2n} x^{2n}$$

Determine A & B from the *boundary conditions*: i.e. the wavefunction must be well-behaved as $x \rightarrow \infty$. (As in the particle in a box case, this leads to a *quantum condition on the energy*.)

The factor $e^{-\alpha x^{**}2/2} \rightarrow 0$ as $x \rightarrow \infty$

But how does the series that multiplies this factor behave as $x \rightarrow \infty$? The series may overwhelm the damping effect of the exponential factor as $x \rightarrow \infty$. Consider the ratio of coefficients of x^{2n+2} and x^{2n} :

For even n, substitute 2j for n in the recursion formula

$$c_{2j+2}/c_{2j} = \{\alpha - 4\alpha j - 2mE/\hbar^2\}/(2j + 1)(2j + 2)$$

The series will be dominated by large x as $x \rightarrow \infty$. So the terms in large j will be important because x is raised to powers of j. For large j,

$$2j + 1 \approx 2j, 2j + 2 \approx 2j, 4\alpha j > 2mE/\hbar^2$$

$$\text{and } c_{2j+2}/c_{2j} \rightarrow 4\alpha j/(2j)(2j) = \alpha/j$$

For odd n, substitute 2j + 1 for n in the recursion formula

$$c_{2j+3}/c_{2j+1} = \{\alpha + 2\alpha(2j + 1) - 2mE/\hbar^2\}/(2j+2)(2j+3)$$

$$\text{For large j, } c_{2j+2}/c_{2j} \rightarrow 4\alpha j/(2j)(2j) = \alpha/j$$

Can we find a power series expansion of some function that has the same ratio of successive coefficients? Yes--

$$e^{\alpha x^{**2}} = 1 + \alpha x^2 + \dots + \alpha^j x^{2j}/j! + \alpha^{j+1} x^{2j+1}/(j+1)! + \dots$$

Coefficient of x^{2j+1} / Coefficient of x^{2j}

$$= [\alpha^{j+1}/(j+1)!] / [\alpha^j/j!] = \alpha/(j+1) \rightarrow \alpha/j \text{ for large } j$$

NOTE: $(j+1)! = (j + 1) j!$

$$\text{So } [\alpha^{j+1}/(j+1)!] / [\alpha^j/j!] = [\alpha^{j+1}/(j+1)j!] / [\alpha^j/j!] = \alpha/(j+1)$$

So each series in ψ must go as $e^{\alpha x^{**2}}$ as j gets large.

But $e^{\alpha x^{**2}} \rightarrow \infty$ for large x

$$\text{So, as } x \rightarrow \infty, \psi \rightarrow A e^{-\alpha x^{**2}/2} e^{\alpha x^{**2}} + B e^{-\alpha x^{**2}/2} e^{\alpha x^{**2}}$$

$$= (A + B) e^{\alpha x^{**2}/2} \rightarrow \infty$$

If the two series could be *truncated* after a certain number of terms, the multiplication by $e^{-\alpha x^{**2}/2}$ would force ψ to 0 as $x \rightarrow \infty$. If the highest term in the truncated series is x^p , then by l'Hospital's Rule

$$\lim_{x \rightarrow \infty} x^p e^{-\alpha x^{**2}/2} = 0$$

If we could truncate the series at some finite value of n , say v , then ψ would be finite at ∞ and would be quadratically integrable. Since for both even & odd n ,

$$c_{n+2} = \{[\alpha + 2\alpha n - 2mE/\hbar^2]/(n+1)(n+2)\} c_n,$$

then $c_{v+2}, c_{v+4}, \text{etc.} = 0$ if

$$\alpha + 2\alpha n - 2mE/\hbar^2 = 0 \quad \text{for } v = n$$

This truncation condition leads to a quantum condition on the energy:

$$E = (\hbar^2/2m) \alpha (1 + 2v), \quad \alpha = 2\pi v m / \hbar$$

$$\text{Or } E = \hbar \pi v (1 + 2v) = \hbar v (1/2 + v), \quad v = 0, 1, 2, \dots$$

So by requiring that ψ be finite as $x \rightarrow \infty$, E becomes quantized.

The general recursion relation can be written by substituting

$$E = (\hbar^2/2m) \alpha (1 + 2v)$$

into

$$c_{n+2} = \{[\alpha + 2\alpha n - 2mE/\hbar^2]/(n+1)(n+2)\} c_n,$$

$$\text{or } c_{n+2} = [2\alpha (n - v)/(n + 1)(n + 2)] c_n$$

So, which series is truncated by quantizing the energy depends on whether v is even or odd. The only way to have the general solution be well-behaved is to set the coefficient of the other series = 0.

$$\text{So } \psi = e^{-\alpha x^{**}2/2} \sum_{j=0}^{\infty} c_{2j+1} x^{2j+1} \text{ or } e^{-\alpha x^{**}2/2} \sum_{j=0}^{\infty} c_{2j} x^{2j}$$

Note that the *energy levels of the harmonic oscillator are equally spaced*:

$$E = h \nu (1/2 + v)$$

$$\Delta E = E_{v+1} - E_v = h \nu (v + 3/2 - v - 1/2) = h \nu$$

For $v = 0$, $E = h \nu / 2$ ground state energy

E is non-zero because $E = 0$ would violate the Uncertainty Principle (both position & momentum would be known exactly).

If $E = 0$, then $T = 0$ & $V = 0$.

$T = 0$ means $\Delta p_x = 0$ (i.e. the momentum is exactly 0)

$V = 0$ means the particle is at exactly 0

Harmonic Oscillator Wavefunctions

$v = 0$ The power series is even; $c_2 = c_4 = \dots = 0$

$$\psi_0 = c_0 e^{-\alpha x^{**2}/2} \quad E_0 = (1/2) h \nu$$

Find c_0 by normalizing ψ_0 : $\int_{-\infty}^{\infty} c_0^2 e^{-\alpha x^{**2}} dx = 1$

$e^{-\alpha x^{**2}}$ is an *even* function of x since replacing x by $-x$ gives the same result.

$$\int_{-\infty}^{\infty} \text{even}(x) dx = 2 \int_0^{\infty} \text{even}(x) dx$$

$$\int_0^{\infty} e^{-\alpha x^{**2}} dx = (1/2) \sqrt{(\pi/\alpha)} \quad (\text{See Appendix for integrals})$$

$$\text{So } 2 c_0^2 (1/2) \sqrt{(\pi/\alpha)} = 1 \rightarrow c_0 = (\alpha/\pi)^{1/4}$$

See Fig. 4.3 for the plot of ψ_v , $v = 0, 1, 2, 3$

ψ_0 is an even function, $\psi_0(x) = \psi_0(-x)$. From the plot it can be seen that $\psi_0 = 0$ only at $x = \pm\infty$ so there are no nodes in ψ_0

$v=1$ The power series is; $c_3 = c_5 = \dots = 0$

$$\psi_1 = c_1 x e^{-\alpha x^2/2} \quad E_1 = (3/2) h\nu$$

Find c_1 by normalizing ψ_1 : $\int_{-\infty}^{\infty} c_1^2 x^2 e^{-\alpha x^2} dx = 1$

$$= 2 \int_0^{\infty} c_1^2 x^2 e^{-\alpha x^2} dx = 2 c_1^2 (1/4) (\pi/\alpha^3)^{(1/2)}$$

$$c_1 = (4\alpha^3/\pi)^{1/4}$$

ψ_1 is odd: $\psi_1(-x) = -\psi_1(x)$; but $|\psi_1|^2$ is even; one node--
at $x = 0$

$v=2$ The power series is; $c_4 = c_6 = \dots = 0$

$$\psi_2 = (c_0 + c_2 x^2) e^{-\alpha x^2/2}$$

Need a recursion relation for c_0 & c_2 for $v = 2$. Set $n = 0$ to obtain

$$c_2 = [2\alpha(0 - 2)/(0 + 1)(0 + 2)] c_0$$

$$\psi_2 = c_0 (1 - 2\alpha x^2) e^{-\alpha x^2/2}$$

Find c_0 by normalizing ψ_2 : $\int_{-\infty}^{\infty} c_0^2 (1 - 2\alpha x^2)^2 e^{-\alpha x^2} dx = 1$

$$c_0 = (\alpha/(4\pi))^{1/4}$$

Note: the number of nodes in the wavefunction, interior to the boundary points at $\pm\infty$, is equal to v .

Note: By squaring the wavefunction it can be seen that there is a non-zero probability of finding the particle anywhere except at the nodes.

Tunneling: As in the particle in a box case, the particle can be found outside the classically-allowed region for which $E > V$. See Fig. 4.4 (i.e. the classically allowed region is that which is inside the parabola defined by $V = (1/2) kx^2$). This indicates quantum mechanical behavior.

To measure that a particle is in the classically forbidden region, one must measure its position. But the act of measurement changes the position, by imparting energy to the system. So an accurate measurement of the position leads to a large uncertainty in the momentum (as well as the kinetic energy)

The Harmonic Oscillator as a Model for the Vibrational Spectra of Diatomic Molecules

How is the wavefunction for the harmonic oscillator related to that of a diatomic molecule?

Consider the line spectrum of H₂. At low resolution one sees a series of thick lines (or bands) that correspond to transitions between electronic energy states. As with the Balmer, Paschen, etc. series for H, the lines have a certain frequency which corresponds to the energy difference between different electronic energy states. At higher resolution, the bands are seen to be made up of several individual lines. The lines are due to the fact that the nuclei aren't infinitely heavy (in fact, nuclear motion is quantized like that of the electron).

Spectral transitions take place between particular vibrational & rotational levels of an excited electronic state & vibrational & rotational levels of the ground state. So a single electronic transition (which shows up as a band at low resolution) can have many different types of transitions between vibrational & rotational levels. These transitions show up as fine structure at high resolution. The simplest spectra to interpret are vibrational-rotational transitions within the same electronic energy level.

Sketch out how to solve for the molecular wavefunction:

Use the Born-Oppenheimer Approximation. Assume that the nuclei are fixed at distance R. This assumes that

$$\Psi = \Psi_{\text{elect}} \Psi_{\text{nucl}}$$

and results in separate eqs. for the electronic & nuclear motions. Solve the Schrödinger Eq. for the electronic energy, E(R). For the vibrational part of the Schrödinger Eq.,

$$-(\hbar^2/2\mu) d^2\chi(R)/dR^2 + E(R) \chi(R) = E_{\text{vib}} \chi(R)$$

where

$$\mu = \text{reduced mass of diatomic molecule} = m_1 m_2 / (m_1 + m_2)$$

R = internuclear separation

$E(R)$ = electronic energy, calculated at various R to give curve

E_{vib} = vibrational energy

χ = vibrational wavefunction

By approximating the form of $E(R)$, one gets an eq. for the vibrational wavefunction similar to that for the harmonic oscillator. Expand $E(R)$ in a Taylor Series around $R = R_e =$ equilibrium internuclear separation:

$$E(R) = E(R_e) + (dE/dR)_{R_e} (R - R_e) + (1/2)(d^2E/dR^2)_{R_e} (R - R_e)^2 + \dots$$

Since the zero of energy falls at $R = R_e$, $E(R_e) = 0$. Also $(dE/dR) \big|_{R_e} = 0$ (i.e. minimum point) at $R = R_e$ So

$$E(R) = (1/2)(d^2E/dR^2) \big|_{R_e} (R - R_e)^2 + \dots$$

Let $\rho = R - R_e$ and $k = (d^2E/dR^2) \big|_{R_e} =$ force constant.

Then $E(\rho) = (1/2) k \rho^2 + \dots$

The first term in the expansion is a parabola with the same minimum & curvature at the minimum as the exact curve $E(R)$.

If this form is used in the Schrödinger Eq. for vibrational motion of the nuclei, the resulting eq. is that of the harmonic oscillator (changing variables from R to ρ):

$$-(\hbar^2/2\mu) d^2\chi(\rho)/d\rho^2 + (1/2) k \rho^2 \chi(\rho) = E_{\text{vib}} \chi(\rho)$$

Therefore, the harmonic oscillator is a good approximation for a diatomic molecule when $R \approx R_e$. So

$$E_{\text{vib}} = E_v = (v + 1/2) h\nu, v = 0, 1, 2, \dots$$

$$\nu = (1/2\pi) (k/\mu)^{1/2}$$

Selection Rules for Transitions Between Vibrational Levels are determined from the time-dependent Schrödinger Eq. (This will be covered in a much later chapter.)

Only if the dipole moment $\epsilon(\rho)$ varies with internuclear separation ρ , as in a heteronuclear diatomic like HCl, is the transition moment non-zero &

$$\Delta v = \pm 1$$

For homonuclear diatomics like H_2 , ϵ is independent of ρ , so no vibrational transition is allowed.

Derive the Selection Rules:

One can calculate the expectation value of ϵ using harmonic oscillator wavefunctions:

$$\langle \epsilon \rangle = \int \psi_v^* \epsilon(\rho) \psi_v \, d\tau$$

If $\Delta v = \pm 1$, then $\langle \epsilon \rangle$ is not equal to zero and the transition is allowed. Calculate the wavenumber of the transition:

$$\text{If } \Delta v = \pm 1, \text{ then } v'' = v' \pm 1$$

$$\Delta E = hc/\lambda = hc \underline{\nu}, \quad \underline{\nu} = 1/\lambda$$

$$\text{For absorption: } v'' = v' + 1$$

$$\begin{aligned} \underline{\nu} &= \Delta E / hc = (1/(hc)) \{ (v''+1/2)hv - (v'+1/2) hv \} \\ &= (v/c) (v'' - v') = v/c \end{aligned}$$

$$\text{For emission: } v'' = v' - 1 \ \& \ \underline{\nu} = v/c$$

An infra red spectrum of a molecule is like a fingerprint. It is particularly important for polyatomic molecules whose spectrum is very complex. Bond stretching & angle bending vibrations are independent of the molecule. So one can determine the molecular structure from the spectra. At high resolution, each of the vibrational peaks will be made up of many other peaks corresponding to rotational transitions (rotational fine structure)

If a molecule were really a harmonic oscillator, it would have only one vibrational transition frequency (calculated above). Its spectrum would be made up of just one line. However, the spectrum is made up of many lines due to the fact that the actual potential function has many *anharmonic terms*.

$$\begin{aligned} E(R) &= (1/2) k (R - R_e)^2 + (1/3!)(d^3E/dR^3) \Big|_{R_e} (R - R_e)^3 \\ &+ (1/4!)(d^4E/dR^4) \Big|_{R_e} (R - R_e)^4 + \dots \end{aligned}$$

These terms cause small non-zero transition moments for $\Delta v = \pm 2, \pm 3, \dots$. Transitions are less intense in these overtones.

Relative Population

N_i = number of molecules in i-th energy level

g_i = degeneracy of the i-th level

T = temperature

B = Boltzmann constant

$$N_i / N_j = (g_i / g_j) e^{-(E_i - E_j)/kT}$$

At room temperature,

light diatomics (H_2 , HCl , CO) - only $v = 0$ is significantly populated

heavy diatomics (I_2) have several levels populated