

# Harmonic Oscillator

Chem 2340

## Classical harmonic oscillator

$$F_x = -kx$$

$$m \frac{d^2 x}{dt^2} + kx = 0$$

$$x = A \sin(2\pi\nu t + b)$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}; \quad \text{or} \quad \omega = 2\pi\nu = \sqrt{\frac{k}{m}} = \text{angular frequency}$$

$$V = -\int F_x dx = \int kx dx = \frac{1}{2} kx^2$$

$$KE = \frac{1}{2} m \left( \frac{dx}{dt} \right)^2$$

$$E = T + V = 2\pi^2 \nu^2 mA^2 = \frac{1}{2} kA^2$$

$k$  = force constant

$x$  completes one period in  $\Delta t = 1/\nu$

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

$$k = 4\pi^2 \nu^2 m$$

Note: here we used  $\cos^2(y) + \sin^2(y) = 1$

## Series solutions to DE's

Consider

$$y'' + c^2 y = 0 \quad \left| \quad \text{here} \quad y'' = d^2 y / dx^2 \right.$$

by inspection, the solutions are

$$y_1 = \sin(cx), y_2 = \cos(cx)$$

But we are not always going to be able to “guess” solutions.

A more general approach is to write

$$y = a_0 + a_1 x + a_2 x^2 + \dots = \sum_{n=0}^{\infty} a_n x^n$$

$$y' = \sum_{n=1}^{\infty} n a_n x^{n-1}$$

So the DE becomes.

$$y'' = \sum_{n=2}^{\infty} n(n-1) a_n x^{n-2}$$

$$\sum_{n=2}^{\infty} n(n-1) a_n x^{n-2} + c^2 \sum_{n=0}^{\infty} a_n x^n = 0$$

This can be rewritten as

$$\sum_{n=0}^{\infty} (n+2)(n+1) a_{n+2} x^n + c^2 \sum_{n=0}^{\infty} a_n x^n = 0$$

$$\sum_{n=0} \left[ (n+2)(n+1)a_{n+2} + a_n c^2 \right] x^n = 0$$

$$\Rightarrow (n+2)(n+1)a_{n+2} + c^2 a_n = 0$$

$$2 \cdot 1 a_2 + c^2 a_0 = 0$$

$$3 \cdot 2 a_3 + c^2 a_1 = 0$$

$$4 \cdot 3 a_4 + c^2 a_2 = 0$$

So  $a_2, a_4, a_6, \dots$  are in terms of  $a_0$   
 $a_3, a_5, a_7, \dots$  are in terms of  $a_1$

What is the significance of this?

Note: the equation relating higher  $n$   $a_n$  to the lower  $n$  coefficients is a **recursion** relation.

Now let's consider the SE for the harmonic oscillator

$$\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \psi + V\psi = E\psi$$

$$\frac{d^2\psi}{dx^2} + \left( \frac{2mE}{\hbar^2} - \alpha^2 x^2 \right) \psi = 0$$

Actually, for a diatomic molecule the mass used would be the reduced mass.

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

$$V = 1/2 kx^2$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}};$$

$$4\pi^2 \nu^2 m = k$$

$$\frac{4\pi^2 \nu^2 m^2}{\hbar^2} = \alpha^2$$

$$\alpha = 2\pi\nu m / \hbar$$

$$\frac{d^2\psi}{dx^2} + \left( \frac{2mE}{\hbar^2} - \alpha^2 x^2 \right) \psi = 0$$

Could directly solve using the series method

Alternatively, we can show that  $e^{-\alpha x^2/2}$  is a solution

$$\psi = e^{-\alpha x^2/2}$$

$$\psi' = -\alpha x e^{-\alpha x^2/2}$$

$$\psi'' = (-\alpha + \alpha^2 x^2) e^{-\alpha x^2/2}$$

$$\left[ -\alpha + \alpha^2 x^2 + \frac{2mE}{\hbar^2} - \alpha^2 x^2 \right] e^{-\alpha x^2/2} = 0 \Rightarrow$$

$$\alpha = \frac{2mE}{\hbar^2}, E = \frac{2\pi\nu m}{\hbar} \frac{\hbar^2}{2m} = \pi\nu\hbar = \frac{\hbar\omega}{2} = \frac{1}{2}h\nu$$

We then look for a general solution of the

$$\psi(x) = e^{-\alpha x^2/2} f(x)$$

We discard the  $e^{\alpha x^2/2}$  solution

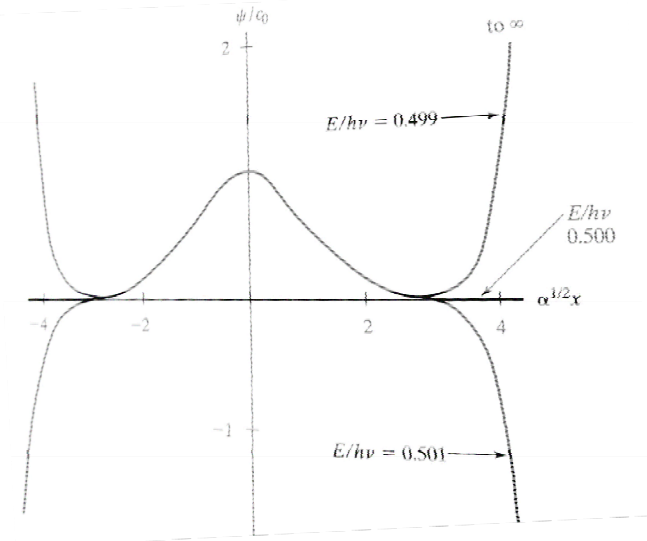


Fig 4.2 from text showing impact of small error in the energy on the wave function In a numerical solution to the problem

$$f'' - 2\alpha x f' + \left( \frac{2mE}{\hbar^2} - \alpha \right) f = 0$$

$$\text{Let } f = \sum_{n=0}^{\infty} c_n x^n$$

$$\text{can show } c_{n+2} = \frac{\alpha + 2\alpha n - 2mE/\hbar^2}{(n+1)(n+2)} c_n$$

Boundary conditions are  $\psi \rightarrow 0$  as  $x \rightarrow \pm \infty$

So  $f(x)$  must not grow faster than  $e^{-\alpha x^2/2}$  falls off as  $x \rightarrow \pm \infty$

$$\text{Ratio test } \frac{c_{2n+2}}{c_n} \sim \frac{\alpha}{n}, \text{ for large } n$$

Can show this implies that the series behaves as  $e^{\alpha x^2}$

So we have a problem. We can solve this by requiring that  $f(x)$  is a finite polynomial rather than an  $\infty$  series.

For the series to truncate some  $n = v$  we require

$$\alpha + 2\alpha v - 2mE / \hbar^2 = 0$$

$$\begin{aligned} \text{Then } E &= \frac{(\alpha + 2\alpha v)}{2m} \hbar^2 = \frac{2\alpha \left[ \frac{1}{2} + v \right]}{2m} \hbar^2 \\ &= \frac{2(2\pi\nu m)}{2m\hbar} \left[ \frac{1}{2} + v \right] \hbar^2 = 2\pi\nu\hbar \left[ \frac{1}{2} + v \right] = \hbar\omega \left[ \frac{1}{2} + v \right] \end{aligned}$$

or  $\hbar\omega \left[ n + \frac{1}{2} \right]$  if we switch back to the  $n$  variable

So the energies are  $\frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \frac{5}{2}\hbar\omega, \dots$

$$c_{n+2} = \frac{2\alpha(n-v)}{(n+1)(n+2)} c_n$$

$$\psi_0 = \left( \frac{\alpha}{\pi} \right)^{\frac{1}{4}} e^{-\alpha x^2/2}$$

$$\psi_1 = \left( \frac{4\alpha^3}{\pi} \right)^{\frac{1}{4}} x e^{-\alpha x^2/2}$$

$$\psi_2 = \left( \frac{\alpha}{4\pi} \right)^{\frac{1}{4}} (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

The polynomials in this sequence are the Hermite polynomials,  $\{H_i\}$

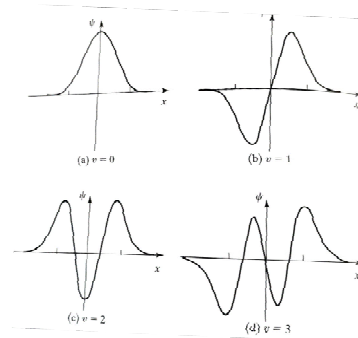


Fig. 4.4 from text showing the wave functions of the first four levels of the HO



$$\langle E \rangle_i = \langle \psi_i | H | \psi_i \rangle = \langle T \rangle_i + \langle V \rangle_i$$

Just as for the classical HO  $\langle T \rangle = \langle V \rangle$

Note it is the  $\{\psi_i\}$  that form an orthogonal set, not the  $H_i$

$$\langle \psi_i | \psi_j \rangle = \int_{-\infty}^{\infty} H_i H_j e^{-\alpha x^2} dx = \delta_{ij}$$

$$\langle x \rangle_i = 0 \quad \leftarrow \text{Do you see why?}$$

$$\langle x^2 \rangle_i \neq 0$$

$$\langle p_x \rangle_i = 0$$

$$\langle p_x^2 \rangle_i \neq 0$$

There are lots of powerful relations involving Hermite polynomials.

Two are

$$H_n(z) = (-1)^n e^{z^2} \frac{d^n}{dz^n} e^{-z^2} \quad \left| \text{generating function} \right.$$

$$2zH_n(z) = nH_{n-1}(z) + \frac{1}{2}H_{n+1}(z) \quad \left| \text{recursion relationship} \right.$$

$$H_0 = 1$$

$$H_1 = 2z$$

$$H_2 = 4z^2 - 2$$

$$H_3 = 8z^3 - 12z$$

$z = \sqrt{\alpha}x$  to get the polynomials in terms of  $\alpha$  and  $x$ .

## Transition matrix element for going from level 0 to level $n$

The operator corresponding to radiation in the  $z$  direction is proportional to  $z$

$$\begin{aligned} &= \langle 0 | z | n \rangle = \int_{-\infty}^{\infty} \psi_0 z \psi_n dz = \int_{-\infty}^{\infty} H_0 \cdot z H_n(z) e^{-z^2} dz \\ &= \int_{-\infty}^{\infty} \left[ \frac{1}{2} H_0 n H_{n-1}(z) + \frac{1}{4} H_0 H_{n+1}(z) \right] e^{-z^2} dz \\ &= n \underbrace{\int_{-\infty}^{\infty} H_0 H_{n-1}(z) e^{-z^2} dz}_{\substack{\downarrow \\ \text{Non-zero only if } n=1}} + \frac{1}{2} \underbrace{\int_{-\infty}^{\infty} H_0 H_{n+1}(z) e^{-z^2} dz}_{\substack{\downarrow \\ 0}} \end{aligned}$$

Here I have not normalized the wave functions. To get the correct value of the integral, when non-zero, one has to use normalized functions and to include the prefactor of the operator

If starting in level  $n$ , the allowed transitions are to  $n \pm 1$

$$\text{Intensity} \propto \left| \langle 0 | z | n \rangle \right|^2$$

In the Dirac notation the identity operator I can be written as:  $\sum_{n=0}^{\infty} |n\rangle\langle n|$

Let's check

$$\begin{aligned} \sum_{n=0}^{\infty} |n\rangle\langle n| \sum_{m=0}^{\infty} |m\rangle\langle m| &= \sum_{n,m} |n\rangle\langle n| m\rangle\langle m| \\ &= \sum_{n=0}^{\infty} |n\rangle\langle n| \quad \text{since } \langle n|m\rangle = \delta_{nm} \end{aligned}$$

Note that the identity operator involves an expansion over all the eigenfunctions of an operator

Also  $\left( \sum_{n=0}^{\infty} |n\rangle\langle n| \right) |m\rangle = |m\rangle$

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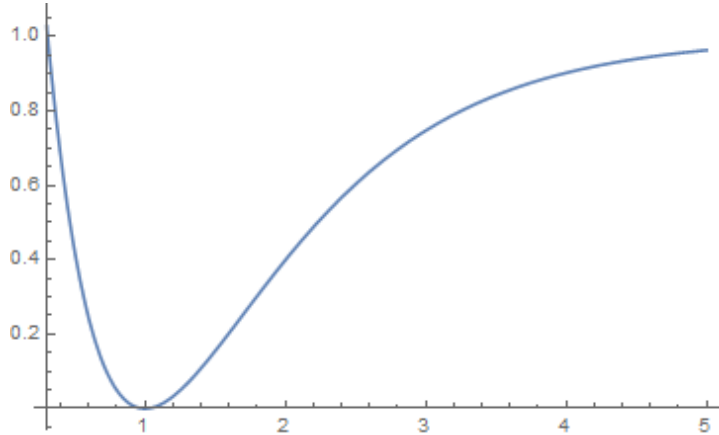
Supposed you want to evaluate:  $\langle 0|z^2|0\rangle$

$$\begin{aligned} \text{We can write: } \langle 0|z^2|0\rangle &= \langle 0|zIz|0\rangle = \sum_{n=0}^{\infty} \langle 0|z|n\rangle\langle n|z|0\rangle \\ &= |\langle 0|z|1\rangle|^2 \end{aligned}$$

$\hbar\omega$

## Realistic potential energy curves of diatomic molecules

For a real molecule the potential energy curve bends over and  $V \rightarrow D_e$  as  $x \rightarrow \infty$



Taylor series expansion about its minimum at  $x = x_0$

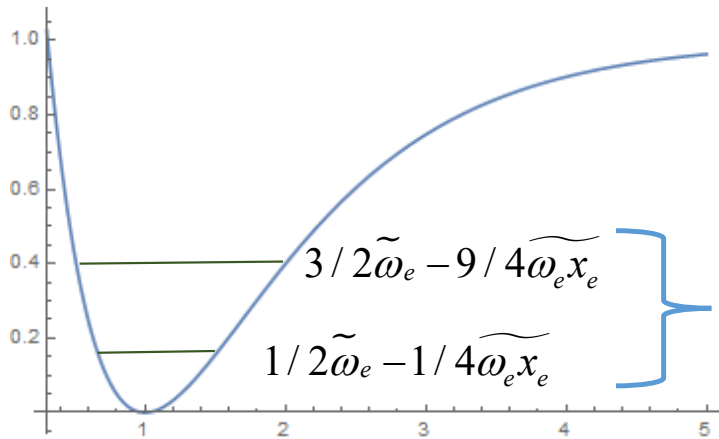
$$V(x) = \frac{d^2V / dx^2}{2} (x - x_e)^2 + \frac{d^3V / dx^3}{3!} (x - x_e)^3 + \frac{d^4V / dx^4}{4!} (x - x_e)^4 + \dots$$

Thus a harmonic potential represents the leading term of the Taylor series expansion of the potential about its minimum at  $x_e$ .

Can show that:

$$E = \left( v + \frac{1}{2} \right) \hbar \omega_e - \left( v + \frac{1}{2} \right)^2 \hbar \omega_e x_e - \dots$$

$\omega_e x_e$  is the first unharmonicity constant  
(generally positive)



in  $\text{cm}^{-1}$  units

### Population of levels at finite T

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

Boltzmann factor  
in exponent

where  $g_i$  is the degeneracy of level  $i$  which is 1 for the 1D vibrational problem.

For chemically bonded diatomic molecules, only the  $n=0$  level has significant population at room temperature.

$kT$  at room temperature  $\sim 200 \text{ cm}^{-1}$ . For typical diatomics,  $\hbar\omega$  (in  $\text{cm}^{-1}$  units) is  $2000\text{-}3000 \text{ cm}^{-1}$ .