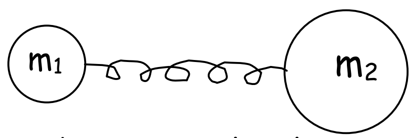
THE HARMONIC OSCILLATOR

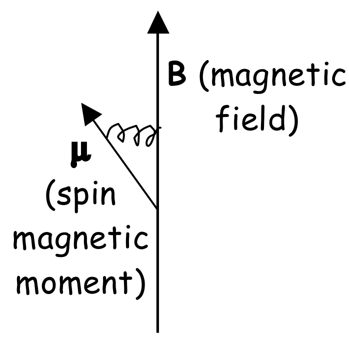
- Nearly any system near equilibrium can be approximated as a H.O.

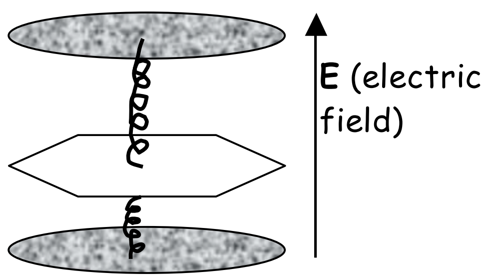
- One of a handful of problems that can be solved exactly in quantum mechanics

examples

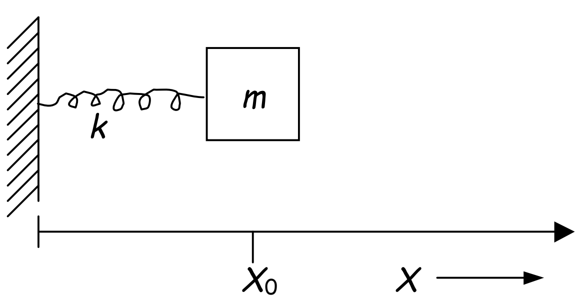


A diatomic molecule





Classical H.O.



Hooke's Law: $f = -k\left(X - X_0\right) \equiv -kx$

(restoring force)

$$f = ma = m\frac{d^2x}{dt^2} = -kx \quad \Rightarrow \quad \frac{d^2x}{dt^2} + \left(\frac{k}{m}\right)x = 0$$

<u>Solve diff. eq.</u>: General solutions are sin and cos functions

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

or can also write as

$$x(t) = C\sin(\omega t + \phi)$$

where *A* and *B* or *C* and ϕ are determined by the initial conditions.

e.g. $x(0) = x_0 \qquad v(0) = 0$

spring is stretched to position x_0 and released at time *t* = 0.

Then

$$x(0) = A\,\cancel{\sin(0)} + B\cos(0) = x_0 \quad \Rightarrow \quad B = x_0$$

$$v(0) = \left.\frac{dx}{dt}\right|_{x=0} = \omega\cos(0) - \omega\,\cancel{\sin(0)} = 0 \quad \Rightarrow \quad A = 0$$

So $\boxed{x(t) = x_0\cos(\omega t)}$

Mass and spring oscillate with frequency: $\omega = \sqrt{\frac{k}{m}}$

and maximum displacement x_0 from equilibrium when cos(ωt)= ±1

<u>Energy of H.O.</u>

<u>Kinetic energy</u> ≡ *K*

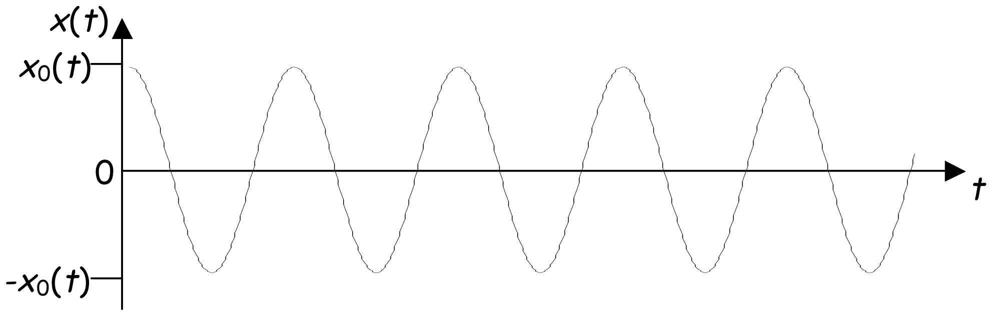
$$K = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2 = \frac{1}{2}m\left[-\omega x_0\sin(\omega t)\right]^2 = \frac{1}{2}kx_0^2\sin^2(\omega t)$$

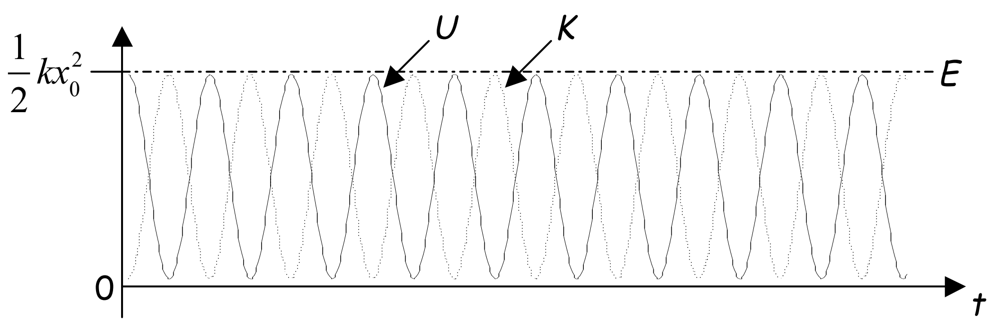
<u>Potential energy</u> ≡ *U*

$$f(x) = -\frac{dU}{dx} \quad \Rightarrow \quad U = -\int f(x)dx = \int(kx)dx = \frac{1}{2}kx^2 = \frac{1}{2}kx_0^2\cos^2(\omega t)$$

Total energy = $K + U = E$

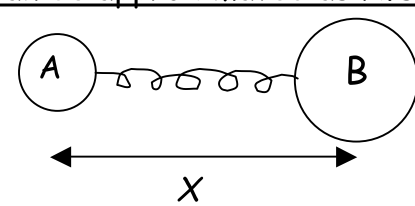
$$E = \frac{1}{2}kx_0^2\left[\sin^2(\omega t) + \cos^2(\omega t)\right] \qquad \boxed{E = \frac{1}{2}kx_0^2}$$

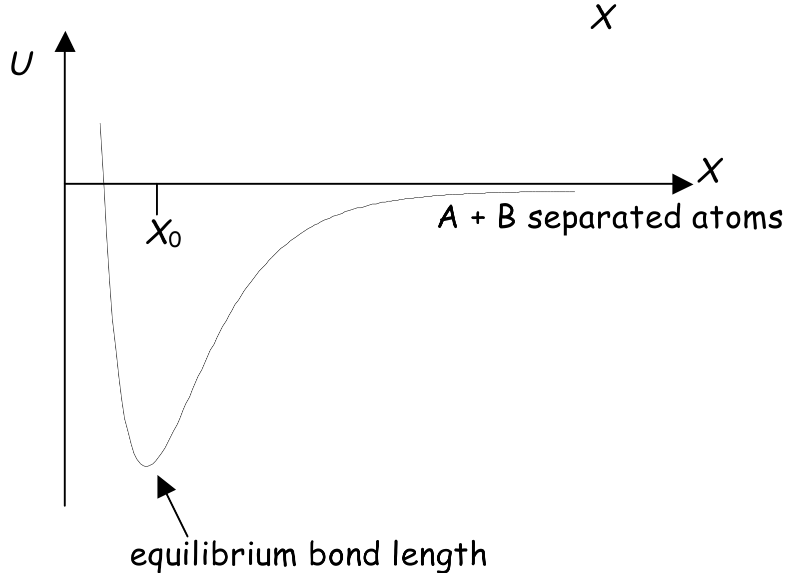




Most real systems near equilibrium can be approximated as H.O.

e.g. Diatomic molecular bond

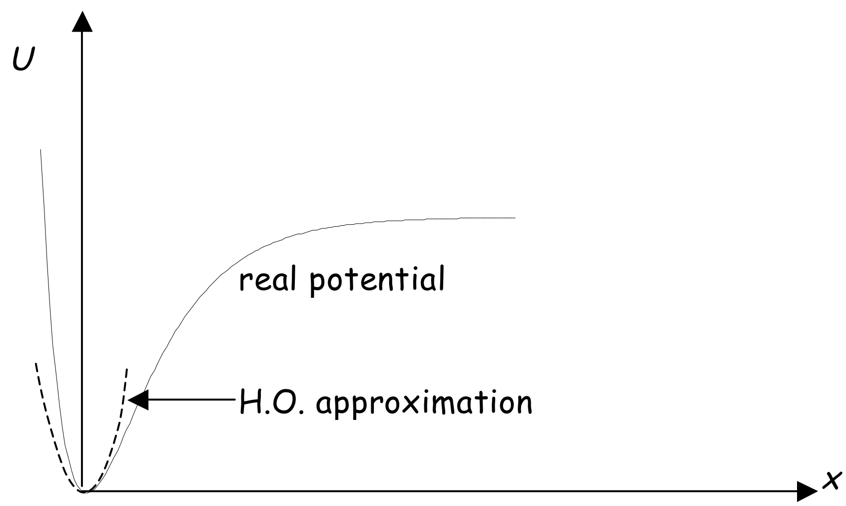




$$U(X) = U(X_0) + \left.\frac{dU}{dX}\right|_{X=X_0}(X - X_0) + \frac{1}{2}\left.\frac{d^2U}{dX^2}\right|_{X=X_0}(X - X_0)^2 + \frac{1}{3!}\left.\frac{d^3U}{dX^3}\right|_{X=X_0}(X - X_0)^3 + \cdots$$

Redefine $x = X - X_0$ and $U(X = X_0) = U(x = 0) = 0$

$$U(x) = \left.\frac{dU}{dx}\right|_{x=0} x + \frac{1}{2}\left.\frac{d^2U}{dx^2}\right|_{x=0} x^2 + \frac{1}{3!}\left.\frac{d^3U}{dx^3}\right|_{x=0} x^3 + \cdots$$

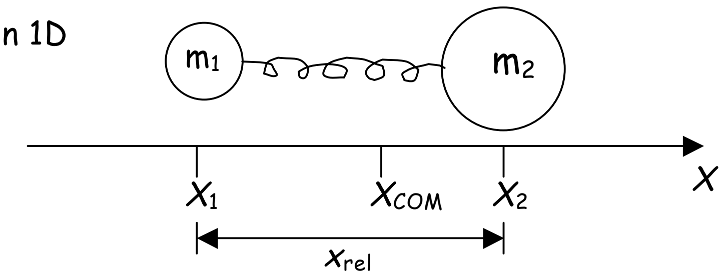


At eq. $\left.\frac{dU}{dx}\right|_{x=0} = 0$

For small deviations from eq. $x^3 << x^2$

$$\therefore \quad U(x) \approx \frac{1}{2}\left.\frac{d^2U}{dx^2}\right|_{x=0} x^2 \equiv \frac{1}{2}kx^2$$

Total energy of molecule in 1D



$$M = m_1 + m_2 \qquad \text{total mass}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad \text{reduced mass}$$

$$X_{COM} = \frac{m_1 X_1 + m_2 X_2}{m_1 + m_2} \qquad \text{COM position}$$

$$x_{rel} = X_2 - X_1 \equiv x \qquad \text{relative position}$$

$$K = \frac{1}{2} m_1 \left(\frac{dX_1}{dt} \right)^2 + \frac{1}{2} m_2 \left(\frac{dX_2}{dt} \right)^2 = \frac{1}{2} M \left(\frac{dX_{COM}}{dt} \right)^2 + \frac{1}{2} \mu \left(\frac{dx}{dt} \right)^2$$

$$U = \frac{1}{2} kx^2$$

$$E = K + U = \frac{1}{2} M \left(\frac{dX_{COM}}{dt} \right)^2 + \frac{1}{2} \mu \left(\frac{dx}{dt} \right)^2 + \frac{1}{2} kx^2$$

COM coordinate describes translational motion of the molecule

$$E_{trans} = \frac{1}{2} M \left(\frac{dX_{COM}}{dt} \right)^2$$

QM description would be free particle or PIB with mass *M*

We'll concentrate on relative motion (describes vibration)

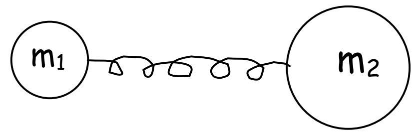
$$E_{vib} = \frac{1}{2} \mu \left(\frac{dx}{dt} \right)^2 + \frac{1}{2} kx^2$$

and solve this problem <u>quantum mechanically</u>.

<u>*THE QUANTUM MECHANICAL HARMONIC OSCILLATOR*</u>

$$\hat{H}\psi(x) = \Big[\underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}_{K} + \underbrace{\frac{1}{2}kx^2}_{U}\Big]\psi(x) = E\psi(x)$$

Note: replace *m* with μ (reduced mass) if



Goal: Find eigenvalues E_n and eigenfunctions $\psi_n(x)$

Rewrite as:

$$\frac{d^2\psi(x)}{dx^2} + \underbrace{\frac{2m}{\hbar^2}\left[E - \frac{1}{2}kx^2\right]}\psi(x) = 0$$

This is not a constant, as it was for P-I-B, so sin and cos functions won't work.

TRY: $f(x) = e^{-\alpha x^2/2}$ (gaussian function)

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

or rewriting, $$\frac{d^2 f(x)}{dx^2} + \alpha f(x) - \alpha^2 x^2 f(x) = 0w$$

which matches our original diff. eq. if

$$\alpha = \frac{2mE}{\hbar^2} \quad \text{and} \quad \alpha^2 = \frac{mk}{\hbar^2}$$

$$\therefore \quad \boxed{E = \frac{\hbar}{2}\sqrt{\frac{k}{m}}}$$

We have found <u>one</u> eigenvalue and eigenfunction

Recall $\omega = \sqrt{\dfrac{k}{m}}$ or $\nu = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{m}}$

$$\therefore \quad \boxed{E = \frac{1}{2}\hbar\omega = \frac{1}{2}h\nu}$$

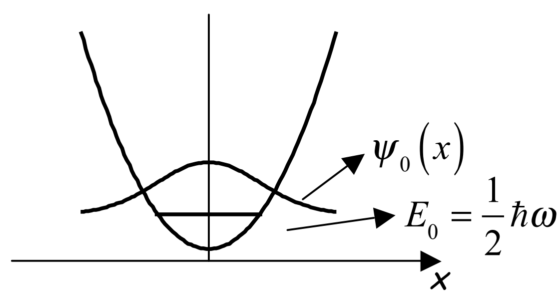
This turns out to be the <u>lowest</u> energy: the "ground" state

For the wavefunction, we need to normalize:

$\psi(x) = Nf(x) = Ne^{-\alpha x^2/2}$ where N is the normalization constant

$$\int_{-\infty}^{\infty} \left|\psi(x)\right|^2 dx = 1 \quad \Rightarrow \quad N^2 \underbrace{\int_{-\infty}^{\infty} e^{-\alpha x^2}}_{\sqrt{\pi/\alpha}} = 1 \quad \Rightarrow \quad N = \left(\frac{\alpha}{\pi}\right)^{1/4}$$

$$\therefore \quad \boxed{\begin{aligned} \psi_0(x) &= \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \\ E_0 &= \frac{1}{2}\hbar\omega = \frac{1}{2}h\nu \end{aligned}}$$



Note $\psi_0(x)$ is symmetric. It is an even function: $\psi_0(x) = \psi_0(-x)$
There are no nodes, & the most likely value for the oscillator displacement is 0.

So far we have just <u>one</u> eigenvalue and eigenstate. What about the others?

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \qquad E_0 = \frac{1}{2}h\nu$$

$$\psi_1(x) = \frac{1}{\sqrt{2}}\left(\frac{\alpha}{\pi}\right)^{1/4} \left(2\alpha^{1/2}x\right)e^{-\alpha x^2/2} \qquad E_1 = \frac{3}{2}h\nu$$

$$\psi_2(x) = \frac{1}{\sqrt{8}}\left(\frac{\alpha}{\pi}\right)^{1/4} \left(4\alpha x^2 - 2\right)e^{-\alpha x^2/2} \qquad E_2 = \frac{5}{2}h\nu$$

$$\psi_3(x) = \frac{1}{\sqrt{48}}\left(\frac{\alpha}{\pi}\right)^{1/4} \left(8\alpha^{3/2}x^3 - 12\alpha^{1/2}x\right)e^{-\alpha x^2/2} \qquad E_3 = \frac{7}{2}h\nu$$

$$\vdots \qquad\qquad \vdots$$

$$\text{with} \quad \alpha = \left(\frac{km}{\hbar^2}\right)^{1/2}$$

These have the general form

$$\boxed{\psi_n(x) = \underbrace{\frac{1}{\left(2^n n!\right)^{1/2}}\left(\frac{\alpha}{\pi}\right)^{1/4}}_{\text{Normalization}} \underbrace{H_n\left(\alpha^{1/2}x\right)}_{\text{Hermite polynomial}} \underbrace{e^{-\alpha x^2/2}}_{\text{Gaussian}} \qquad n = 0,1,2,\ldots}$$

Normalization Gaussian

Hermite polynomial (pronounced "air-MEET")

$$H_0(y) = 1 \qquad \text{even} \quad (n = 0)$$

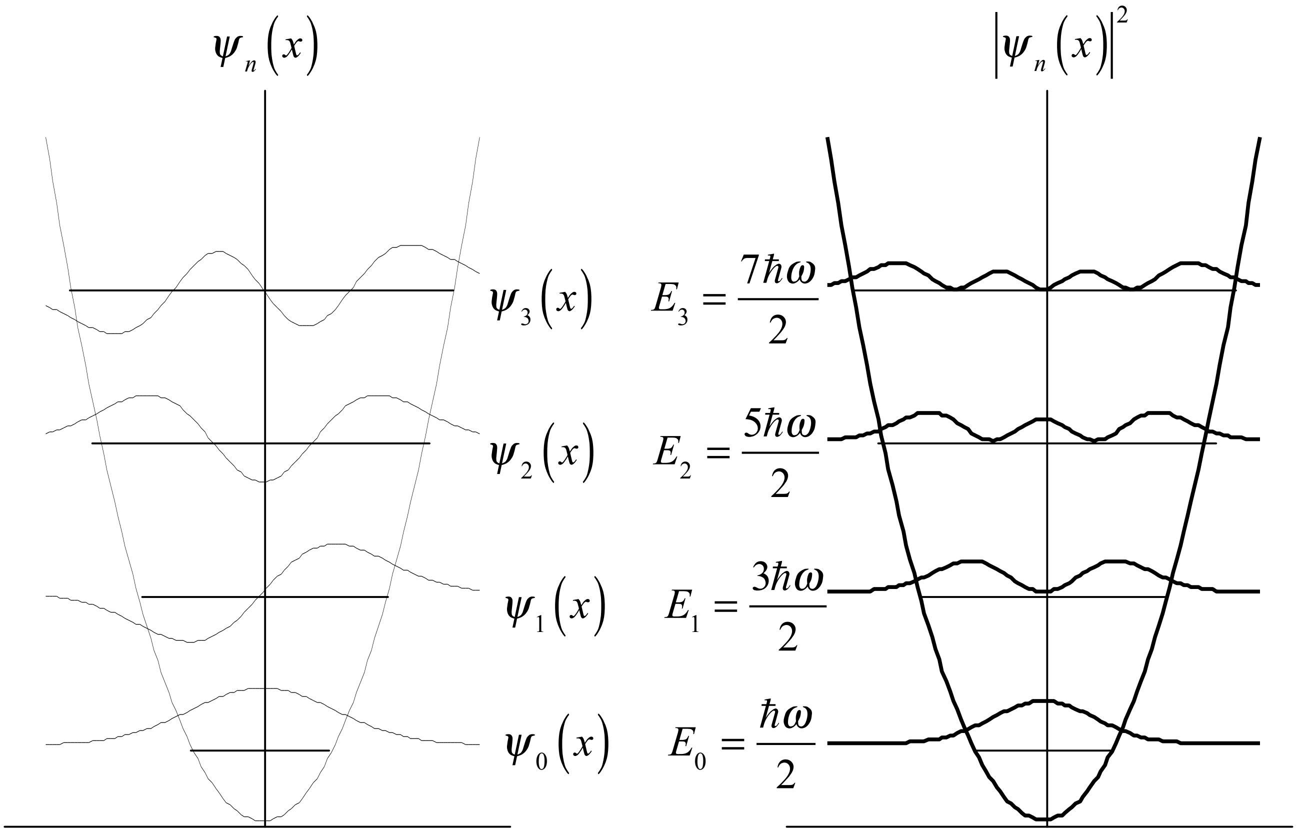
$$H_1(y) = 2y \qquad \text{odd} \quad (n = 1)$$

$$H_2(y) = 4y^2 - 2 \qquad \text{even} \quad (n = 2)$$

$$H_3(y) = 8y^3 - 12y \qquad \text{odd} \quad (n = 3)$$

$$H_4(y) = 16y^4 - 48y^2 + 12 \qquad \text{even} \quad (n = 4)$$

$$\vdots \qquad\qquad \vdots$$



Energies are $\boxed{E_n = \left(n + \frac{1}{2}\right)h\nu}$

Note *E* increases linearly with *n*.

⇒ Energy levels are <u>evenly spaced</u>

$$E_{n+1} - E_n = \left(\left(n+1\right) + \frac{1}{2}\right)h\nu - \left(n + \frac{1}{2}\right)h\nu = h\nu \quad \text{regardless of } n$$

There is a "<u>zero-point</u>" energy $E_0 = \frac{1}{2}h\nu$

E = 0 is not allowed by the Heisenberg Uncertainty Principle.

Symmetry properties of ψ's

$\psi_{0,2,4,6,....}$ are *even* functions $\psi(-x)=\psi(x)$

$\psi_{1,3,5,7,....}$ are *odd* functions $\psi(-x)=-\psi(x)$

Useful properties:

(even) $\cdot$(even) = even
(odd) $\cdot$(odd) = even
(odd) $\cdot$(even) = odd

$$\frac{d(\text{odd})}{dx}=(\text{even}) \qquad \frac{d(\text{even})}{dx}=(\text{odd})$$

$$\int_{-\infty}^{\infty}(\text{odd})\,dx=0 \qquad \int_{-\infty}^{\infty}(\text{even})\,dx=2\int_{0}^{\infty}(\text{even})\,dx$$

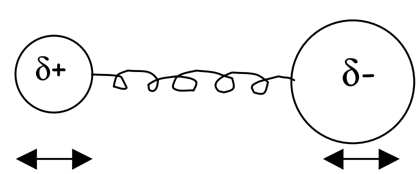
Just from symmetry:

$$\langle x\rangle_n=\int_{-\infty}^{\infty}\underbrace{\psi_n^*(x)\,x\,\psi_n(x)}_{\text{odd}}dx=0 \qquad \langle p\rangle_n=\int_{-\infty}^{\infty}\underbrace{\psi_n^*\left(-ih\frac{d}{dx}\right)\psi_n(x)}_{\text{odd}}dx=0$$

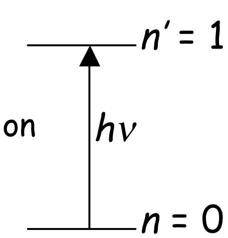
Average displacement & average momentum = <u>0</u>

IR spectroscopy $\Rightarrow$ H.O. selection rules

Intensity of vibrational absorption features



Vibrational transition



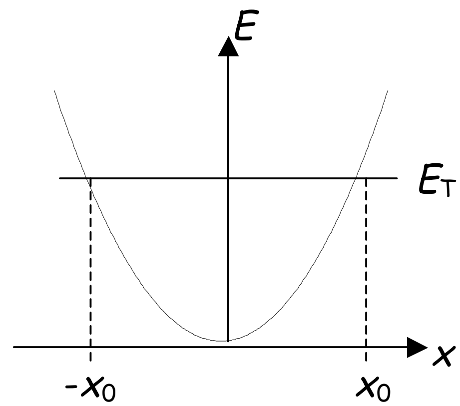
Intensity $$I_{nn'} \propto \left| \frac{d\mu}{dx} \int_{-\infty}^{\infty} \psi_n^* x \psi_{n'} dx \right|^2$$

1) Dipole moment of molecule must change as molecule vibrates ⇒ HCl can absorb IR radiation, but N_2, O_2, H_2 cannot.

2) Only transitions with $n' = n \pm 1$ allowed (selection rule). (Prove for homework.)

QUANTUM MECHANICAL HARMONIC OSCILLATOR & TUNNELING

Classical turning points



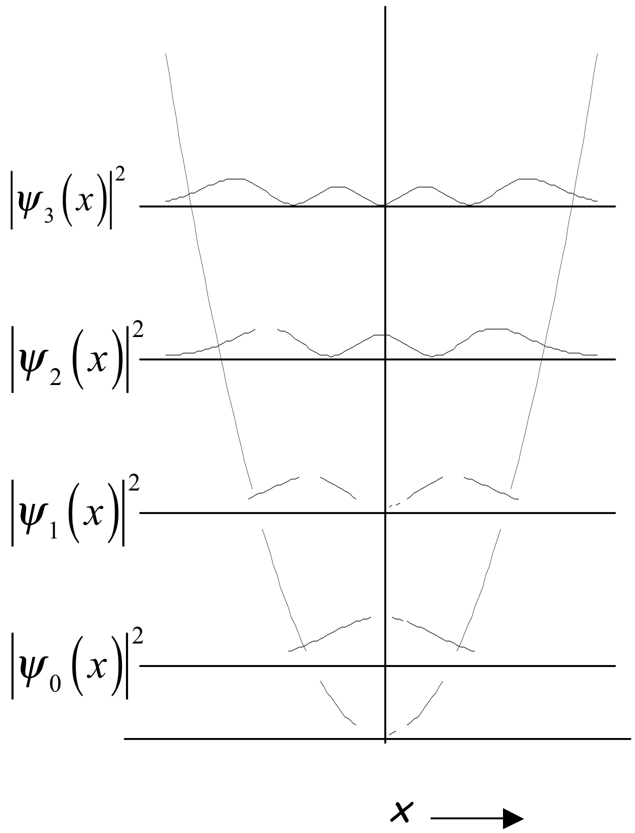
Classical H.O.: Total energy $E_T = \frac{1}{2} k x_0^2$ oscillates between K and U.

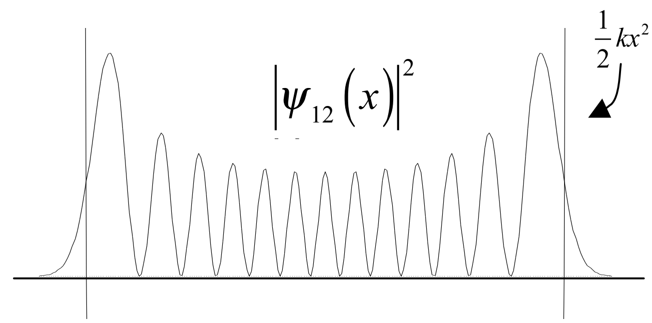
Maximum displacement x_0 occurs when all the energy is potential.

$$x_0 = \sqrt{\frac{2E_T}{k}}$$ is the "classical turning point"

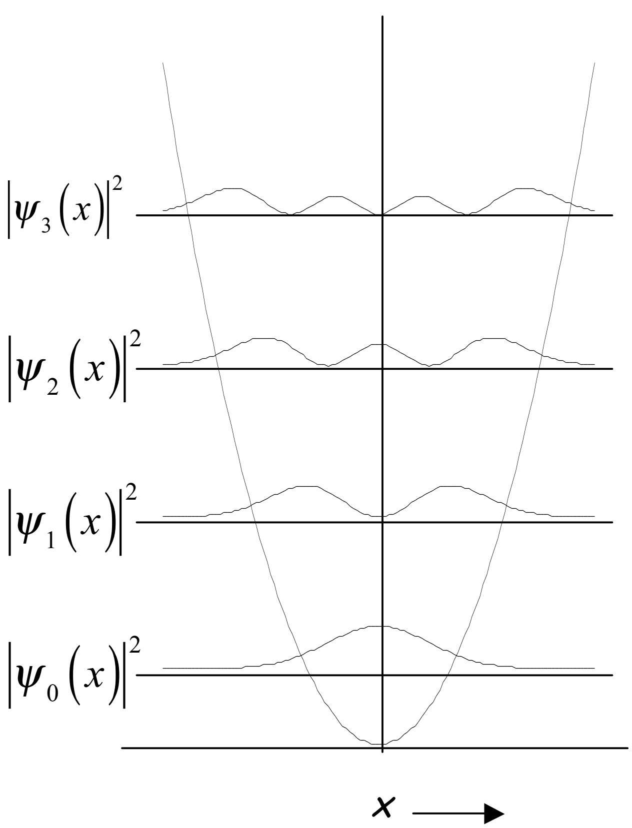
The classical oscillator with energy E_T can never exceed this displacement, since if it did it would have more potential energy than the total energy.

Quantum Mechanical Harmonic Oscillator.





At high n, probability density begins to look classical, peaking at turning points.



Non-zero probability at $x > x_0$!
Prob. of ($x > x_0$, $x < -x_0$):

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

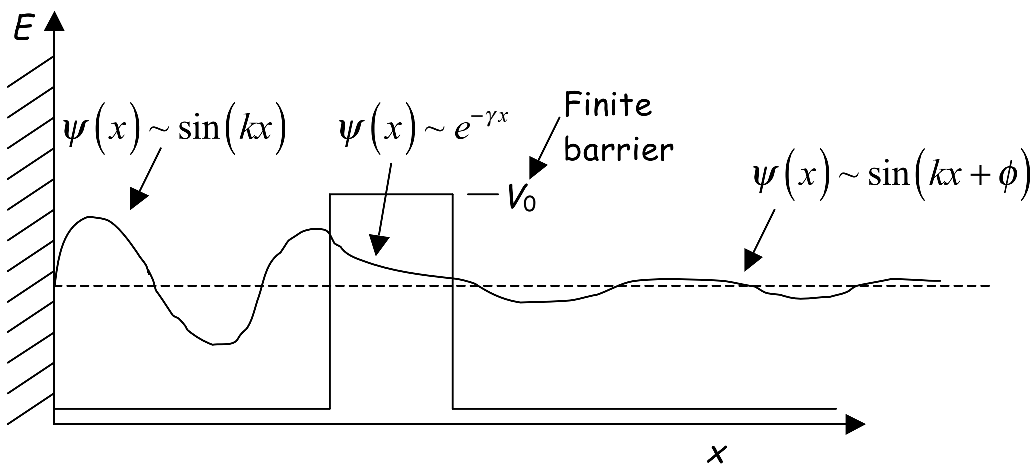
$$= \frac{2}{\pi^{1/2}} \int_{1}^{\infty} e^{-y^2} dy = \underbrace{\mathrm{erfc}(1)}$$

"Complementary error function" tabulated or calculated numerically

Prob. of ($x > x_0$, $x < -x_0$) = erfc(1) = 0.16
Significant probability!

The oscillator is "tunneling" into the classically forbidden region. This is a purely QM phenomenon!

Tunneling is a general feature of QM systems, especially those with very low mass like e- and H.



Even though the energy is less than the barrier height, the wavefunction is nonzero within the barrier! So a particle on the left may escape or "tunnel" into the right hand side.

Inside barrier: $$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V_0\right]\psi(x)=E\psi(x)$$

or $$\frac{d^2\psi(x)}{dx^2}=\left[\frac{2m(V_0-E)}{\hbar^2}\right]\psi(x)\equiv\gamma^2\psi(x)$$

Solutions are of the form $$\psi(x)=Be^{-\gamma x} \quad \text{with} \quad \gamma=\left[\frac{2m(V_0-E)}{\hbar^2}\right]^{\frac{1}{2}}$$

Note $$\gamma \propto (V_0-E)^{1/2} \quad \text{and} \quad \gamma \propto m^{1/2}$$

If barrier is not too much higher then the energy and if the mass is light, then tunneling is significant.
Important for protons (e.g. H-bond fluctuations, tautomerization)

Important for electrons (e.g. scanning tunneling microscopy)

Nonstationary states of the QM H.O.

System may be in a state other than an eigenstate, e.g.

$\psi = c_0\psi_0 + c_1\psi_1$ with $|c_0|^2 + |c_1|^2 = 1$ (normalization), e.g. $|c_0| = |c_1| = \dfrac{1}{\sqrt{2}}$

Full time-dependent eigenstates can be written as

$$\Psi_0(x,t) = \psi_0(x)e^{-i\omega_0 t} \qquad \Psi_1(x,t) = \psi_1(x)e^{-i\omega_1 t}$$

where

$$\hbar\omega_0 = E_0 = \frac{1}{2}\hbar\omega_{vib} \;\Rightarrow\; \omega_0 = \frac{1}{2}\omega_{vib} \qquad \hbar\omega_1 = E_1 = \frac{3}{2}\hbar\omega_{vib} \;\Rightarrow\; \omega_1 = \frac{3}{2}\omega_{vib}$$

System is then time-dependent:

$$\Psi(x,t) = \frac{1}{\sqrt{2}}e^{-i\omega_0 t}\psi_0(x) + \frac{1}{\sqrt{2}}e^{-i\omega_1 t}\psi_1(x) = c_0(t)\psi_0(x) + c_1(t)\psi_1(x)$$

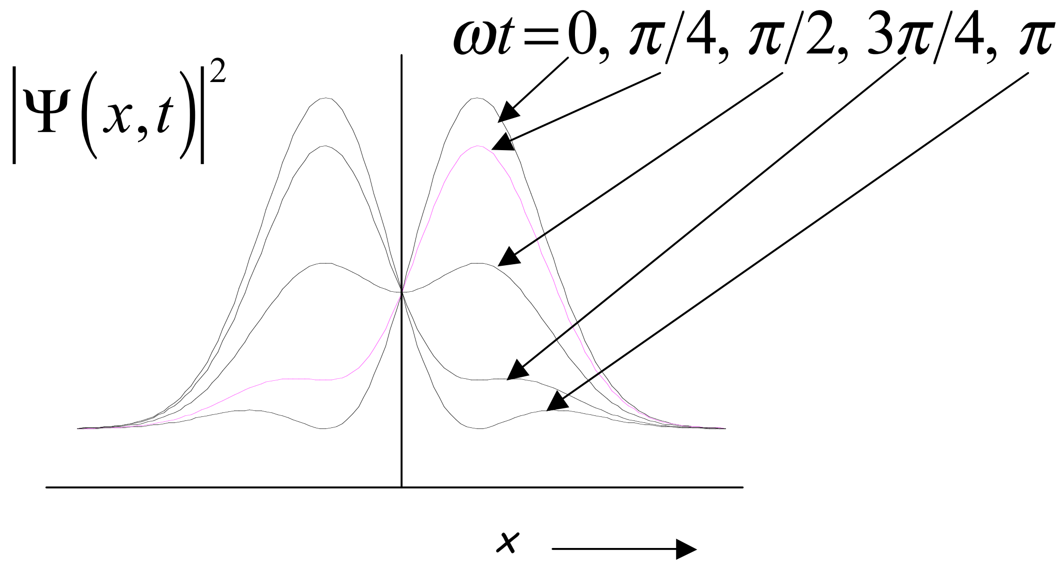
$$\text{where} \quad c_0(t) = \frac{1}{\sqrt{2}}e^{-i\omega_0 t} \qquad c_1(t) = \frac{1}{\sqrt{2}}e^{-i\omega_1 t}$$

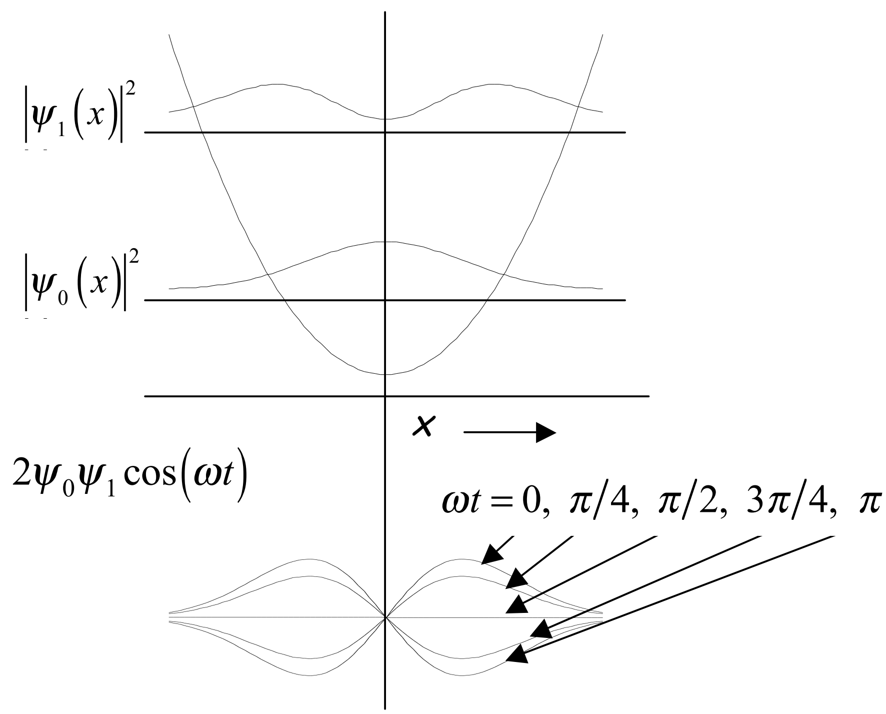
What is probability density?

$$\Psi^*(x,t)\Psi(x,t) = \frac{1}{2}\left[\psi_0^*(x)e^{i\omega_0 t} + \psi_1^*(x)e^{i\omega_1 t}\right]\left[\psi_0(x)e^{-i\omega_0 t} + \psi_1(x)e^{-i\omega_1 t}\right]$$

$$= \frac{1}{2}\left[\psi_0^*\psi_0 + \psi_1^*\psi_1 + \psi_1^*\psi_0 e^{i(\omega_1-\omega_0)t} + \psi_0^*\psi_1 e^{-i(\omega_1-\omega_0)t}\right] = \frac{1}{2}\left[\psi_0^2 + \psi_1^2 + 2\psi_0\psi_1\cos(\omega_{vib}t)\right]$$

Probability density oscillates at the vibrational frequency!





What happens to the expectation value <x>?

$$\langle x\rangle = \int_{-\infty}^{\infty}\Psi^*(x,t)\hat{x}\Psi(x,t)\,dx$$

$$= \frac{1}{2}\int_{-\infty}^{\infty}\left[\psi_0^*(x)e^{i\omega_0 t} + \psi_1^*(x)e^{i\omega_1 t}\right]x\left[\psi_0(x)e^{-i\omega_0 t} + \psi_1(x)e^{-i\omega_1 t}\right]dx$$

$$= \frac{1}{2}\left[\underbrace{\int_{-\infty}^{\infty}\psi_0^* x\psi_0\,dx}_{\langle x\rangle_0 = 0} + \underbrace{\int_{-\infty}^{\infty}\psi_1^* x\psi_1\,dx}_{\langle x\rangle_1 = 0} + \int_{-\infty}^{\infty}\psi_1^* x\psi_0 e^{i(\omega_1-\omega_0)t}dx + \int_{-\infty}^{\infty}\psi_0^* x\psi_1 e^{-i(\omega_1-\omega_0)t}dx\right]$$

$$= \cos(\omega_{vib}t)\int_{-\infty}^{\infty}\psi_0 x\psi_1\,dx$$

<x>(t) oscillates at the vibrational frequency, like the classical H.O.!

Vibrational amplitude is $\int_{-\infty}^{\infty}\psi_0 x\psi_1\,dx$

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\alpha x^2/2} \qquad \psi_1(x) = \frac{1}{\sqrt{2}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\left(2\alpha^{1/2}x\right)e^{-\alpha x^2/2}$$

$$\Rightarrow \quad x\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} xe^{-\alpha x^2/2} = (2\alpha)^{-1/2}\,\psi_1(x)$$

$$\therefore \quad \int_{-\infty}^{\infty}\psi_0 x\psi_1\,dx = (2\alpha)^{-1/2}\int_{-\infty}^{\infty}\psi_0^2\,dx = (2\alpha)^{-1/2} \quad \boxed{\langle x\rangle(t) = (2\alpha)^{-1/2}\cos(\omega_{vib}t)}$$

<u>Relations among Hermite polynomials</u>

Recall H.O. wavefunctions

$$\psi_n(x) = \underbrace{\frac{1}{\left(2^n n!\right)^{1/2}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}}_{\text{Normalization}}\underbrace{H_n\left(\alpha^{1/2}x\right)}_{\text{Hermite polynomial}}\underbrace{e^{-\alpha x^2/2}}_{\text{Gaussian}} \qquad n = 0,1,2,\ldots$$

$$
\begin{array}{lll}
H_0(y)=1 & \text{even} & (n=0) \\
H_1(y)=2y & \text{odd} & (n=1) \\
H_2(y)=4y^2-2 & \text{even} & (n=2) \\
H_3(y)=8y^3-12y & \text{odd} & (n=3) \\
H_4(y)=16y^4-48y^2+12 & \text{even} & (n=4) \\
\vdots & & \vdots
\end{array}
$$

Generating formula for <u>all</u> the H_n:

$$H_n(y)=(-1)^n e^{y^2}\frac{d^n}{dy^n}e^{-y^2}$$

A useful derivative formula is:

$$\frac{dH_n(y)}{dy}=(-1)^n 2ye^{y^2}\frac{d^n}{dy^n}e^{-y^2}+(-1)^n e^{y^2}\frac{d^{n+1}}{dy^{n+1}}e^{-y^2}=2yH_n(y)-H_{n+1}(y)$$

Another useful relation among the H_n's is the <u>recursion formula</u>:

$$H_{n+1}(y)-2yH_n(y)+2nH_{n-1}(y)=0$$

Substituting $2yH_n(y)=H_{n+1}(y)+2nH_{n-1}(y)$ above gives

$$\frac{dH_n(y)}{dy}=2nH_{n-1}(y)$$

Use these relations to solve for momentum $\langle p\rangle(t)$

$$
\begin{aligned}
\langle p\rangle &= \int_{-\infty}^{\infty}\Psi^*(x,t)\,\hat{p}\,\Psi(x,t)\,dx \\
&= \frac{1}{2}\int_{-\infty}^{\infty}\left[\psi_0^*(x)e^{i\omega_0 t}+\psi_1^*(x)e^{i\omega_1 t}\right]\hat{p}\left[\psi_0(x)e^{-i\omega_0 t}+\psi_1(x)e^{-i\omega_1 t}\right]dx \\
&= \frac{1}{2}\Bigg[\underbrace{\int_{-\infty}^{\infty}\psi_0^*\hat{p}\psi_0\,dx}_{\langle p\rangle_0=0}+\underbrace{\int_{-\infty}^{\infty}\psi_1^*\hat{p}\psi_1\,dx}_{\langle p\rangle_1=0}+\int_{-\infty}^{\infty}\psi_1^*\hat{p}\psi_0 e^{i(\omega_1-\omega_0)t}dx+\int_{-\infty}^{\infty}\psi_0^*\hat{p}\psi_1 e^{-i(\omega_1-\omega_0)t}dx\Bigg]
\end{aligned}
$$

$$\frac{d}{dx}\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}(-\alpha x)e^{-\alpha x^2/2} = -\left(\frac{\alpha}{2}\right)^{\frac{1}{2}}\psi_1(x)$$

$$\therefore \quad \int_{-\infty}^{\infty}\psi_1^*\hat{p}\psi_0 e^{i(\omega_1-\omega_0)t}dx = i\hbar\left(\frac{\alpha}{2}\right)^{\frac{1}{2}} e^{i(\omega_1-\omega_0)t}\int_{-\infty}^{\infty}\psi_1^*\psi_1 dx = i\hbar\left(\frac{\alpha}{2}\right)^{\frac{1}{2}} e^{i\omega_{vib}t}$$

To solve integral $\int_{-\infty}^{\infty}\psi_0^*\hat{p}\psi_1 e^{-i(\omega_1-\omega_0)t}dx$ use relations among H_n's

$$\frac{d}{dx}\psi_1(x) = \frac{d}{dx}\left[N_1 H_1\left(\alpha^{1/2}x\right)e^{-\alpha x^2/2}\right] = \alpha^{1/2}N_1\frac{d}{dy}\left[H_1(y)e^{-y^2/2}\right]$$

$$\text{with} \quad y \equiv \alpha^{1/2}x \quad dy = \alpha^{1/2}dx \quad dx = \alpha^{-1/2}dy \quad \frac{d}{dx} = \alpha^{1/2}\frac{d}{dy}$$

$$\frac{d}{dx}\psi_1(x) = \alpha^{1/2}N_1\left[\frac{d}{dy}H_1(y)e^{-y^2/2} - yH_1(y)e^{-y^2/2}\right]$$

$$\frac{d}{dy}H_1(y) = 2nH_0(y) = 2H_0(y)$$

$$yH_1(y) = \frac{1}{2}\left[2nH_0(y) + H_2(y)\right] = H_0(y) + \frac{1}{2}H_2(y)$$

$$\frac{d}{dx}\psi_1(x) = \alpha^{1/2}N_1\left[H_0(y)e^{-y^2/2} - \frac{1}{2}H_2(y)e^{-y^2/2}\right] = \alpha^{1/2}N_1\left[\frac{1}{N_0}\psi_0(x) - \frac{1}{2N_2}\psi_2(x)\right]$$

$$\int_{-\infty}^{\infty}\psi_0^*\hat{p}\psi_1 e^{-i(\omega_1-\omega_0)t}dx = e^{-i(\omega_1-\omega_0)t}(-i\hbar)\int_{-\infty}^{\infty}\psi_0^*\frac{d}{dx}\psi_1 dx$$

$$= e^{-i(\omega_1-\omega_0)t}(-i\hbar)\alpha^{1/2}N_1\left[\frac{1}{N_0}\int_{-\infty}^{\infty}\psi_0^*\psi_0 dx - \frac{1}{2N_2}\int_{-\infty}^{\infty}\psi_0^*\psi_2 dx\right]$$

$$= e^{-i(\omega_1-\omega_0)t}(-i\hbar)\alpha^{1/2}\frac{N_1}{N_0} = -i\hbar\left(\frac{\alpha}{2}\right)^{\frac{1}{2}}e^{-i\omega_{vib}t}$$

Finally

$$\langle p\rangle(t)=\frac{1}{2}\left[i\hbar\left(\frac{\alpha}{2}\right)^{\frac{1}{2}}\left(e^{i\omega_{vib}t}-e^{-i\omega_{vib}t}\right)\right]=-\hbar\left(\frac{\alpha}{2}\right)^{\frac{1}{2}}\sin\left(\omega_{vib}t\right)$$

Average momentum also oscillates at the vibrational frequency.