

## Harmonic Oscillator – 09 update – use pib to “think through”

Consider one ball on a spring  
 Hook's law states that restoring force

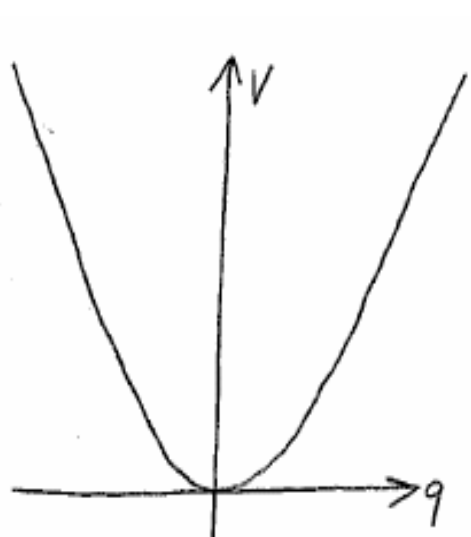
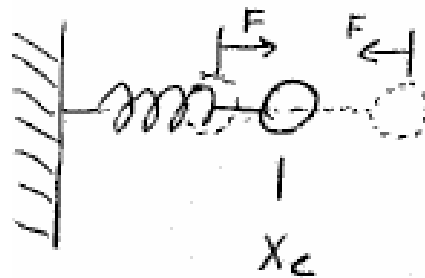
$$F = -k(x - x_e) = -kq$$

$$q = \Delta x \quad \leftarrow \text{displacement}$$

$$F = -\partial V / \partial q \quad [\text{recall: } d(kq^2)/dq = 2kq]$$

$$V = \frac{1}{2} kq^2 \quad k = \text{force constant}$$

$$T = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial q^2}$$



$$H\psi = \left( \frac{-\hbar^2}{2m} \frac{d^2}{dq^2} + (1/2) kq^2 \right) \psi = E\psi$$

T                      V

- a) like a box with sloped sides  
 – softer potential - **expect penetrate**
- b) still a well - **expect oscillator**
- c) must be integrable – **expect damping, i.e. w/f goes to 0 at  $q = \pm\infty$**

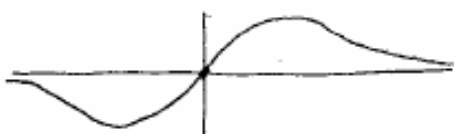
Trial:  $\psi \sim f(q)e^{-\alpha q}$  only will work on one side

**Solution:**  $\psi \sim f(q)e^{-\alpha q^2}$  works both -- ( $\alpha$  must positive)

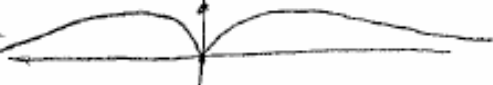
$f(q) \sim \text{const}$



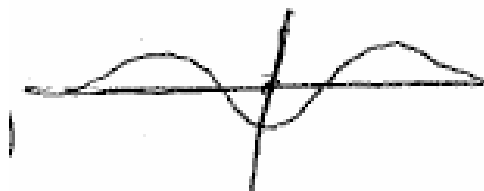
$\sim q$



$\sim q^2$



$f(q)$  – polynomial form works  
 $f_0 \sim \text{const}$  orthog.  $f_1 \sim q$  (odd-even)



→ orthog. if  $f_2(q) \sim q^2 - \text{const}$

Result – see text nice pictures-  
not worked out, just picture

Wave function

– modify variable to simplify:

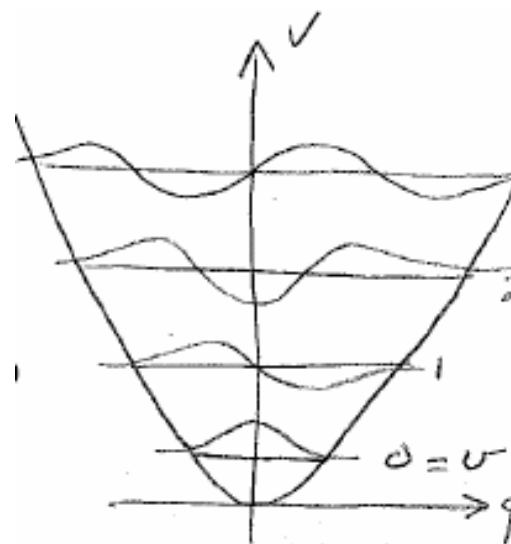
$$\psi_v(y) = H_v(y) e^{-y^2/2}$$

$v = 0, 1, 2, \dots$  (quantize)

recursion formula:

$$H_v(y) = (-1)^v e^{y^2} d^v/dy^v (e^{-y^2})$$

$$y = \alpha^{1/2} q \quad \alpha = 2\pi\sqrt{mk}/h = \sqrt{mk}/\hbar$$



non-classical: see wavefunction penetrate potential

Chemistry Place addresses difference with classical

Hermite polynomials:

ex:  $H_0 = 1$

$$H_1 = 2y$$

$$H_2 = 4y^2 - 2$$

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

**note:** – odd - even progression

– alternate exponents

–  $\infty$  number solutions

– exponential damping

thus:  $\psi_v = A_v H_v(y) e^{-y^2/2}$   $y = \alpha^{1/2} q$   $A_v = (2^n n!)^{-1/2} (\alpha/\pi)^{1/4}$

Homework: insert  $\psi_v$  into Schrödinger equation to get:

$$\begin{aligned} E_v &= (v + 1/2) \hbar\omega & \omega &= \sqrt{k/m} \\ &= (v + 1/2) h\nu & \nu &= \omega/2\pi \end{aligned}$$

note: – even energy spacing:  $\Delta E = h\nu$

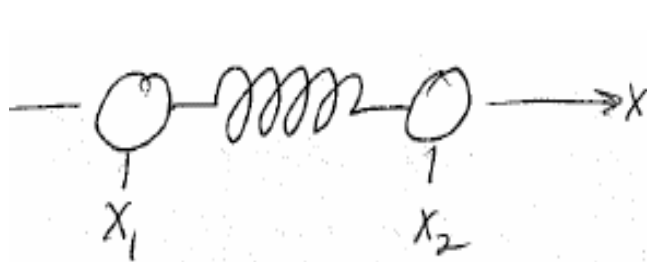
– zero point energy:  $1/2 h\nu$

– heavier mass }  $\Delta E \rightarrow 0$  classical

– weaker force constant  $\Delta E \rightarrow 0$

**Probabilities:** low  $\nu$  – high -middle; high  $\nu$  – high- edge  
 This fits classical, turnaround points  $\rightarrow$  slower motion

To describe two masses on a spring (relate to molecules)



need **change variable**

$$q = (x_2 - x_1) - (x_2^0 - x_1^0)$$

$$= \mathbf{r} - \mathbf{r}_{eq} \quad (3\text{-D represent})$$

$$\mathbf{r} = x_2 - x_1 \quad \text{relative 1-D position}$$

in this case:  $\mu = m_1 m_2 / (m_1 + m_2) \rightarrow$  reduced mass into  $H$

2-mass harmonic oscillator:

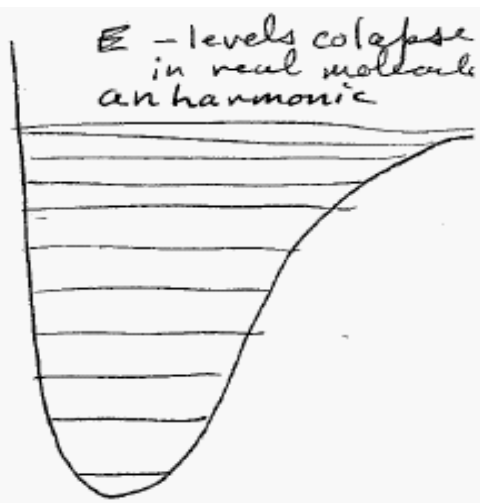
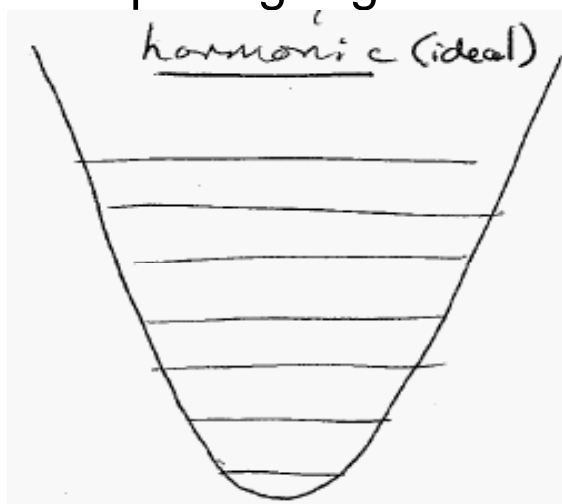
$$H\psi = [(-\hbar^2/2\mu) d^2/dq^2 + 1/2 kq^2]\psi_\nu = E_\nu \psi_\nu$$

and get  $E_\nu = (\nu + 1/2)\hbar\omega = (\nu + 1/2)h\nu$      $\omega = \sqrt{k/\mu}$      $\nu = 1/2\pi\sqrt{k/\mu}$

Use to model vibration of a diatomic molecule – low  $\nu$

harmonic (ideal)  
 spacing regular

E-levels collapse in  
 real molec.  $\rightarrow$  anharmonic



multiatom  $3n - 6$  relative coord – complex but separable

## Two-dimensional Harmonic oscillator:

$$H = T + V$$

$$T = -\hbar^2/2m (\partial^2/\partial x^2 + \partial^2/\partial y^2)$$

$$\begin{aligned} V &= V(x, y) \quad \text{expand about } x=0, y=0 \rightarrow \text{use } f(x) = \sum_n [1/n!] d^n f/dx^n|_{x_0} (x-x_0)^n \\ &= V(0, 0) + \partial V/\partial x|_0 x + \partial V/\partial y|_0 y + \frac{1}{2} \partial^2 V/\partial x^2|_0 x^2 \\ &\quad + \frac{1}{2} \partial^2 V/\partial y^2|_0 y^2 + \frac{1}{2} \partial^2 V/\partial x \partial y|_0 xy + 1/6 \partial^3 V/\partial x^3|_0 x^3 \dots \text{etc.} \end{aligned}$$

- more complex potential – many terms, Taylor expansion
- not separated -- cross-terms like  $\partial^2 V/\partial x \partial y$  mix variables
- $V(0, 0) = 0$  – arbitrary constant - ignore (part of E)
  - $\partial V/\partial x|_0 = \partial V/\partial y|_0 = 0$  – evaluate derivative at min. choose  $x = 0, y = 0$  as the minimum
  - —same as choosing  $q=0$  as  $x_e-x$

Then 
$$\begin{aligned} V &= \frac{1}{2} (\partial^2 V/\partial x^2)_0 x^2 + \frac{1}{2} (\partial^2 V/\partial y^2)_0 y^2 + \frac{1}{2} (\partial^2 V/\partial x \partial y)_0 xy \\ &= \frac{1}{2} k_x x^2 + \frac{1}{2} k_y y^2 + \frac{1}{2} k_{xy} xy + \dots \end{aligned}$$

where  $k_x = (\partial^2 V/\partial x^2)_0$  etc. – force constant

- so form just like harmonic oscillator, if neglect high order terms, like  $x^3$  and solvable if can separate
  - do change of variable  $x, y \rightarrow q_1, q_2$  where  $q_1, q_2$  chosen so that potential is not coupled, mixed coord.
  - $V(q_1, q_2) = \frac{1}{2} k_1 q_1^2 + \frac{1}{2} k_2 q_2^2$
- call this diagonalized potential – use matrix approach can do to arbitrary accuracy
  - also works for n-dimensions:  $(3n - 6)$  vibration

Basis for vibrational spectroscopy – IR and Raman