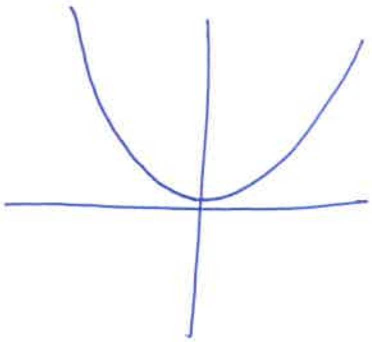
Harmonic Oscillator ~~Part I~~



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

Classically, $x = A\cos(\omega t + \phi)$, with $\omega = \sqrt{\frac{k}{m}}$

Only one frequency here. We expect that to show up also in osc. of Schr. waves

$$H = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

We will find e.f.s by 19th century math tricks. Later we will do a more elegant approach. But nothing is mysterious here — just solving dif. eq.s

Find e.f.s $\psi_n(x)$

s.t. $H\psi_n(x) = E_n\psi_n(x)$

First, simplify by rescaling:

$$\beta = \left[\frac{mk}{\hbar^2}\right]^{1/4} = \left[\frac{m\omega}{\hbar}\right]^{1/2}$$

$k = \omega^2 m$

So that

$$\frac{1}{2}\underbrace{\left[\frac{\hbar^2 k}{m}\right]^{1/2}}_{\hbar\omega}\cdot\left[-\frac{d^2}{d(\beta x)^2}+(\beta x)^2\right]\varphi_n(x)=E_n\,\varphi_n(x)$$

Progress. Now define $z=\beta x=\left[\frac{m\omega}{\hbar}\right]^{1/2}x$ & $\mathcal{E}_n=\frac{E_n}{\hbar\omega}$

rescaled distance   rescaled energy

~~18th cent math skills for problems like this~~

$\cancel{\frac{1}{2}\left(-\frac{d^2}{dz^2}\right.}$

$$\boxed{\frac{1}{2}\left(-\frac{d^2}{dz^2}+z^2\right)\varphi_n(z)=\mathcal{E}_n\,\varphi_n(z)}$$

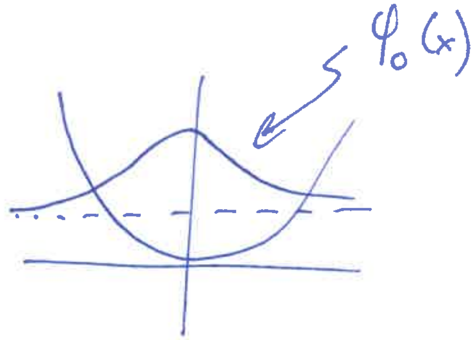
Guess one solution:

$$\varphi_0(z)=e^{-z^2/2}$$

$$-\frac{d^2}{dz^2}\left(e^{-z^2/2}\right)=-\frac{d}{dz}\left(-z\,e^{-z^2/2}\right)=\left(-z^2+1\right)e^{-z^2/2}$$

$$\Rightarrow\ \frac{1}{2}\left(-\frac{d^2}{dz^2}+z^2\right)e^{-z^2/2}=\frac{1}{2}\,e^{-z^2/2}$$

This is an e.f. of the form



$$E_0 = \hbar\omega\,\varepsilon_0 = \tfrac{1}{2}\hbar\omega$$

Famous h.m. zero-point energy. Same idea we saw with particle in box.

To find other e.f.s, write

$$\varphi_n(z) = h_n(z)e^{-z^2/2}$$

$$-\frac{d^2}{dz^2}\left(h_n(z)e^{-z^2/2}\right) = -\frac{d}{dz}\left(\left(h_n' - z h_n\right)e^{-z^2/2}\right)$$

$$= -\left(+h_n'' - z h_n' - z h_n' - h_n + z^2 h_n\right)e^{-z^2/2}$$

$$= \left(-h_n'' + 2z h_n' - z^2 h_n + h_n\right)e^{-z^2/2}$$

So $\Rightarrow$ $\frac{1}{2}\left(-\frac{d^2}{dz^2}+z^2\right)h_n e^{-z^2/2} = \varepsilon_n h_n e^{-z^2/2}$

becomes

$$\boxed{-h_n'' + 2z h_n' = \lambda_n h_n} \quad , \text{ where } \lambda_n = (2\varepsilon_n - 1)$$

At first, this e.v. problem looks as bad as original.

However, try simple functions: (But this is where 19th cent math shines, solving stuff like this)

$h_0(z) = 1$. Satisfies eqn if $\lambda_0 = 0$

$h_1(z) = z$. " " " $\lambda_1 = 2$

(won't quite work, so use tilde)

$\tilde{h}_2(z) = z^2$ gives $-\tilde{h}_2'' + 2z\tilde{h}_2' = 4z^2 - 2$

Almost. (z^2 on RHS part right) patch up by adding a constant (LHS stays same + RHS gets addition of ~~constant~~ -2)

$h_2(z) = z^2 - \frac{1}{2}$ satisfies eqn if $\lambda_2 = 4$

$(4 \times -\frac{1}{2} = -2 \checkmark)$

Similarly

$h_3 = z^3 - \frac{3}{2}z$ ~~gives~~ works with $\lambda_3 = 6$

Almost clear by now that this Pattern emerges:

For any n, we can write

$$h_n = z^n - a_2 z^{n-2} - a_4 z^{n-4} - \dots$$

Then leading terms are (those w/ highest power of z):

LHS $\qquad\qquad\qquad\qquad\qquad\qquad$ RHS

$$2z h_n' = 2n z^n - \dots \qquad = \lambda_n h_n = \lambda_n z^n - \dots$$

$$\Rightarrow \lambda_n = 2n$$

Then we can take it order by order to determine $a_2, a_4, \dots$ to make this polynomial an e.f.

- It is conventional to normalize these polynomials so that the leading term is $(2z)^n$
- Then these are the Hermite polynomials $H_n(z)$, which are characterized by

$$\left[\frac{d^2}{dz^2} - 2z\frac{d}{dz} + 2n\right] H_n(z) = 0$$

Successive H_n give an inf series of

soln's to Schr eqn:

$$\varphi_n(x) = H_n(\beta x)\, e^{-\frac{1}{2}(\beta x)^2} \quad , \left(\beta = \left(\frac{m\omega}{\hbar}\right)^{1/2} \ \& \ \varepsilon_n = \frac{E_n}{\hbar\omega}\right)$$

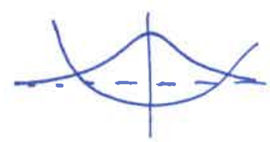
$$E_n = \left(n + \tfrac{1}{2}\right)\hbar\omega$$

b/c $\lambda_n = 2\varepsilon_n - 1$

& $\lambda_n = 2n$ $\Rightarrow \varepsilon_n = n + \frac{1}{2}$

Writing first few

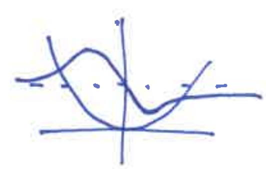
$$\varphi_0 = e^{-\frac{1}{2}(\beta x)^2}$$



0 nodes

$$\varphi_1 = \beta x\, e^{-\frac{1}{2}(\beta x)^2}$$

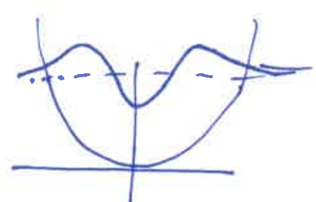
Gaussian × line



1 node

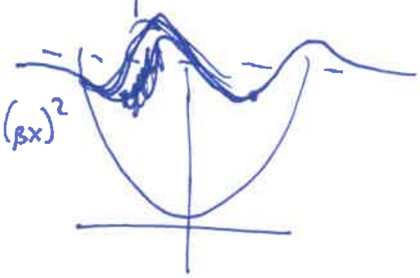
$$\varphi_2 = \left(4(\beta x)^2 - 2\right) e^{-\frac{1}{2}(\beta x)^2}$$

Gaussian × quadratic w/ min < 0



2 nodes

$$\varphi_3 = \left(8(\beta x)^3 - 12(\beta x)\right) e^{-\frac{1}{2}(\beta x)^2}$$



3 nodes

~~[illegible]~~

Arguments from last lecture imply

① Completeness

$(\varepsilon_n \neq \varepsilon_m$ for $n \neq m$ $\Rightarrow$ non degenerate)

+ ② Orthogonality $\rightarrow \int dz\, e^{-z^2} H_n(z) H_m(z) = 0$ for $n \neq m$

- Both can be proven ~~[illegible]~~ explicitly, but we already know they must be true ~~[illegible]~~ from ~~[illegible]~~ valid arguments

- Normalization takes some not so fun ~~t~~edious work, but

$$\int dz\, e^{-z^2} (H_n(z))^2 = \sqrt{\pi}\, 2^n n!$$

Normalized

$$\boxed{\Rightarrow \varphi_n(x) = \left[\frac{\beta}{\sqrt{\pi}} \frac{1}{2^n n!}\right]^{1/2} H_n(\beta x) e^{-\frac{1}{2}(\beta x)^2} \qquad E_n = \hbar\omega\left(n+\tfrac{1}{2}\right) \qquad \int dx\, \varphi_n(x)\varphi_m(x) = \begin{cases} 1 & n=m \\ 0 & n \neq m \end{cases}}$$

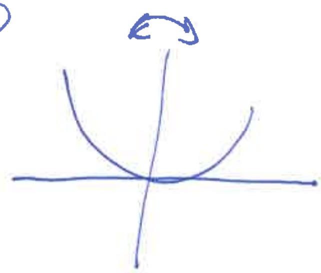
Harmonic Oscillator, Part II

Symmetry of potential has implications

$V(x)$ is symmetric w.r.t. $x \to -x$

(A) $\frac{1}{2}kx^2 = \frac{1}{2}k(-x)^2$

(B)



Saying same thing

Does this mean that e.f. of Schr. eqn. are also symmetric?

No! Need to be able to sum them to get arb. functions, so they cannot be:

But... let's look

$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right)\varphi_n(x) = E_n\varphi_n(x)$$

for $x \to -x$

$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right)\varphi_n(-x) = E_n\varphi_n(-x)$$

Schr. eqn w/ this potential unchanged if we flip axis, or equivalently look at the potential from the opposite direction

G

So, if ~~Since~~ $\varphi_n(x)$ is an e.f., then $\varphi_n(-x)$ is also,

with same eigenvalue.

$\Rightarrow$ $\varphi_n(-x)$ is prop to $\varphi_n(x)$

$$\Rightarrow \varphi_n(x) = c\,\varphi_n(-x)$$

If that's true, then taking $x \to -x$ again in 2nd equation yields...

$$= c\left[c\,\varphi_n(x)\right]$$

$$= c^2\,\varphi_n(x)$$

$$\Rightarrow c^2 = 1 \quad \Rightarrow c = \pm 1$$

"even parity" $\varphi_n(-x) = +\varphi_n(x)$ — Here $n = 0, 2, 4, \ldots$

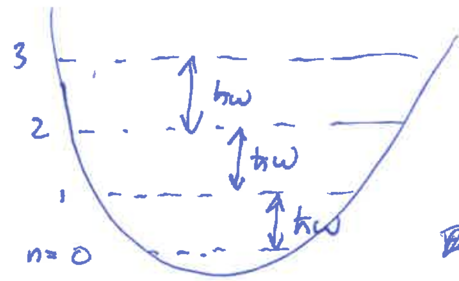
"odd parity" $\varphi_n(-x) = -\varphi_n(x)$ — $n = 1, 3, 5, \ldots$

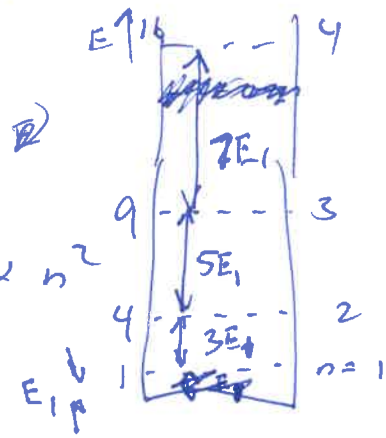
~~4/12-17, 2016, Week 3, Day~~

H.O. spectrum is interesting

No fundamental here

$E = (n+\frac{1}{2})\hbar\omega$





(Recall particle in box had $E \propto n^2$)

- Will discuss later in course how light is emitted when system jumps.

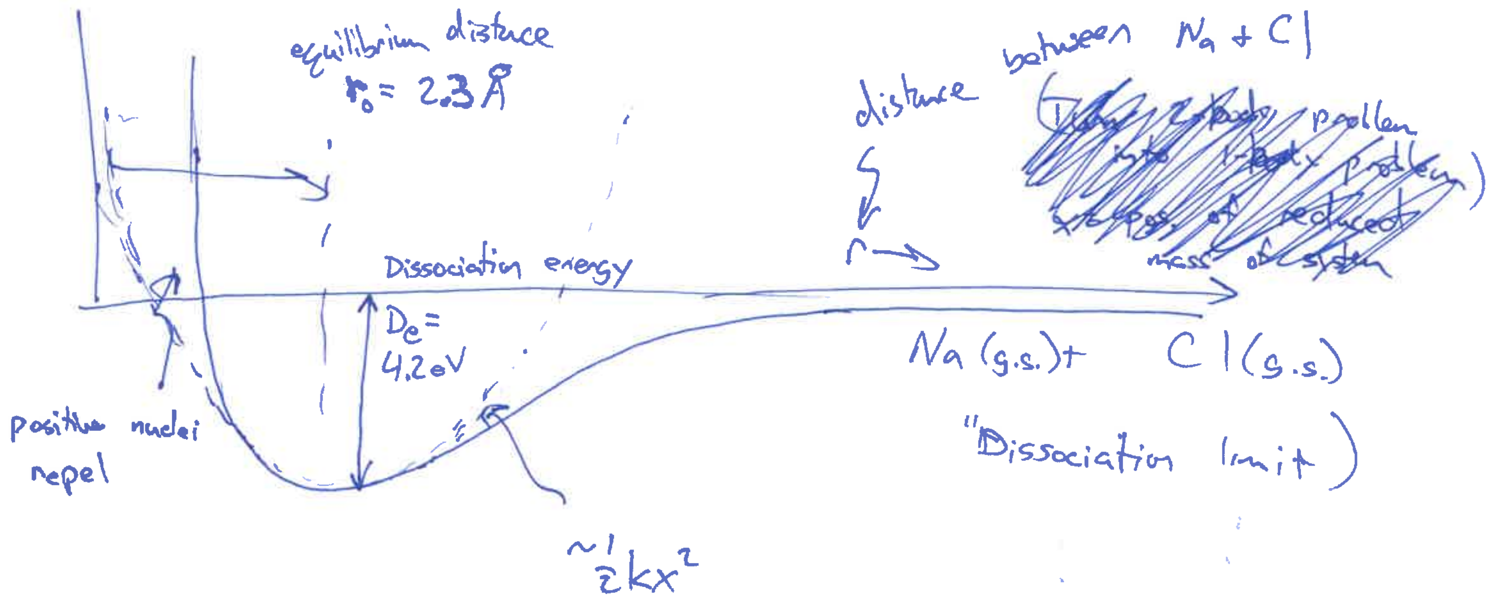
- With H.M., doesn't matter – always same color γ

- Connected with special aspect of classical HM – Period of motion ind. of energy. (Compare w/ part in box, where $E\uparrow \Rightarrow T\downarrow$) T= period

Can think of classically & see QM incarnation too

- All potential minima ~ H.O. locally.

- Consider diatomic molecule NaCl



- Get r_0 + D_e from either measurements of spectrum or "quantum chemistry" theory.

(Rough estimates from glancing @ potential) Bond length $\sim 2Å$, $E \sim 4eV$

- What is k? Need $\frac{1}{2}kx^2 \approx 4\,eV$ for $\Delta x = 2Å$

$$\Rightarrow k \approx 2\,eV/Å^2$$

Reduced mass

$$m = \frac{m_{Na}\, m_{Cl}}{m_{Na} + m_{Cl}} = \frac{22 \cdot 35}{22+35}\,amu = 13\,amu$$

$$\Rightarrow \omega = \sqrt{\frac{k}{m}} = \left(\frac{2\,eV/Å^2}{13\,amu}\right)^{1/2} = \left(\frac{2 \times 1.6\times10^{-19}\,J/(10^{-10})^2\,m^2}{13 \times 1.6\times10^{-27}\,kg}\right)^{1/2}$$

$\boxed{5}$

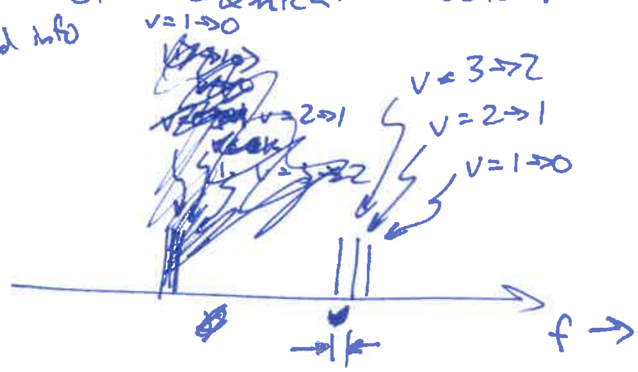
$$\approx \left(\frac{2}{13}\cdot 10^{28}\right)^{1/2} s^{-1} = 0.4\times 10^{14}\ s^{-1} \qquad f = \frac{\omega}{2\pi} = 6\times 10^{12}\ \mathrm{Hz} = 6\ \mathrm{THz}$$

$$\lambda = \frac{c}{f} = \frac{2\pi c}{\omega} = 25\ \mu m$$

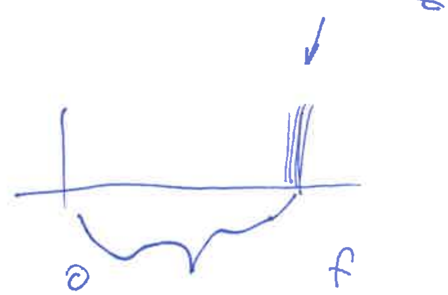
Near IR

⇒ Near IR spectroscopy tells you about details of chemical bond.

e.g. ⓪ What is f?
① What is frequency ⇒ bond info
②



$\Delta f = 0$ for H.M.



or

(How harmonic is well?)

Does QM HM Oscillate?

probability density

$$P_{x,x+\Delta x} = \rho(x)\,\Delta x$$

$$\rho(x) = |\psi(x,t)|^2$$

~~Ret~~ If we are in one eigenstate

$$\psi(x,0) = \varphi_n(x)$$

$$\psi(x,t) = \varphi_n(x)\,e^{-i\omega_n t} \qquad \omega_n = \frac{E}{\hbar} = (n+\tfrac{1}{2})\omega\,, \quad \omega = \sqrt{\frac{k}{m}}$$

$$= H_n(x)\,e^{-\frac{1}{2}(\beta x)^2}\,e^{-i(n+\frac{1}{2})\hbar\omega t}$$

$$|\psi(x,t)|^2 = H_n^2(x)\,e^{-(\beta x)^2}$$

No time dep.

"Stationary state"

- In what ways does QM osc. behave like classical osc.?

- Lets consider $P_x = |\psi(x,t)|^2$.

(write last) $e^{-i\frac{\omega}{2}t}$

$$\psi(x,t) = \sum_{n=0}^{\infty} c_n H_n(\beta x) e^{-\frac{1}{2}(\beta x)^2} e^{-in\omega t}$$

Since $E_n = (n+\frac{1}{2})\hbar\omega$

$$\Rightarrow \omega_n = \frac{E_n}{\hbar} = (n+\tfrac{1}{2})\omega$$

- First prefactor is unimportant for $|\psi(x,t)|^2$, since

$$|e^{i\alpha(t)}|^2 = 1 \qquad e^{im\omega t} e^{-in\omega t} = e^{i(m-n)\omega t}$$

- So, notice that $|\psi(x,t)|^2$ will be periodic with period $T = \frac{2\pi}{\omega}$.

(Fundamental $|m-n|=1$ has that period & $|m-n|=2$ twice as fast b is a periodic there also)

Take superposition of adjacent states

$$\psi(x,t) = \frac{1}{\sqrt{2}}\varphi_2(x)e^{-i2\omega t} + \frac{1}{\sqrt{2}}\varphi_3 e^{-i3\omega t}$$

$$|\psi(x,t)|^2 = \left(\frac{1}{2}\right)\left|e^{-i2\omega t}\right|^2 \left|\left(\varphi_2(x) + \varphi_3(x)e^{-i\omega t}\right)\right|^2$$

$|\alpha\beta| = |\alpha|\,|\beta|$

$a = \alpha e^{i\phi_a}$ $\quad a, b$ real

$b = \beta e^{i\phi_b}$

$ab = \alpha\beta e^{i(\phi_a+\phi_b)}$

$|ab| = \alpha\beta = |\alpha|\,|\beta|$

$$= \frac{1}{2}\left|\varphi_2(x)e^{+i\frac{\omega}{2}t} + \varphi_3(x)e^{-i\frac{\omega t}{2}}\right|^2$$

$$= \left(\frac{1}{2}\right)(\varphi_2\gamma + \varphi_3\gamma^*)(\varphi_2^*\gamma^* + \varphi_3\gamma)$$

$$= \left(\frac{1}{2}\right)\left[\varphi_2^2 + \varphi_3^2 + (\varphi_2\varphi_3)\underbrace{(\gamma\gamma + \gamma^*\gamma^*)}_{e^{i\omega t} + e^{-i\omega t} = 2\cos\omega t}\right]$$

$$|\psi(x,t)|^2 = \left(\frac{1}{2}\right)\left(\varphi_2^2(x) + \varphi_3(x)^2 + 2\varphi_2(x)\varphi_3(x)\cos\omega t\right)$$

Would have same form ~~but~~ same frequency (but not same spatial dep) for any adj levels. Not so for $\square$