Energy and wavefunctions of H. O. and vibrational spectroscopy

Note Title 26-10-2009

Administrative Business

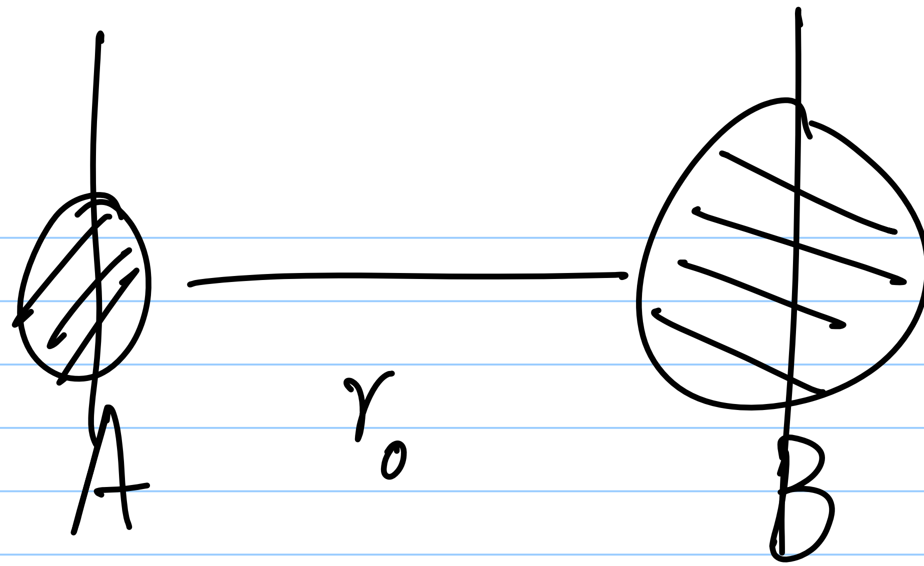
Reminor I and II

Friday, Oct. 30, 1715 hrs.

Confirm with NDK/SD before Thursday Oct. 29 if you have a valid medical reason (MC required)

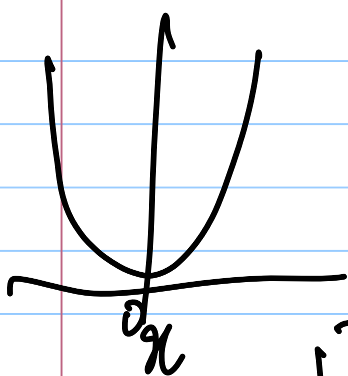
Quiz II - 1st week of November. Details to TBA

No re-quizzes!



Restoring force $\propto$ displacement from equilibrium

$$V = \frac{1}{2} k x^2$$



$$\left(-\frac{\hbar^2}{2\mu/m}\frac{d^2}{dx^2} + \tfrac{1}{2}kx^2\right)\psi = E\psi$$

displacement from equilibrium

$$\boxed{\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}}$$

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

(classical)

$y = \alpha x$ $\qquad \alpha = \left(\dfrac{mk}{\hbar^2}\right)^{1/4}$

dimensionless length $\qquad \dfrac{1}{m^4}$

dimensionless energy $\lambda = \dfrac{2E}{\hbar\omega}$

① — $\dfrac{d^2\psi}{dy^2} + (\lambda - y^2)\psi = 0$

Asymptotic solution

$$\frac{d^2\psi}{dy^2} - y^2\psi = 0$$

$$\psi \sim e^{\pm \frac{1}{2} y^2}$$

$$\psi_{asymp} = e^{-\frac{1}{2}y^2}$$

$$\boxed{\psi(y)} = (\text{polynomial in } y) \times e^{-y^2/2}$$

$$= \boxed{H(y) \times e^{-y^2/2}} \quad \text{--- } ②$$

$$H(y) = a_0 + a_1 y + a_2 y^2 + \cdots$$

$$\frac{d^2H}{dy^2} - 2y\frac{dH}{dy} + (\lambda - 1)H = 0$$

$$a_{s+2} = \frac{2s+1-\lambda}{(s+2)(s+1)} a_s, \quad s \geq 0$$

→ Recurrence relation

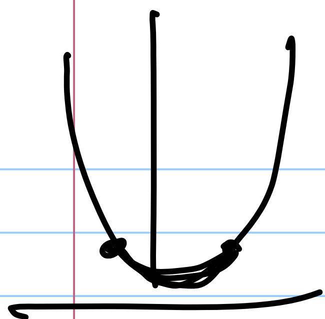
$a_1 = 0$ (even terms)

$a_0 = 0$ (odd terms)

$$e^{y^2} \times e^{-y^2/2}$$

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

$$E = (n + 1/2)\hbar\omega$$



$$\psi = a_0' + a_1' y + a_2' y^2 + \cdots$$

Frobenius series solution

$$a_k = ?\, a_k'$$

ZPE $= \frac{1}{2}\hbar\omega$

$n\hbar\omega$

$(n + \boxed{\tfrac{1}{2}})\hbar\omega$

$0, 1, 2, \ldots$

$H_0 = 1$

$$\psi(n=0) = H_0 e^{-y^2/2} \quad / \quad \tfrac{1}{2}\hbar\omega$$

$$\psi(n=1) = H_1 e^{-y^2/2} \quad / \quad \tfrac{3}{2}\hbar\omega$$

$$\psi(n=2) = H_2 e^{-y^2/2} \quad / \quad \tfrac{5}{2}\hbar\omega$$

$$\vdots$$

"Hermite polynomials" $H_0 = 1$

"even parity"

$H_1 = 2y$

"odd parity" $H_2 = 4y^2 - 2$

$e^{-y^2/2}$

even

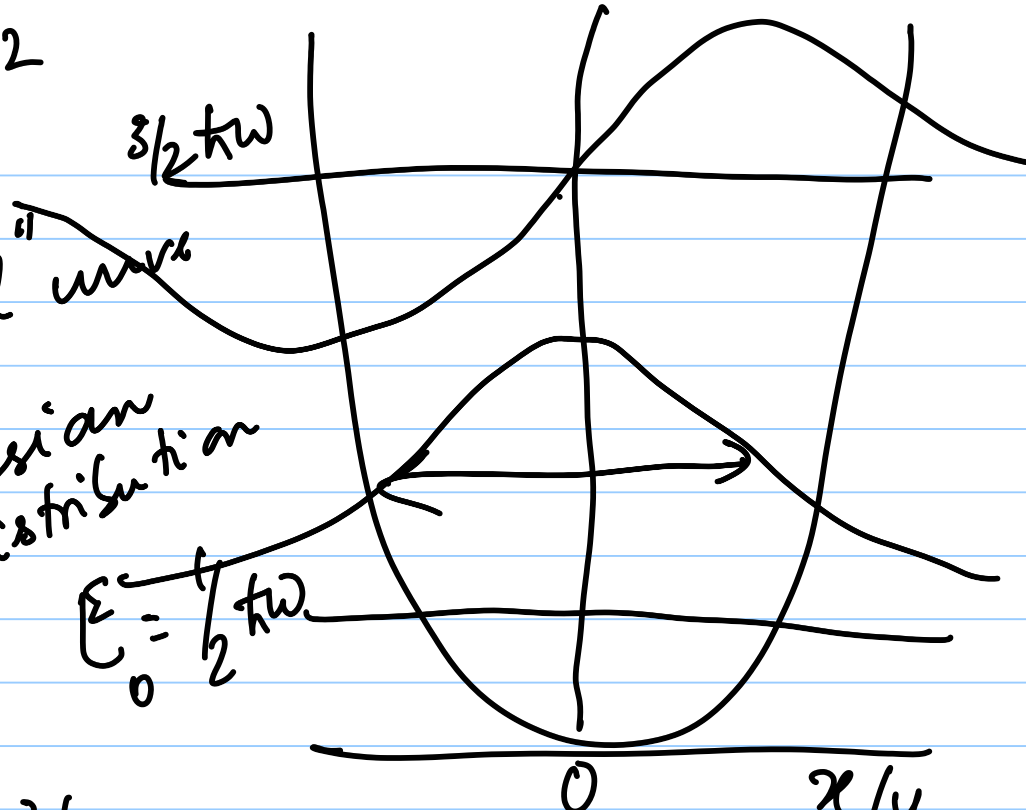
$H_3 = 8y^3 - 12y$

$H_{n+1} = 2y\, H_n(y) - 2n\, H_{n-1}(y)$

$$\psi_0 = e^{-y^2/2}$$

"Bell" curve

Normal / Gaussian distribution



$$\psi_1 = 2y\, e^{-y^2/2}$$

$$\psi_2 = (4y^2 - 2)\, e^{-y^2/2}$$

$$N_n = \frac{1}{\sqrt{2^n n!}} \sqrt{\frac{\alpha}{\sqrt{\pi}}}$$

$$\alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4}$$

Always

$$\psi = H_n\left(\frac{x}{\alpha}\right) e^{-\frac{x^2/\alpha^2}{2}}$$

$$\langle x \rangle = \int_{-\infty}^{\infty} \underbrace{\psi_0^*}_{\text{even}} \; \underbrace{x}_{\text{odd}} \; \underbrace{\psi_0}_{\text{even}} \, dx$$

$$= 0$$

$$\underset{\uparrow}{\mathcal{H}} \psi = E \psi$$

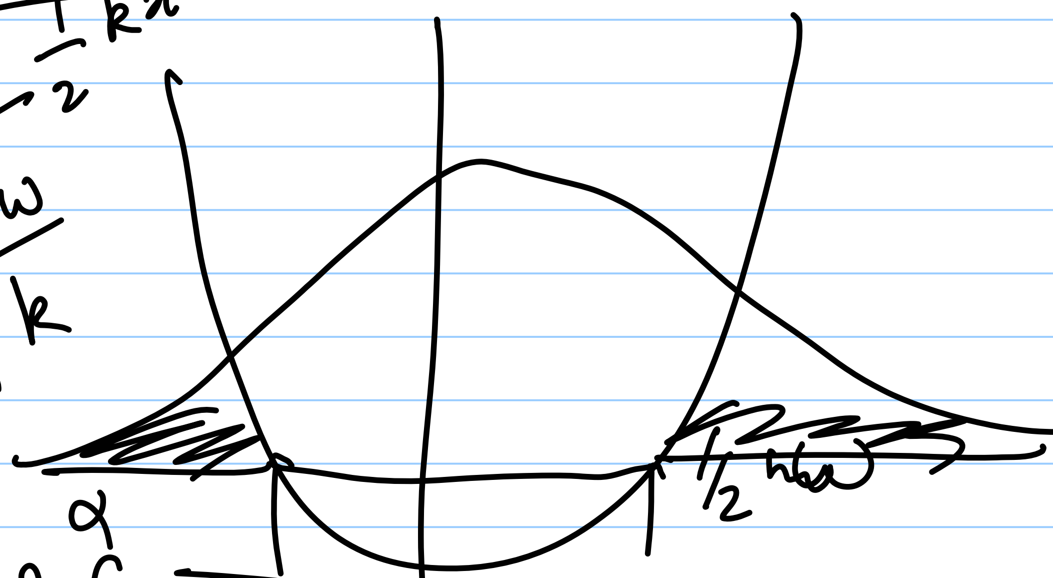
$$\langle V \rangle = \left\langle \frac{1}{2} k x^2 \right\rangle = \frac{1}{2} k \langle x^2 \rangle$$

$$= E/2$$

Prob. of finding the oscillator in the classically forbidden region

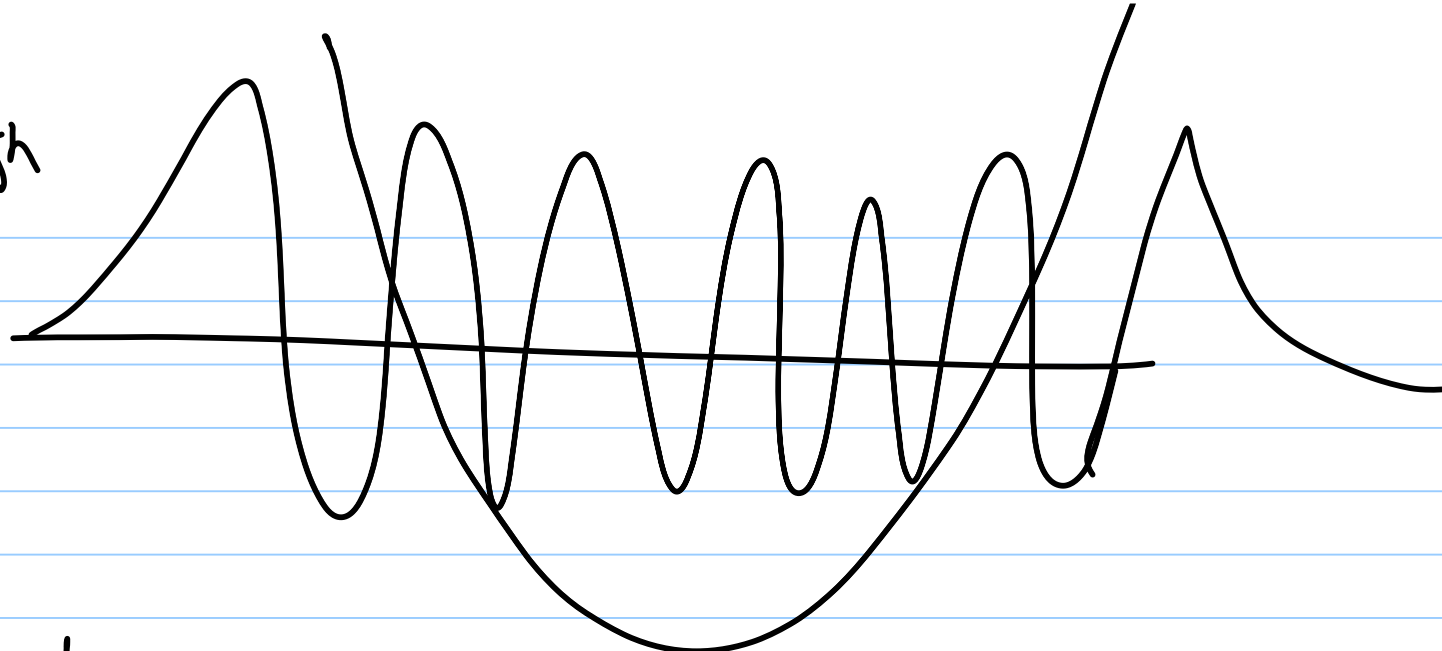
$$E = \frac{1}{2}\hbar\omega = \frac{1}{2}kx^2$$

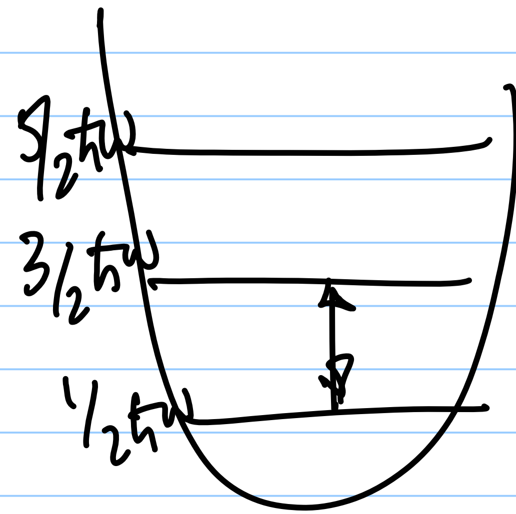
$$x_{tp} = \pm\sqrt{\frac{\hbar\omega}{k}}$$

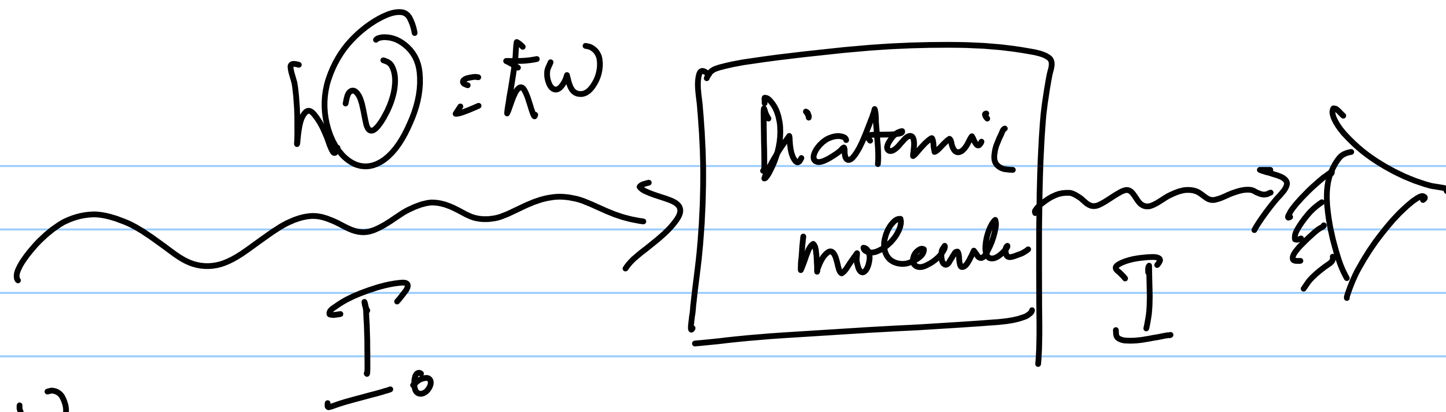


$$P(>x_{tp}) = 2\int_{x_{tp}}^{\infty} \psi_0^* \psi_0 \, dx \neq 0$$

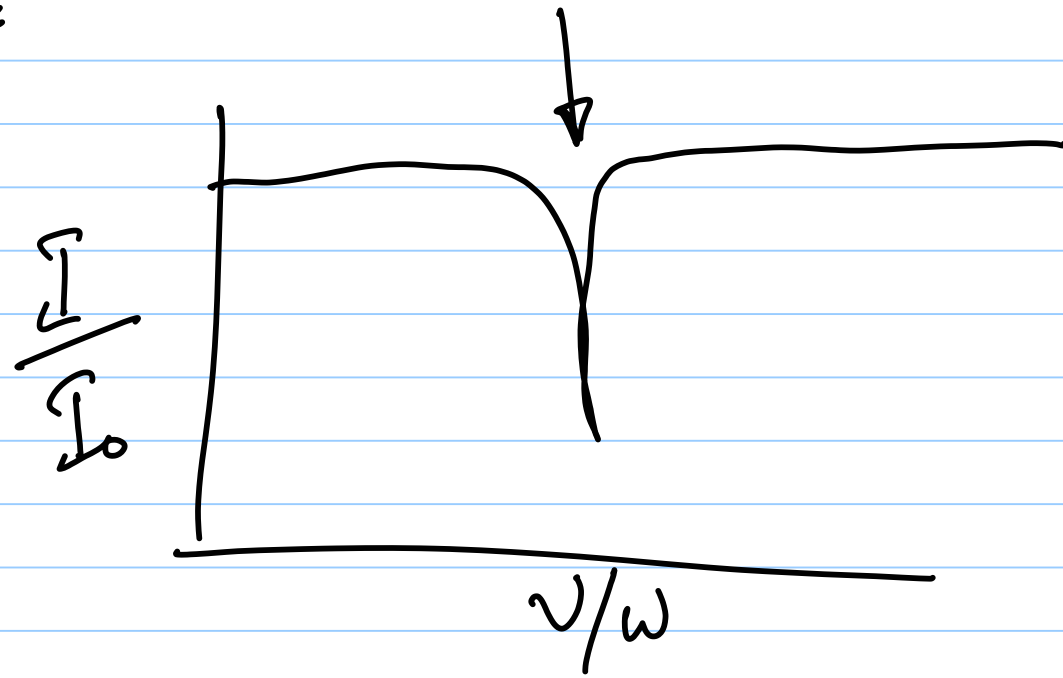
very high







$\Delta E = \hbar\omega$



$400 - 4000\ \mathrm{cm}^{-1}$ (Infrared)

$$\omega = \sqrt{\frac{k}{\mu}}$$

$\hbar\omega$

$1000\ \mathrm{cm}^{-1}$

$Ni(CO)_4$

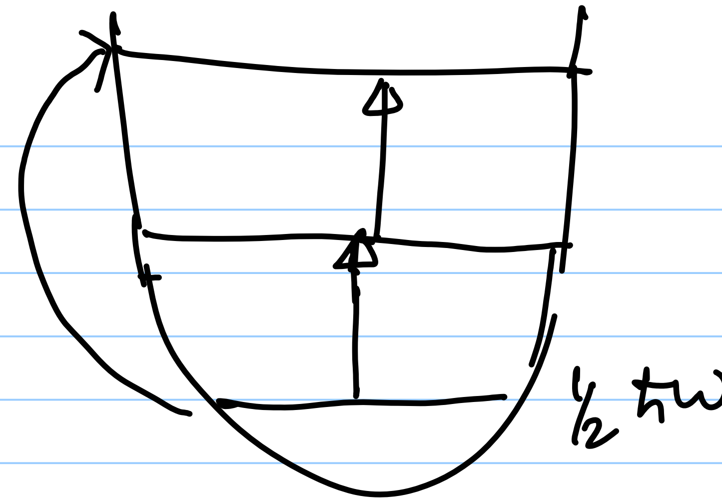
typical values
$k \approx 100\ \mathrm{N/m}$

$C \overset{k}{-} H \quad \mu_{C-H}$

$C \overset{k}{-} D \quad \mu_{C-D}$

$$\boxed{C \equiv O}$$

$$M - C \underset{k'}{\overset{k}{\equiv}} O$$



$$E = \left(n + \tfrac{1}{2}\right)\hbar\omega \qquad \omega = \sqrt{\frac{k}{m}}$$

$$n = 0, 1, 2, 3, \ldots$$

$$\psi_n = N_n \underbrace{H_n}_{\text{odd/even}}(\alpha x)\, \underbrace{e^{-\alpha^2 x^2}}_{\text{even}}$$

$$\boxed{\langle x^2 \rangle = \int_{-\infty}^{\infty} e^{-kx^2} x^2 \, dx}$$

$$\underbrace{\quad}_{I_1 I_2} \quad I_1^2 \qquad \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-k(x^2+y^2)} x^2 y^2 \, dx \, dy$$

$$I_1^2 \quad \int_{-\infty}^{\infty} e^{-kx^2} x^2 \, dx$$

$$I_2 = \int_{-\infty}^{\infty} e^{-ky^2} y^2 \, dy$$