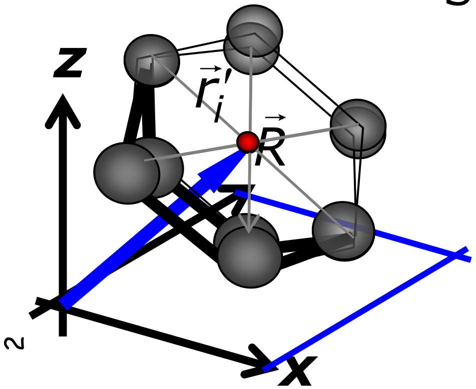
# Harmonic Oscillator

# Harmonic Vibrations of N-Body Systems

Separation of overall (center-of-mass "com"), rot and vib motion:



$$\boxed{\begin{aligned}\hat H(\vec r_1,\vec r_2,..,\vec r_N) &= \hat H_{com}+\hat H_{rot}+\\ &+\hat H_{vib}(\{|\vec r_i-\vec r_j|,|\vec p_i-\vec p_j|\}_{i\neq j})+\hat H_{...}(...)\end{aligned}}$$

Superposition of $N_{vib}$ independent vibrational "normal modes", normal coordinates $\{q_j\}$

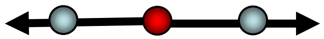
$$\hat H_{vib}(\{|\vec r_i-\vec r_j|,|\vec p_i-\vec p_j|\}_{i\neq j})=\sum_{j=1}^{N_{vib}}\hat H_{vib}(j)$$

$$\hat H_{vib}(j)=-\frac{\hbar^2}{2\mu_j}\frac{\partial^2}{\partial q_j^2}+U(q_j)$$

**No interaction with other degrees of freedom i≠j**

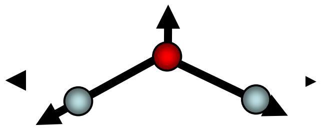
**3 Normal modes of linear molecules**

symmetric stretch (infrared)



asymmetric stretch

bend (2 x)



Generic example: Diatomic molecule (H-Cl),..
Discrete bound (stationary) states at low excitations
Dissociation at high excitations

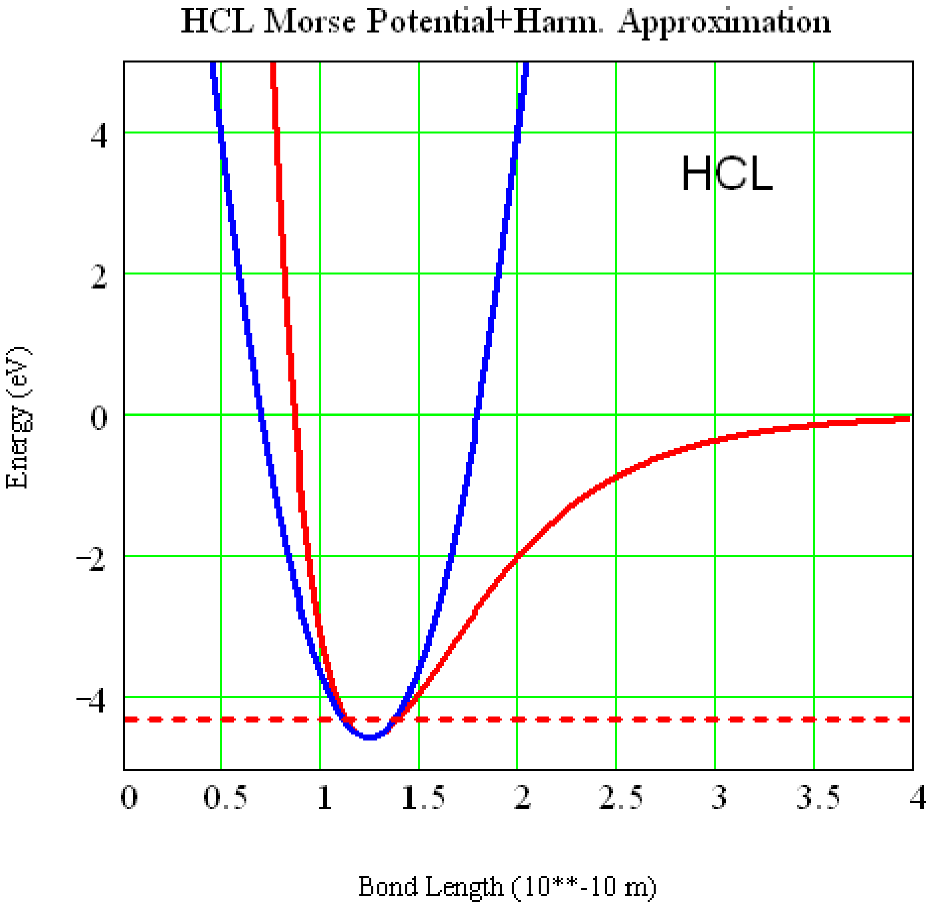
**Dissociation**

Classical vibrational frequency $\varpi_j=\sqrt{\frac{c_j}{\mu_j}}$

$\boldsymbol{c_j}$= Hooke's constant

# Morse Potential and Harmonic Approximation

$$\hat{H}_{vib}(j) = -\frac{\hbar^2}{2\mu_j}\frac{\partial^2}{\partial q_j^2} + U(q_j) = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial q_j^2} + \frac{1}{2}c\left(q_j - q_{j0}\right)^2 + U(q_{j0})$$



Equilibrium bond length

$$\left.\frac{\partial}{\partial q_j}U(q_j)\right|_{q_j=q_{j0}} = 0 \qquad \to q_{j0}$$

Taylor expansion about $q_{j0}$

$$U(q_j) = U(q_{j0}) +$$

$$+(q_j - q_{j0})\cancel{\left[\frac{\partial}{\partial q_j}U(q_j)\right]_{q_{j0}}}$$

$$+\frac{1}{2}(q_j - q_{j0})^2 \underbrace{\left[\frac{\partial^2}{\partial q_j^2}U(q_j)\right]_{q_{j0}}}_{=:c}$$

$$+ .......(higher\ orders)$$

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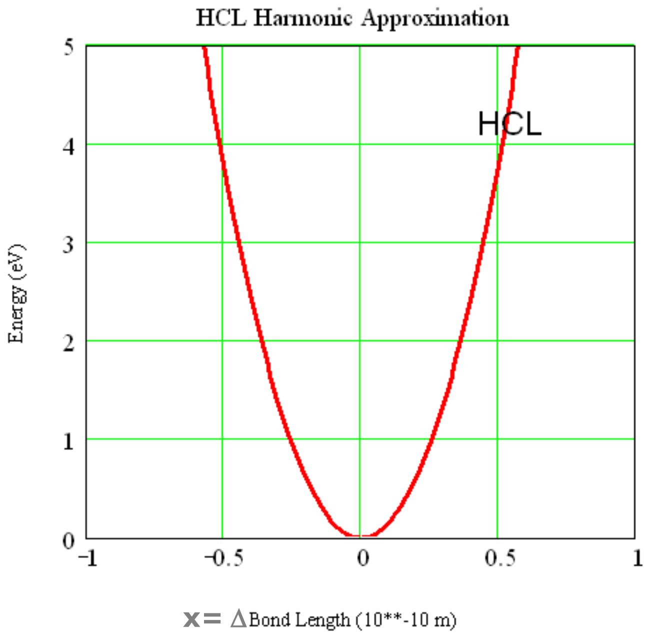

$$\hat{H}_{ho} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial q^2} + \frac{1}{2}c\underbrace{\left(q-q_0\right)}_{=:x}^2 + \xcancel{U(q_0)}$$

Reset energy scale → $U(q_0)=0$
***x*** **:=** displacement from equilibrium

$$\hat{H}_{ho} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2}cx^2 \qquad \mu := \text{reduced mass}$$

## Stationary Schrödinger Equation

$$\boxed{\hat{H}_{ho}\psi(x) = \left\{-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2}cx^2\right\}\psi(x) = E\psi(x)}$$

Symmetric potential →

$$\left[\hat{\Pi}, \hat{H}_{ho}\right] = 0 \rightarrow \psi = \hat{\Pi} - EF$$

***ψ(x)*** : spatially either symmetric or asymmetric

**Energy eigen states**

$$k^2 = \frac{2\mu}{\hbar^2}E; \quad \lambda^2 = \frac{\mu c}{\hbar^2}$$

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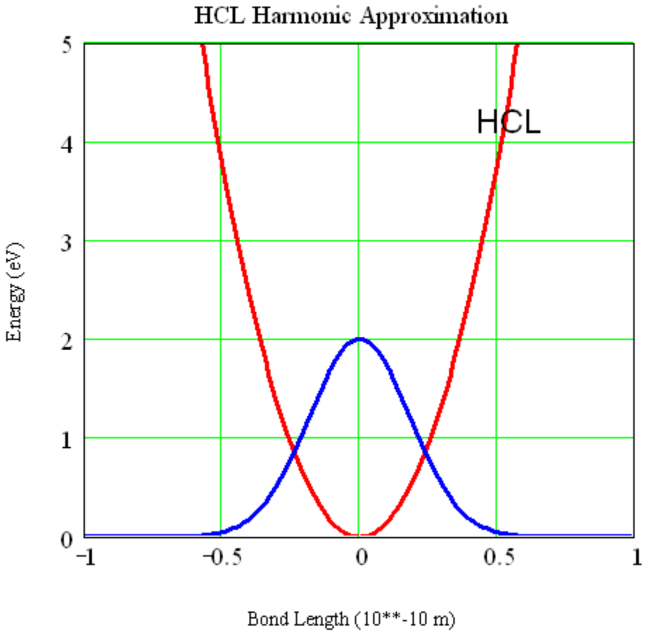
# Harmonic Oscillator: Asymptotic Behavior



$$\left\{\frac{\partial^2}{\partial x^2} + k^2 - \lambda^2 x^2\right\}\psi(x) = 0$$

$$\boxed{k^2 = \frac{2\mu}{\hbar^2}E \qquad \lambda^2 = \frac{\mu c}{\hbar^2}}$$

$$\left\{\frac{\partial^2}{\lambda\partial x^2} + \frac{k^2}{\lambda} - \lambda x^2\right\}\psi(x) = 0$$

$$\left\{\frac{\partial^2}{\partial \xi^2} + \frac{k^2}{\lambda} - \xi^2\right\}\psi(\xi) = 0$$

$$\boxed{\xi := \sqrt{\lambda}\, x}$$

$$\left[\hat{\Pi}, \hat{H}_{ho}\right] = 0 \rightarrow \psi = \hat{\Pi} - EF$$

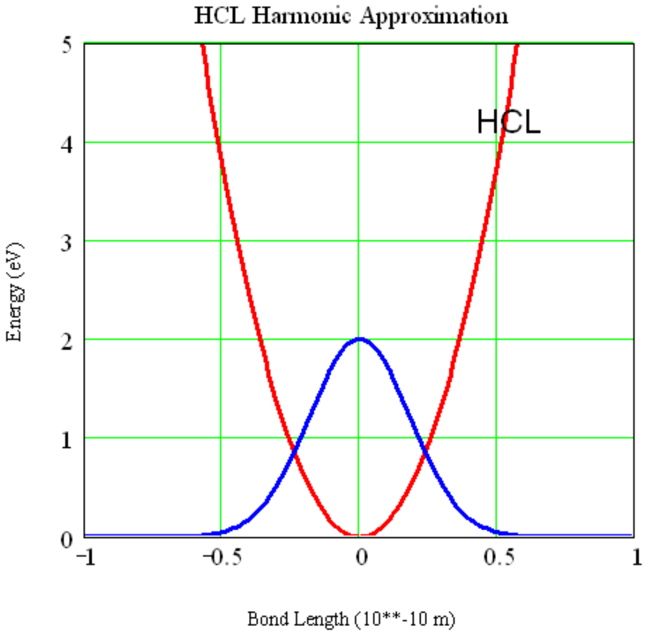
Asymptotic boundary conditions (***$\psi(x)$*** in classically forbidden region)?

$\xi^2 \gg$ ***$k^2/\lambda \rightarrow k^2 \ll \lambda^2 x^2$***

$$\frac{\partial^2}{\partial \xi^2}\psi(\xi) \simeq \xi^2 \psi(\xi) \quad \text{solved } \textit{app.} \text{ by } \boxed{\psi(\xi) \simeq e^{-\xi^2/2}}$$

Gaussian decay of wf in forbidden region, faster for heavy particles ($\mu$) and steep potential ***(c)*** . For *HCL*: $\lambda$ ***~ 84 Å$^{-2}$***

# Harmonic Oscillator Eigen Value Equation



$$\left[\hat{\Pi},\hat{H}_{ho}\right]=0\rightarrow\psi=\hat{\Pi}-EF$$

Found one energy eigen value and eigen function (= ground state of qu. oscillator)

$$\left\{\frac{\partial^2}{\partial\xi^2}+\frac{k^2}{\lambda}-\xi^2\right\}\psi(\xi)=0$$

$$\boxed{\begin{aligned}k^2&=\frac{2\mu}{\hbar^2}E\\ \lambda^2&=\frac{\mu c}{\hbar^2}\end{aligned}}$$

$$\boxed{\xi:=\sqrt{\lambda}\,x}$$

Trial: $\psi(\xi)\simeq e^{-\xi^2/2}$

$$\frac{\partial^2}{\partial\xi^2}\psi(\xi)=\left(\xi^2-1\right)\psi(\xi)$$

$\boxed{\psi_{n=0}(x)=e^{-\frac{\sqrt{\mu c}}{2\hbar}x^2}}$ =exact solution for $\frac{k^2}{\lambda}=1$

$$\frac{k^2}{\lambda}=1\rightarrow E=\frac{\hbar^2}{2\mu}k^2=\frac{\hbar^2}{2\mu}\sqrt{\frac{\mu c}{\hbar^2}}=\frac{1}{2}\hbar\sqrt{\frac{c}{\mu}}$$

$\boxed{E_0=\frac{1}{2}\hbar\varpi}$ *classical frequency* $\boxed{\varpi=\sqrt{\frac{c}{\mu}}}$

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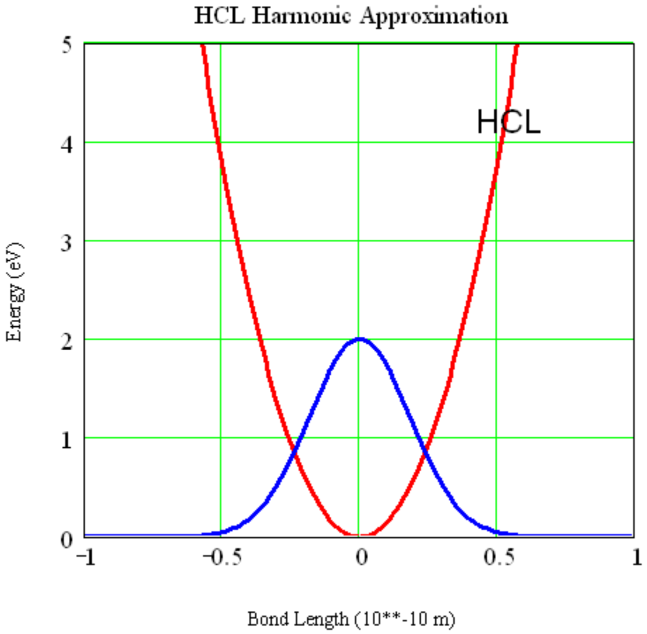
# Harmonic Oscillator: Hermite’s Differential Equ.



$$\left\{\frac{\partial^2}{\partial\xi^2}+\frac{k^2}{\lambda}-\xi^2\right\}\psi(\xi)=0$$

$$k^2=\frac{2\mu}{\hbar^2}E$$

$$\lambda^2=\frac{\mu c}{\hbar^2}$$

$$\xi:=\sqrt{\lambda}\,x$$

All asymptotic: $\psi(\xi)\simeq e^{-\xi^2/2}$

Trial function $\boxed{\psi(\xi)=H(\xi)e^{-\xi^2/2}}$

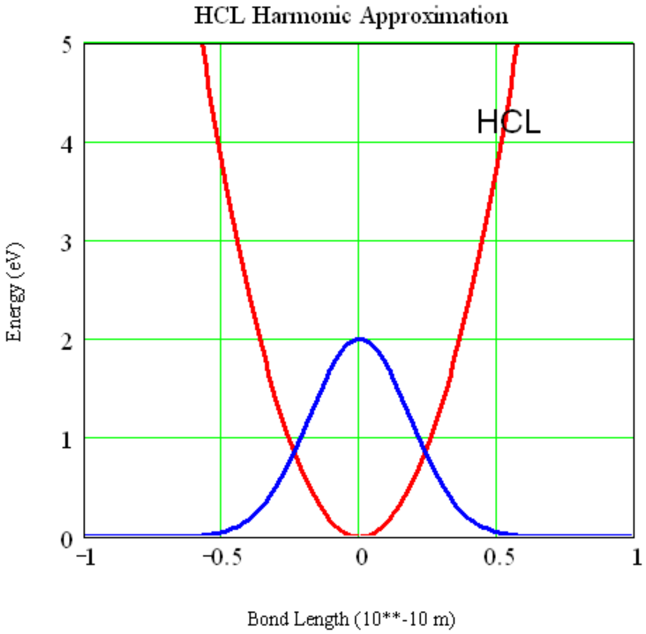
$$\left\{\frac{\partial^2}{\partial\xi^2}+\frac{k^2}{\lambda}-\xi^2\right\}H(\xi)e^{-\xi^2/2}=0$$

$$\frac{\partial^2}{\partial\xi^2}H(\xi)e^{-\xi^2/2}=\left\{\left(\frac{\partial^2}{\partial\xi^2}H\right)-2\xi\left(\frac{\partial}{\partial\xi}H\right)+\xi^2H-H\right\}e^{-\xi^2/2}$$

Hermite’s DEqu. $\boxed{\left\{\frac{\partial^2}{\partial\xi^2}-2\xi\frac{\partial}{\partial\xi}+\left(\frac{k^2}{\lambda}-1\right)\right\}H(\xi)=0}$

Asymptotic behavior: *H(ξ)* not exponential → ***H*** = finite power series

# Solving with Series Method



$$\boxed{\psi(\xi) = H(\xi)e^{-\xi^2/2}}$$

Hermite's DEqu.

$$\boxed{\left\{\frac{\partial^2}{\partial\xi^2} - 2\xi\frac{\partial}{\partial\xi} + \left(\frac{k^2}{\lambda} - 1\right)\right\}H(\xi) = 0}$$

$$k^2 = \frac{2\mu}{\hbar^2}E$$

$$\lambda^2 = \frac{\mu c}{\hbar^2}$$

$$\xi := \sqrt{\lambda}\,x$$

Asymptotic behavior → *H(ξ)* not exponential
→ *H*= finite power series

$$\left[\hat{\Pi}, \hat{H}_{ho}\right] = 0 \rightarrow \psi = \hat{\Pi} - EF$$

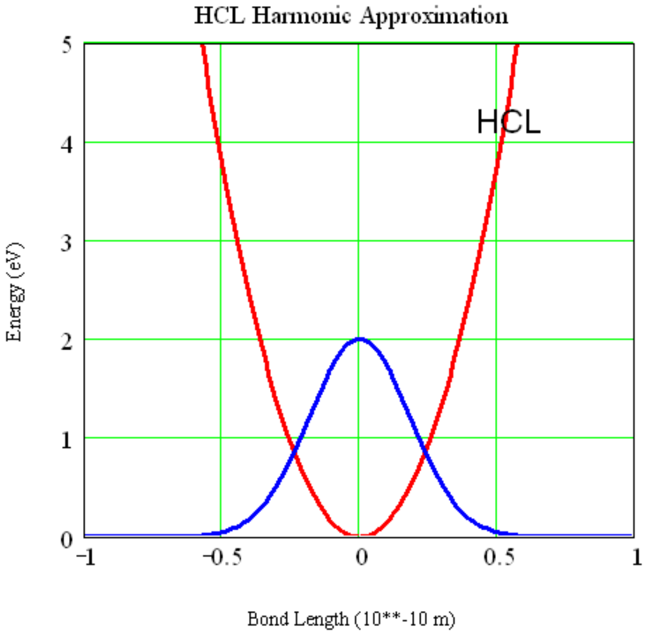
$$\boxed{H_n(\xi) = \sum_{i=0}^{n} a_i \xi^i}$$

Discrete EV spectrum,
count states *n*=,*0, 1,…*
***a<sub>i</sub>*** from differential equ.

$$\left.\begin{aligned}
\frac{\partial^2}{\partial\xi^2}\sum_{i=0}^{n} a_i\xi^i &= \sum_{i=0}^{n} a_{i+2}(i+2)(i+1)\xi^i \\
-2\xi\frac{\partial}{\partial\xi}\sum_{i=0}^{n} a_i\xi^i &= \sum_{i=0}^{n}(-2i)a_i\xi^i \\
\left(\frac{k_n^2}{\lambda} - 1\right)\sum_{i=0}^{n} a_i\xi^i &= \sum_{i=0}^{n} a_i\left(\frac{k_n^2}{\lambda} - 1\right)\xi^i
\end{aligned}\right\}$$

$$0 = \sum_{i=0}^{n}\underbrace{\left\{\begin{aligned}(i+2)(i+1)a_{i+2} \\ (-2i)a_i \\ \left(k_n^2/\lambda - 1\right)a_i\end{aligned}\right\}}_{\text{all }=0}\xi^i$$

# Energy Spectrum of Harmonic Oscillator



$$\boxed{\psi_n(\xi) = H_n(\xi)e^{-\xi^2/2}}$$

$$\boxed{H_n(\xi) = \sum_{i=0}^{n} a_i \xi^i}$$

$$\boxed{E_n = \frac{\hbar^2 k_n^2}{2\mu} \qquad \lambda^2 = \frac{\mu c}{\hbar^2}}$$

$$\boxed{\xi := \sqrt{\lambda}\, x}$$

Recursion relations for $a_i$ terminate at $i = n$

$$(i+2)(i+1)a_{i+2} = \left\{(2i+1) - \left(k_n^2/\lambda\right)\right\} a_i$$

i = even or $i$ = odd.

$$\boxed{k_n^2 = (2n+1)\lambda}$$

$$\left[\hat{\Pi}, \hat{H}_{ho}\right] = 0 \rightarrow \psi = \hat{\Pi} - EF$$

$$E_n = \frac{\hbar^2}{2\mu}k_n^2 = \frac{\hbar^2}{2\mu}(2n+1)\sqrt{\frac{\mu c}{\hbar^2}} = \left(n+\frac{1}{2}\right)\hbar\underbrace{\sqrt{\frac{c}{\mu}}}_{\omega}$$

Energy eigen values of qu. harmonic oscillator

$$\boxed{E_n = \left(n+\frac{1}{2}\right)\hbar\varpi \qquad n = 0,1,2,...}$$

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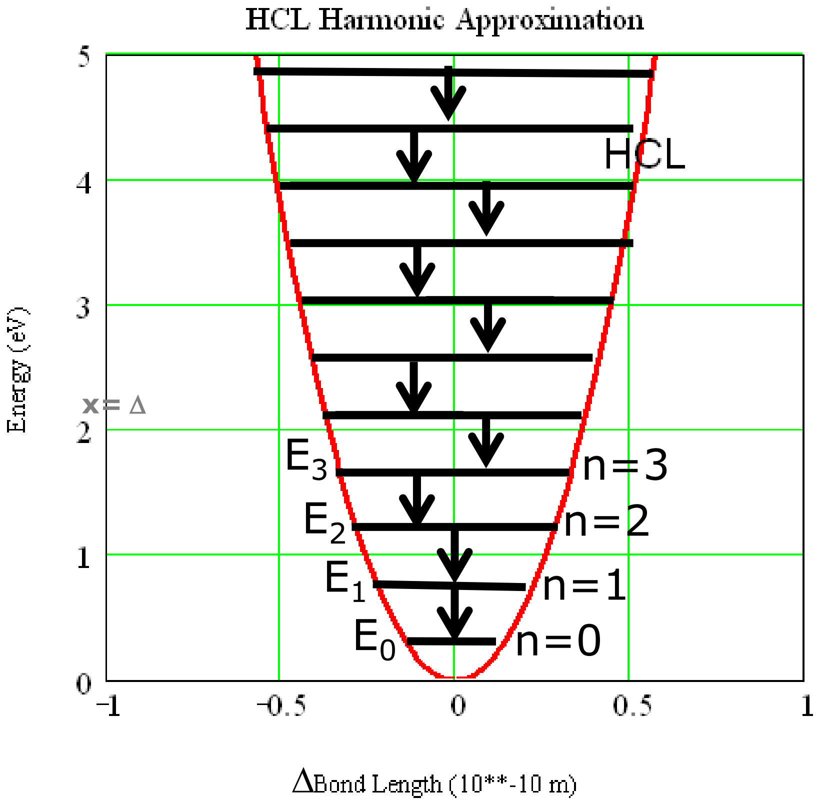
# Harmonic Oscillator Level Scheme



Equidistant level scheme

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\varpi \qquad n = 0,1,2,...}$$

unbounded, n → ⍰

*HCl*

$$E_0 = \frac{1}{2}\hbar\omega = 0.27\,eV$$ Zero-point energy

$$\varpi = 8.2 \cdot 10^{14} s^{-1}$$

Elm. E1 transitions:

***Δn = ± 1***

+1: absorption

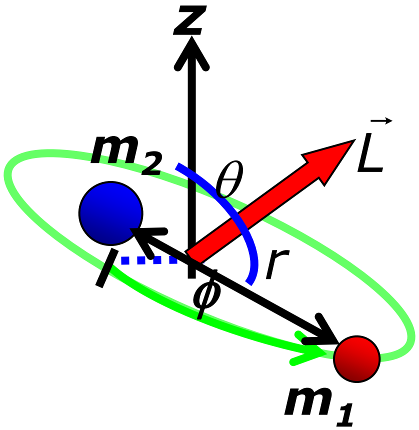
-1: emission

Absorption and emission in *infra-red* spectral region

$$HCl : \nu = \frac{\varpi}{2\pi} = 5.85 \cdot 10^{13} Hz \rightarrow \lambda = 5.12 \mu m$$

# Rot-Vib Spectra of Molecules

Assume independent rot and vib → neglect centrifugal stretching



$$\hat{H} = \hat{H}_{com} + \hat{H}_{rot} + \hat{H}_{vib} + \hat{H}_{el}(...)$$

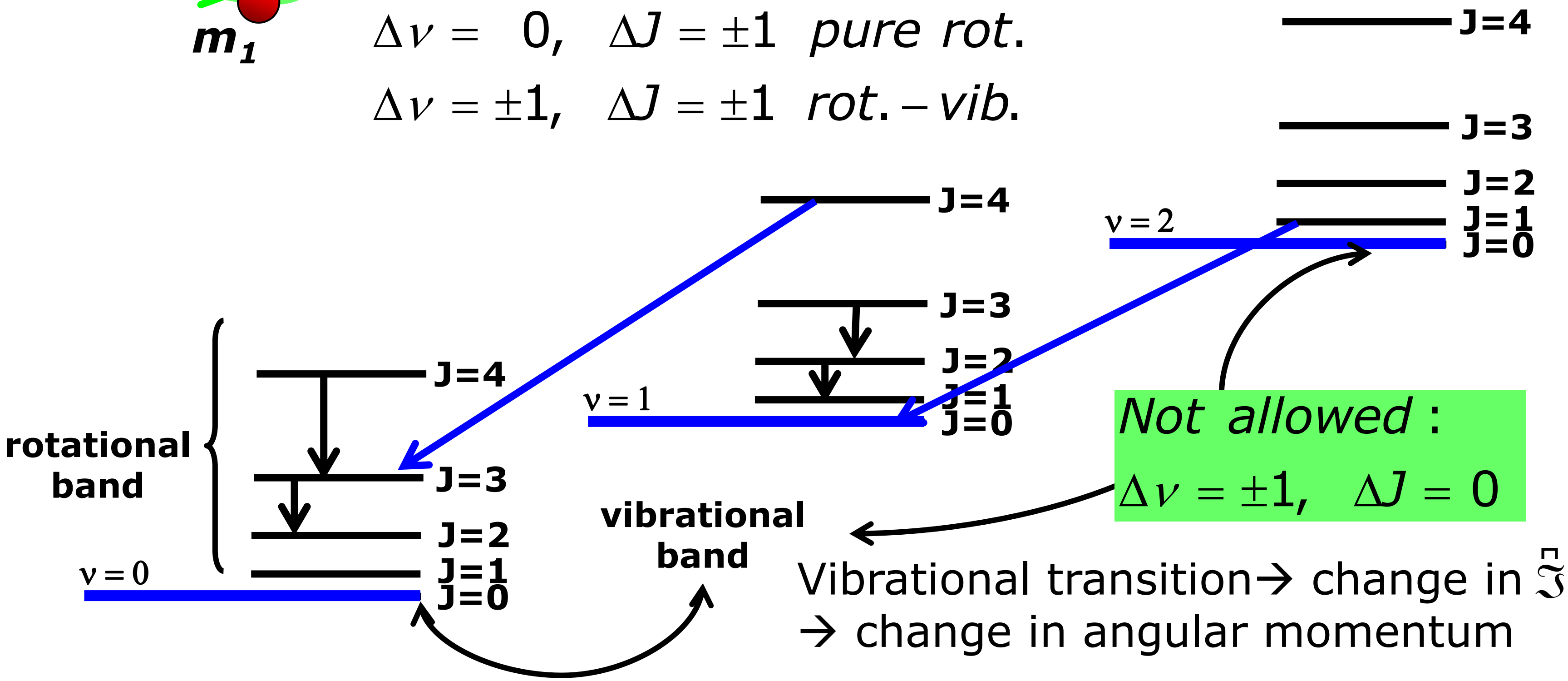
Very different energy scales

$$E = \frac{P^2}{2M} + \frac{\hbar^2}{2\Im} J(J+1) + \hbar\varpi(\nu + \frac{1}{2}) + ...$$

Selection rules for elm transitions:

$\Delta\nu = \; 0, \quad \Delta J = \pm 1 \quad$ *pure rot.*

$\Delta\nu = \pm 1, \quad \Delta J = \pm 1 \quad$ *rot.-vib.*

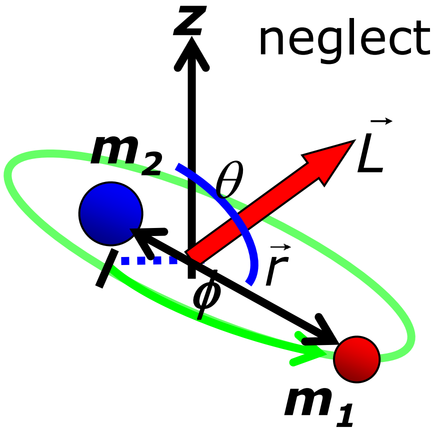


*Not allowed* :

$\Delta\nu = \pm 1, \quad \Delta J = 0$

Vibrational transition → change in $\Im$
→ change in angular momentum

# Rot-Vib Spectra of Molecules



Assume independent rot and vib
neglect centrifugal stretching

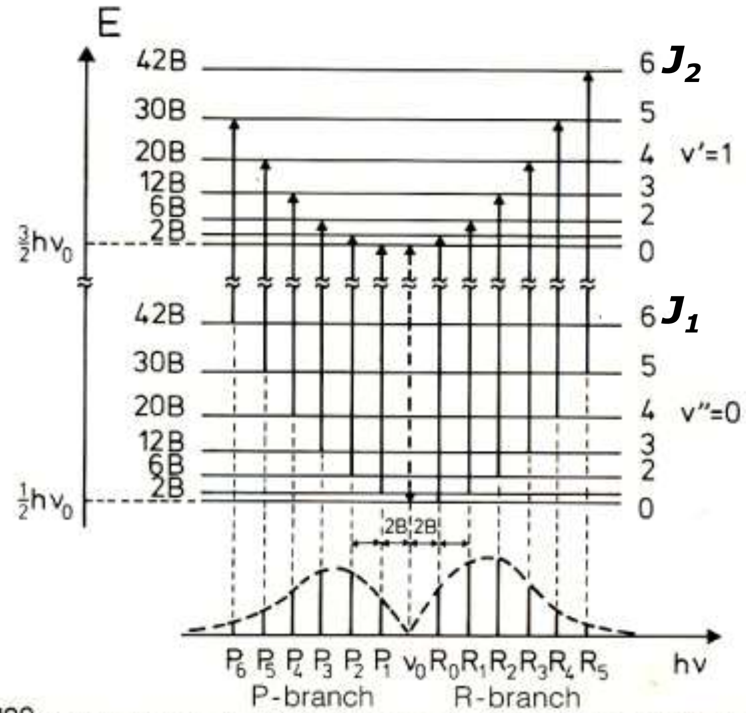
$$\hat{H} = \hat{H}_{com} + \hat{H}_{rot} + \hat{H}_{vib}$$

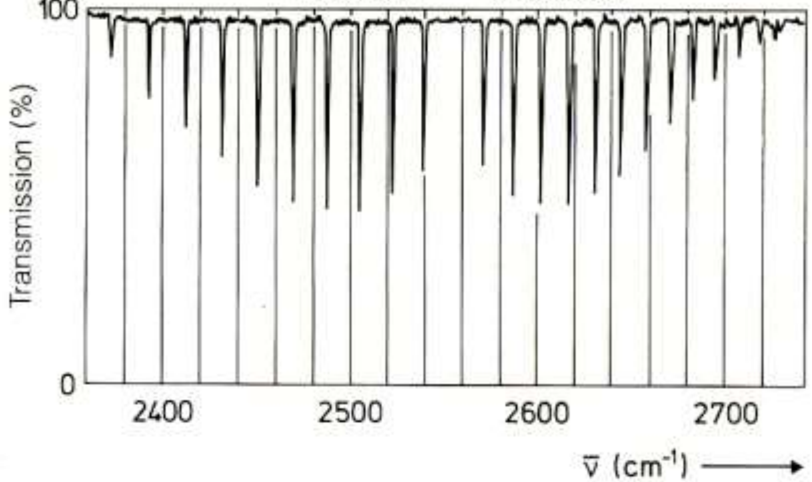
$$E = \frac{P^2}{2M} + \frac{\hbar^2}{2\Im} J(J+1) + \hbar\varpi(\nu + \frac{1}{2})$$

Rot-vib absorption/emission branches

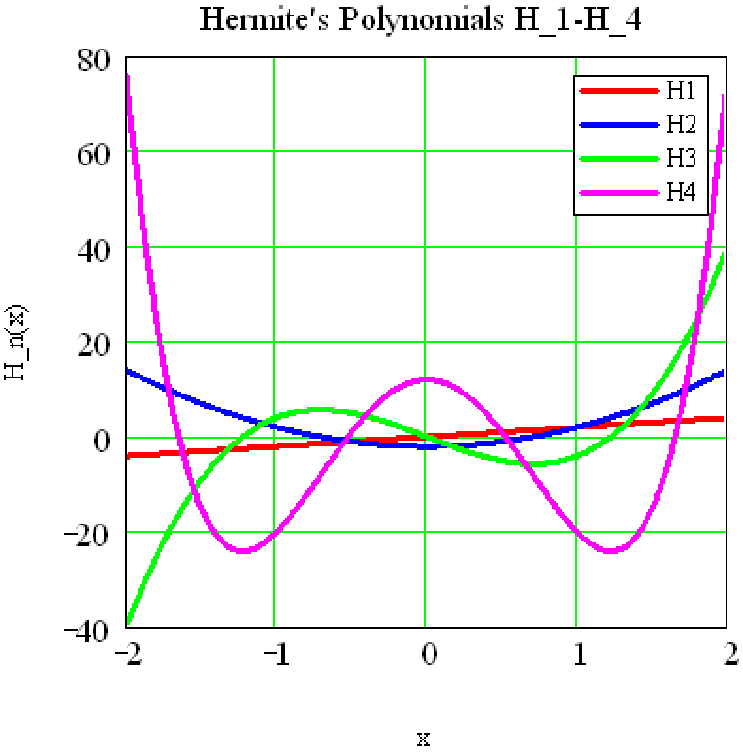
$$\Delta E_{J_1 \to J_2 = J_1+1} = B\left[(J_1+1)(J_1+2) - J_1(J_1+1)\right] = 2B(J_1+2) \quad \boxed{R-Branch}$$

$$\Delta E_{J_1 \to J_2 = J_1-1} = B\left[(J_1-1)J_1 - J_1(J_1+1)\right] = -2B(J_1+2) \quad \boxed{P-Branch}$$





# HOsc-Wave Functions: Hermite's Polynomials



$$H_n(\xi) = \sum_{i=0}^{n} a_i \xi^i$$

$$a_{i+2} = \frac{2(i-n)}{(i+2)(i+1)} a_i$$

$$E_n = \frac{\hbar^2 k_n^2}{2\mu}$$

$$\lambda^2 = \frac{\mu c}{\hbar^2}$$

$$\xi := \sqrt{\lambda}\, x$$

Definite parity **$\pi$=+1** , **$\pi$=-1**

$$H_0(x) = 1$$

$$H_1(x) = 2x$$

$$H_2(x) = 4x^2 - 2$$

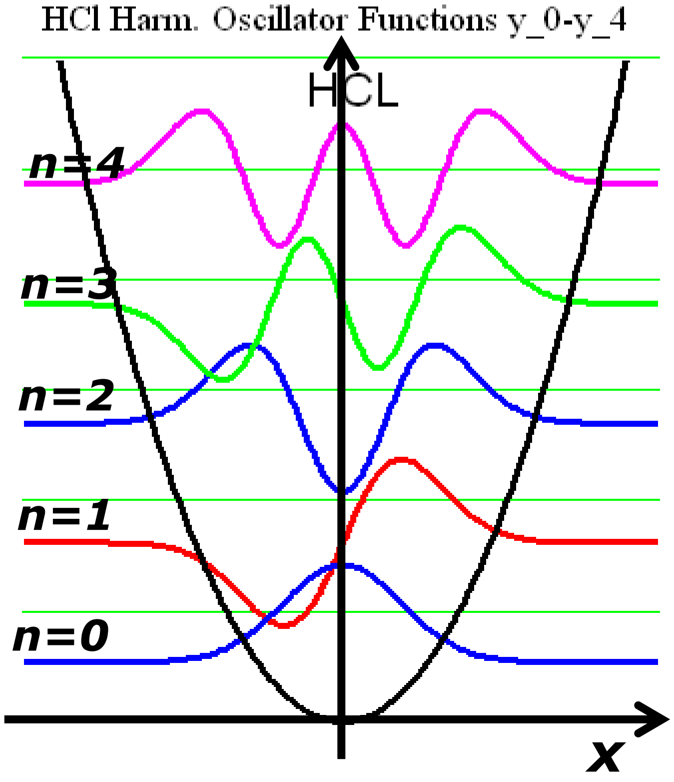
$$H_3(x) = 8x^3 - 12x$$

$$H_4(x) = 16x^4 - 48x^2 + 12$$

$$H_5(x) = 32x^5 - 160x^3 + 120x$$

$$H_6(x) = 64x^6 - 480x^4 + 720x^2 - 120$$

# Oscillator Eigenfunctions



Unnormalized:

$$\boxed{\psi(\xi) \propto H(\xi) e^{-\xi^2/2}}$$

$$\boxed{E_n = \frac{\hbar^2 k_n^2}{2\mu} \qquad \lambda^2 = \frac{\mu C}{\hbar^2}}$$

$$\boxed{\xi := \sqrt{\lambda}\, x}$$

$$\lambda^2 = \frac{\mu C}{\hbar^2} = \frac{\mu^2 \varpi^2}{\hbar^2}$$

$$\boxed{\psi_n(x) = \left( \frac{\lambda}{\sqrt{\pi} 2^n n!} \right)^{1/2} H_n(\sqrt{\lambda} x) e^{-\lambda x^2}}$$

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

All have definite parity,

$$\pi_n = (-1)^n$$

spatial symmetry.

n = # of nodes

$\hbar\omega = 0.54 eV$ $\lambda = 84.14 \overset{o}{A}^{-2}$

$\sqrt{\lambda} = 5.454 \overset{o}{A}^{-1}$; $1/\lambda = 0.012 \overset{o}{A}^{2}$

# Calculating Expectation Values

$$\boxed{\psi_n(x) = \left(\frac{\lambda}{\sqrt{\pi}2^n n!}\right)^{1/2} H_n(\sqrt{\lambda}x)e^{-\lambda x^2}}$$

Mean square deviation from equilibrium bond length

$$\left\langle x^2 \right\rangle_n = \int_{-\infty}^{+\infty} x^2 \left|\psi_n(x)\right|^2 dx$$

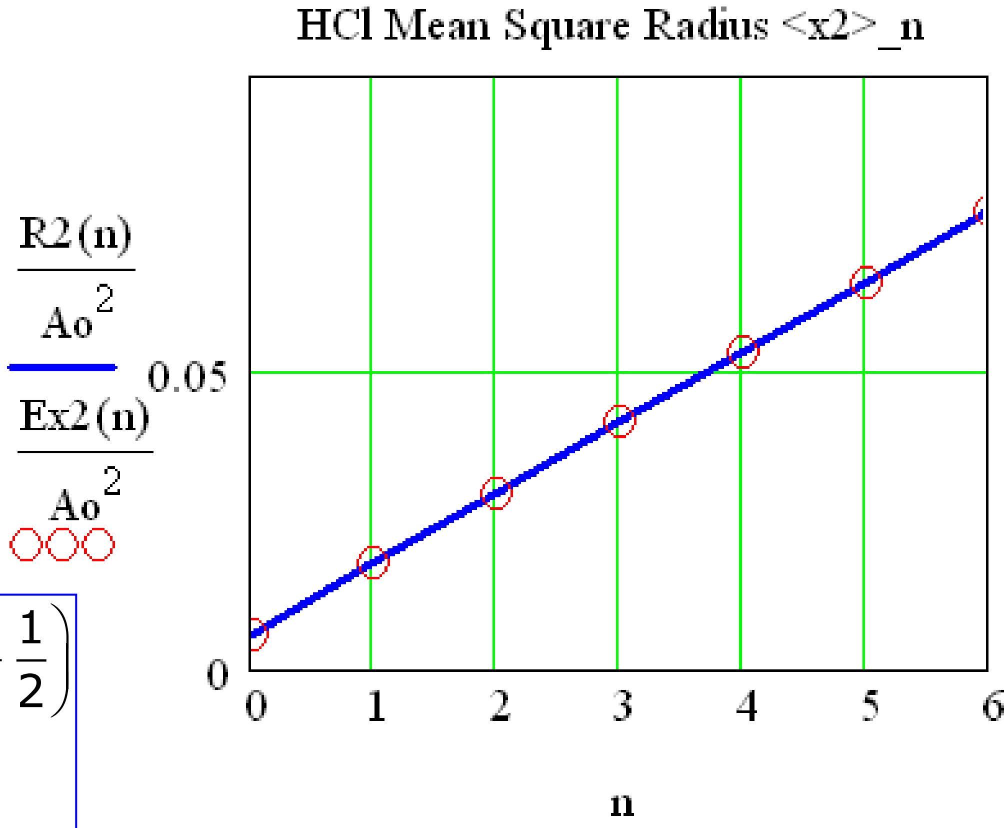
*HCl*

$\hbar\omega = 0.54eV \qquad \lambda = 84.14\,\overset{o}{A}{}^{-2} \quad \sqrt{\lambda} = 5.454\,\overset{o}{A}{}^{-1};\ 1/\lambda = 0.012\,\overset{o}{A}{}^{2}$

MathCad rendition: $s\lambda := \sqrt{\lambda}$

$$\psi(n,x) := N_n \cdot H(s\lambda \cdot x)_n \cdot e^{\frac{-\lambda}{2}\cdot x^2}$$

$$Ex2(n) := \int_{\frac{-10}{s\lambda}}^{\frac{10}{s\lambda}} x^2 \cdot (|\psi(n,x)|)^2\, dx$$



Deviation from equilibrium bond length

$$\boxed{\begin{aligned}\left\langle x^2 \right\rangle_n &= \frac{1}{\lambda}\left(n+\frac{1}{2}\right) = 0.012\,\overset{o}{A}{}^{2}\left(n+\frac{1}{2}\right)\\ \left\langle x \right\rangle_{rms,n} &= 0.109\,\overset{o}{A}\left(n+\frac{1}{2}\right)^{1/2}\end{aligned}}$$

# End of Section