Lecture 2 B

Application of Quantum mechanics

II- Vibrational motion

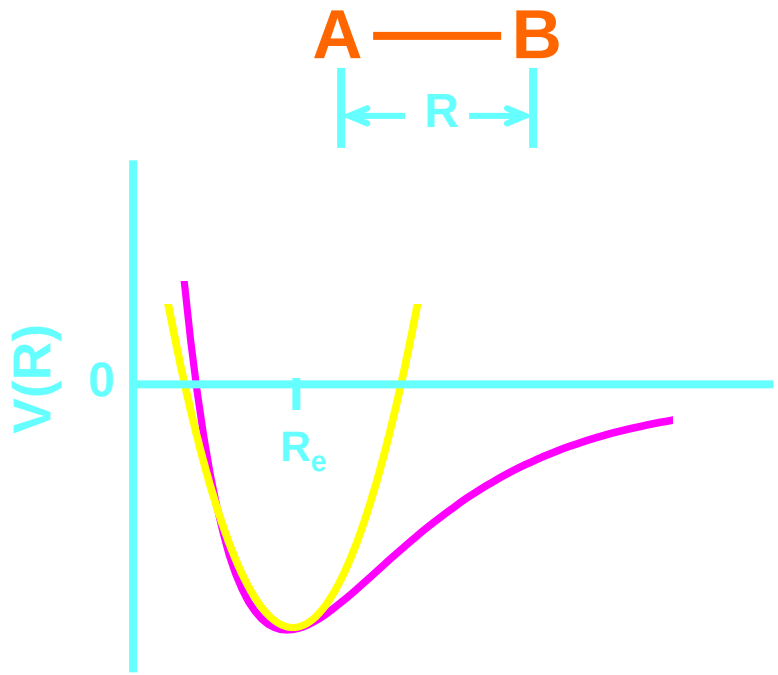
Harmonic Oscillator Models

Harmonic Oscillator

Many physical system including molecular with configuration near to equilibrium position can be described by Hamiltonian of the Harmonic Oscillator

1.The Classical Harmonic Oscillator

The Potential Energy of a Diatomic Molecule



Harmonic Oscillator Approximation

$V(R) \approx \frac{1}{2}k(R-R_e)^2$ k is the force constant

or $V(x) \approx \frac{1}{2}kx^2$ $x = R-R_e$

Hooke's Law and Newton's Equation

Force: $$f = -\frac{dV}{dx} = -\frac{d}{dx}\left(\frac{1}{2}kx^2\right) = -kx$$

Newton's Equation: $$f = \mu a = \mu \frac{d^2x}{dt^2}$$ where $$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Reduced Mass

Therefore: $$\mu \frac{d^2x}{dt^2} = -kx$$

Solution

$$\mu \frac{d^2x}{dt^2} = -kx$$

Assume: $x(t) = A\sin(\omega t) + B\cos(\omega t)$

$$\frac{d^2x}{dt^2} = -\omega^2 A\sin(\omega t) - \omega^2 B\cos(\omega t)$$

$$= -\omega^2 x$$

$$\frac{d^2x}{dt^2} = -\frac{k}{\mu}x$$

$$-\omega^2 x = -\frac{k}{\mu}x$$

$$\downarrow$$

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

or $$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

or $$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

Initial Conditions (like BC's)

$$x(t) = A\sin(\omega t) + B\cos(\omega t)$$

$$\frac{dx}{dt} = \omega A\cos(\omega t) - \omega B\sin(\omega t)$$

$$\left(\frac{dx}{dt}\right)_{t=0} = \omega A = 0$$

$$\downarrow$$

$$x(t) = B\cos(\omega t)$$

and $x(0) = x_0 = B$ $\longrightarrow$

$$\boxed{\begin{aligned} x(t) &= x_0\cos(\omega t) \\ \nu &= \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \end{aligned}}$$

Let's assume that the HO starts out at rest stretched out to $x = x_0$.

$$x(0) = x_0$$

$$\left(\frac{dx}{dt}\right)_{t=0} = 0$$

Conservation of Energy

$$x(t) = x_0 \cos(\omega t) \longrightarrow \frac{dx}{dt} = -\omega x_0 \sin(\omega t) \qquad \omega = \sqrt{\frac{k}{\mu}}$$

Potential Energy (V) **Kinetic Energy (T)** **Total Energy (E)**

$$V = \frac{1}{2}kx^2 \qquad T = \frac{1}{2}\mu\left(\frac{dx}{dt}\right)^2 \qquad E = T + V$$

$$T = \frac{1}{2}\mu\omega^2 x_0^2 \sin^2(\omega t)$$

$$V = \frac{1}{2}kx_0^2 \cos^2(\omega t) \qquad T = \frac{1}{2}kx_0^2 \sin^2(\omega t) \qquad E = \frac{1}{2}kx_0^2$$

$\omega t = 0, \pi, 2\pi, \ldots \longrightarrow x = \pm x_0$

$$V = \frac{1}{2}kx_0^2 \qquad T = 0 \qquad E = \frac{1}{2}kx_0^2$$

$\omega t = \pi/2, 3\pi/2, \ldots \longrightarrow x = 0$

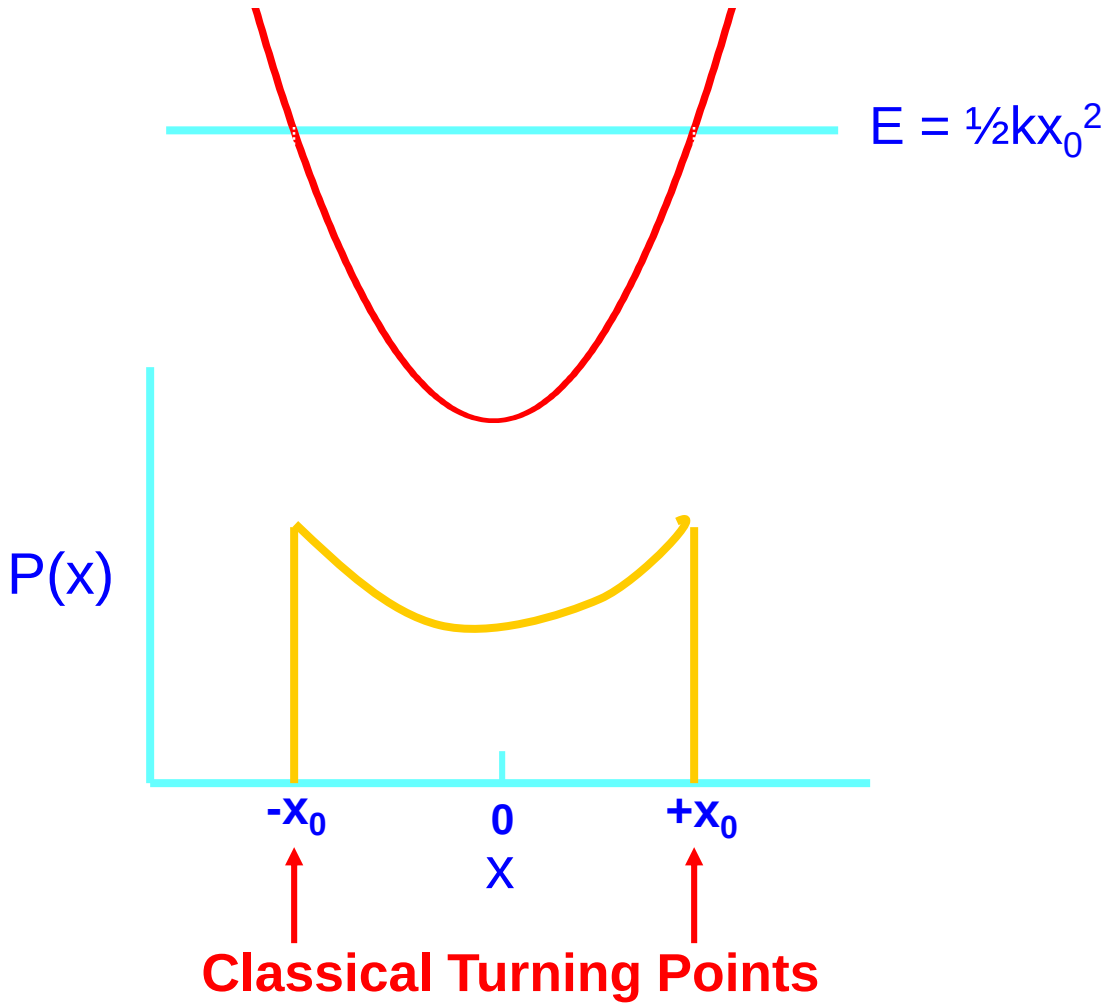
$$V = 0 \qquad T = \frac{1}{2}kx_0^2 \qquad E = \frac{1}{2}kx_0^2$$

Classical HO Properties

Energy: $E = T + V = \frac{1}{2}kx_0^2 = \text{Any Value}$ i.e. no energy quantization

If $x_0 = 0$, $E = 0$ i.e. no Zero Point Energy

Probability:

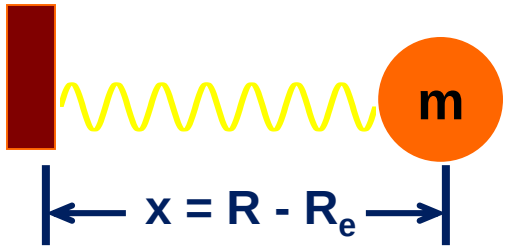


The Quantum Mechanical Harmonic Oscillator

Schrödinger Equation

Particle vibrating against wall

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



Two particles vibrating against each other

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2}+\frac{1}{2}kx^2\psi = E\psi$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Boundary Condition: $\psi \rightarrow 0$ as $x \rightarrow \pm\infty$

Solution of the HO Schrödinger Equation

Rearrangement of the Equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2}+\frac{1}{2}kx^2\psi = E\psi$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2}+\left(\frac{1}{2}kx^2-E\right)\psi = 0$$

$$\frac{d^2\psi}{dx^2}-\frac{2\mu}{\hbar^2}\left(\frac{1}{2}kx^2-E\right)\psi = 0$$

$$\frac{d^2\psi}{dx^2}+\left(\frac{2\mu E}{\hbar^2}-\frac{k\mu}{\hbar^2}x^2\right)\psi = 0$$

$$\frac{d^2\psi}{dx^2}+\left(\lambda-\alpha^2x^2\right)\psi = 0$$

Define

$$\lambda \equiv \frac{2\mu E}{\hbar^2}$$

$$\alpha^2 \equiv \frac{k\mu}{\hbar^2} = \frac{\mu^2\omega^2}{\hbar^2} \qquad \omega = \sqrt{\frac{k}{\mu}}$$

HO Energies and Wavefunctions

Harmonic Oscillator Energies

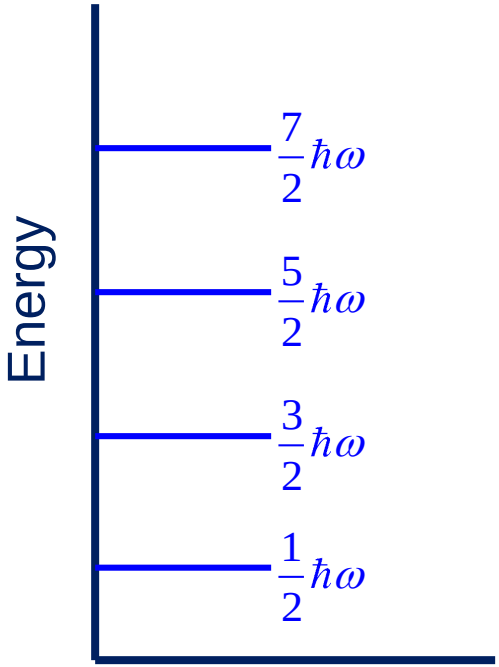
$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega = \left(n + \frac{1}{2}\right)h\nu \qquad n = 0, 1, 2, 3, \ldots$$

Angular Frequency: $\omega = \sqrt{\frac{k}{\mu}}$

Circular Frequency: $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

Wavenumbers: $\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

where $\tilde{\nu} = \frac{1}{\lambda(cm)} = \frac{\nu}{c\,(cm/s)}\ cm^{-1}$

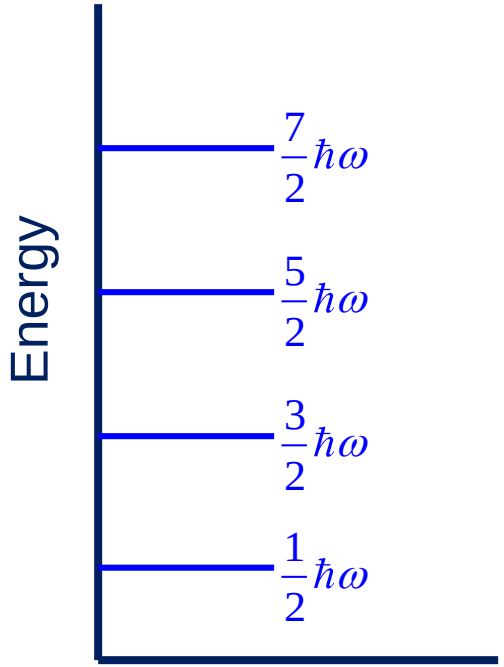


Quantized Energies

Only certain energy levels are allowed and the separation between levels is:

$$\Delta E = \hbar\omega$$

The classical HO permits any value of E.



Zero Point Energy

The minimum allowed value for the energy is:

$$E_0 = \frac{1}{2}\hbar\omega$$

The classical HO can have E=0.

Note: All “bound” particles have a minimum ZPE.
This is a consequence of the Uncertainty Principle.

The Correspondence Principle

The results of Quantum Mechanics must not contradict those of classical mechanics when applied to macroscopic systems.

The fundamental vibrational frequency of the H_2 molecule is 4200 cm^{-1}. Calculate the energy level spacing and the ZPE, in J and in kJ/mol.

$\hbar = 1.05 \times 10^{-34}$ J•s
$c = 3.00 \times 10^{8}$ m/s
$= 3.00 \times 10^{10}$ cm/s
$N_A = 6.02 \times 10^{23}$ mol^{-1}

$$\omega = 2\pi\nu = 2\pi c\tilde{\nu} = 2(3.14)(3.00x10^{10}\ cm/s)(4200\ cm^{-1}) = 7.92x10^{14}\ s^{-1}$$

Spacing: $$\Delta E = \hbar\omega = (1.05x10^{-34}\ J \cdot s)(7.92x10^{14}\ s^{-1}) = 8.3x10^{-20}\ J$$

$$N_A \cdot \Delta E = (6.02x10^{23}\ mol^{-1})(8.3x10^{-20}\ J) = 5.00x10^{4}\ J/mol = \boxed{50\ kJ/mol}$$

ZPE: $$E_0 = \frac{1}{2}\hbar\omega = \frac{1}{2}(1.05x10^{-34}\ J \cdot s)(7.92x10^{14}\ s^{-1}) = 4.15x10^{-20}\ J$$

$$N_A \cdot E_0 = (6.02x10^{23}\ mol^{-1})(4.15x10^{-20}\ J) = 2.5x10^{4}\ J/mol = \boxed{25\ kJ/mol}$$

Macroscopic oscillators have ***much*** lower frequencies than molecular sized systems. Calculate the energy level spacing and the ZPE, in J and in kJ/mol, for a macroscopic oscillator with a frequency of 10,000 cycles/second.

$\hbar = 1.05x10^{-34}$ J•s
$c = 3.00x10^{8}$ m/s
$= 3.00x10^{10}$ cm/s
$N_A = 6.02x10^{23}$ mol^{-1}

$$\omega = 2\pi\nu = 2(3.14)(1.00x10^{4}\ s^{-1}) = 6.28x10^{4}\ s^{-1}$$

Spacing: $\Delta E = \hbar\omega = (1.05x10^{-34}\ J\cdot s)(6.28x10^{4}\ s^{-1}) = 6.6x10^{-30}\ J$

$$N_A \cdot \Delta E = (6.02x10^{23}\ mol^{-1})(6.6x10^{-30}\ J) = 4.0x10^{-6}\ J/mol = \boxed{4.0x10^{-9}\ kJ/mol}$$

ZPE: $E_0 = \frac{1}{2}\hbar\omega = \frac{1}{2}(1.05x10^{-34}\ J\cdot s)(6.28x10^{4}\ s^{-1}) = 3.3x10^{-30}\ J$

$$N_A \cdot E_0 = (6.02x10^{23}\ mol^{-1})(3.3x10^{-30}\ J) = 2.0x10^{-6}\ J/mol = \boxed{2.0x10^{-9}\ kJ/mol}$$

Harmonic oscillator wavefunction

$$\psi_v = N_v H_v(y) e^{-y^2/2} \qquad y = \left(\frac{x}{\alpha}\right) \quad \alpha = \left[\frac{\hbar^2}{mk_f}\right]^{1/4}$$

$$\psi_v = \left[\frac{1}{\sqrt{\pi}\, 2^v v! \alpha}\right]^{1/2} H_v(y) e^{-y^2/2} \qquad y = \left(\frac{x}{\alpha}\right) \quad \alpha = \left[\frac{\hbar^2}{mk_f}\right]^{1/4}$$

$$N_v = \left[\frac{1}{\alpha\sqrt{\pi}\, 2^v v!}\right]^{1/2}$$

in general

v	$H(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
6	$64y^6 - 480y^4 + 720y^2 - 120$

$$\int H_m H_n e^{-y^2} dy = \begin{pmatrix} 0 & n \neq m \\ \sqrt{\pi}\, 2^v v! & n = m \end{pmatrix}$$

Harmonic Oscillator Wavefunctions

$$\psi = \left(\sum_{n=0}^{\infty} a_n x^n \right) e^{-\alpha x^2/2}$$

Application of the recursion formula yields a different polynomial for each value of n.

$$\psi_n = N_n H_n(\sqrt{\alpha}\, x) e^{-\alpha x^2/2}$$

These polynomials are called Hermite polynomials, H_n

or

$$\psi_n = N_n H_n(y) e^{-y^2/2} \quad \text{where} \quad y = \sqrt{\alpha}\, x$$

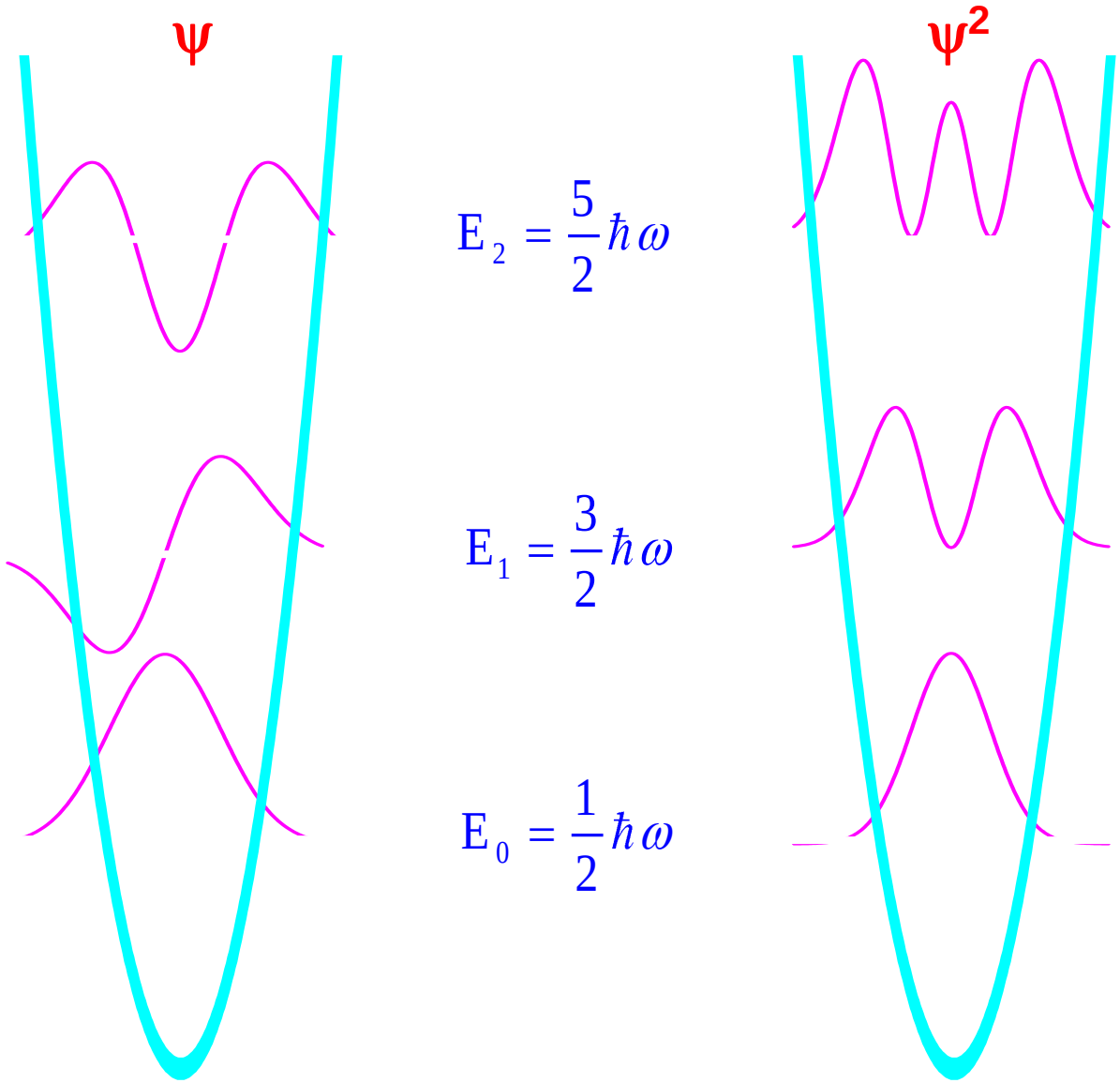
Some specific solutions

n = 0 $\quad \psi_0 = N_0 e^{-\alpha x^2/2} = N_0 e^{-z^2/2}$ **Even**

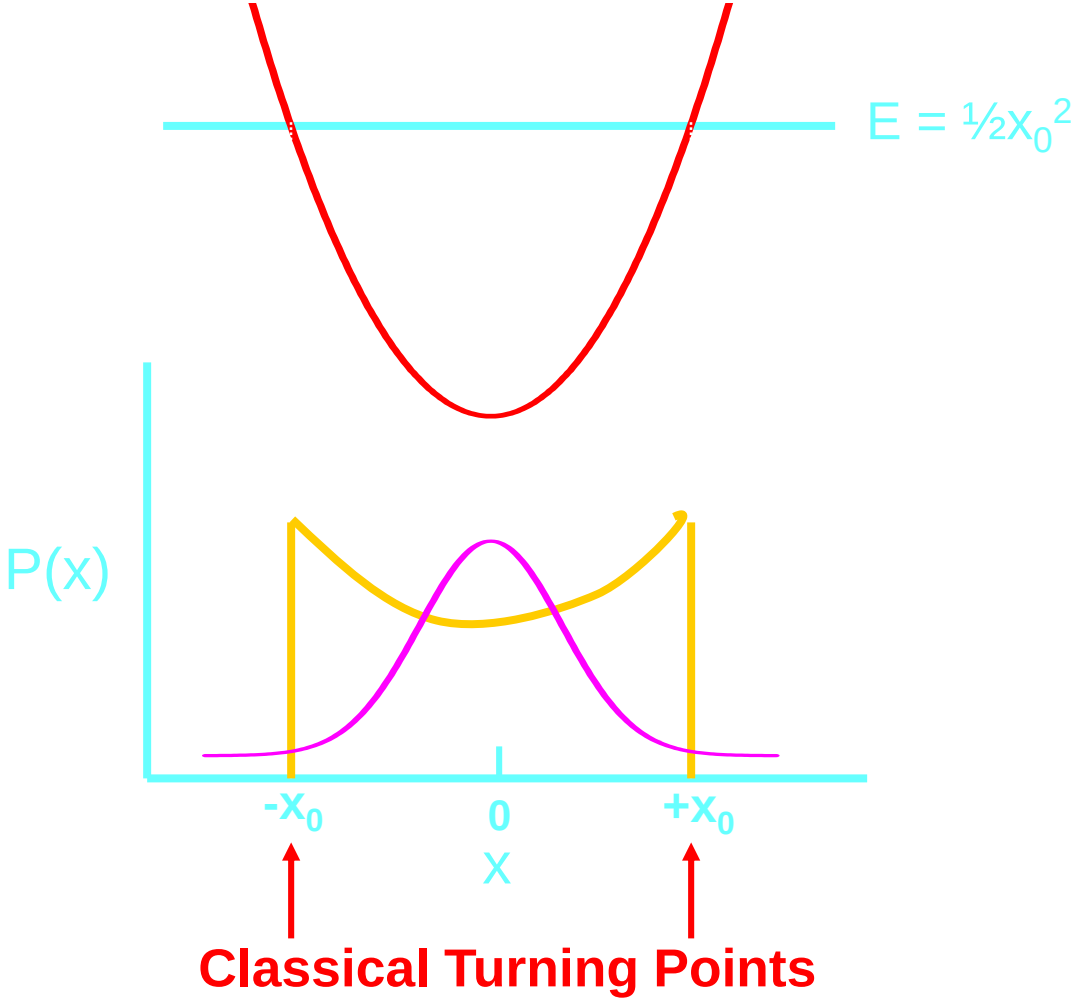
n = 1 $\quad \psi_1 = N_1 (2\sqrt{\alpha}\, x) e^{-\alpha x^2/2} = N_1 (2z) e^{-z^2/2}$ **Odd**

n = 2 $\quad \psi_2 = N_2 (4\alpha x^2 - 2) e^{-\alpha x^2/2} = N_2 (4z^2 - 2) e^{-z^2/2}$ **Even**

n = 3 $\quad \psi_3 = N_3 (8\alpha^{3/2} x^3 - 12\sqrt{\alpha}\, x) e^{-\alpha x^2/2} = N_3 (8z^3 - 12z) e^{-z^2/2}$ **Odd**


ψ
ψ2
$E_2 = \frac{5}{2}\hbar\omega$
$E_1 = \frac{3}{2}\hbar\omega$
$E_0 = \frac{1}{2}\hbar\omega$

Quantum Mechanical vs. Classical Probability



Classical

P(x) minimum at x=0

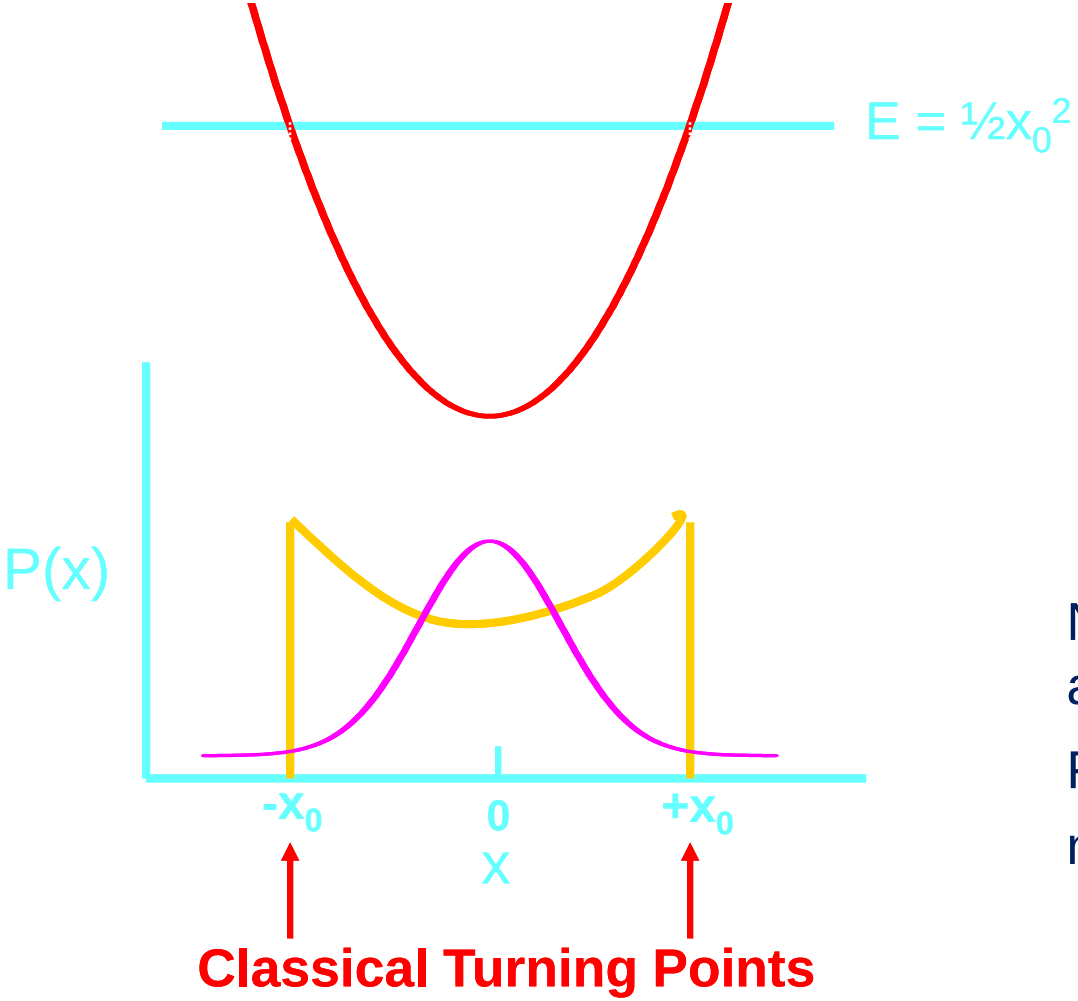
P(x) = 0 past $\pm x_0$

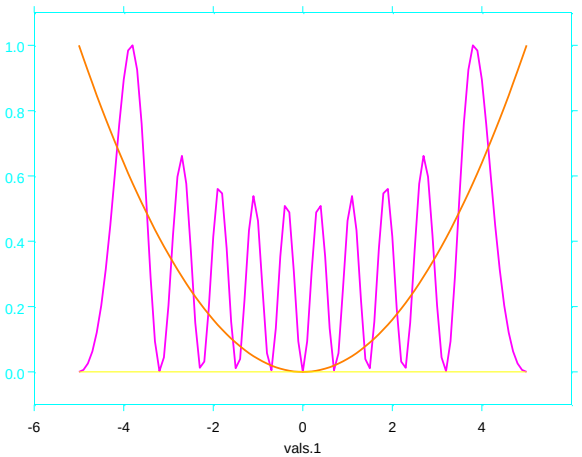
QM (n=0)

P(x) maximum at x=0

P(x) $\neq$ 0 past $\pm x_0$

Correspondence Principle





$(x \;\; \psi 2 \;\; V \;\; zero)$

n=9

Note that as n increases, P(x) approaches the classical limit.

For macroscopic oscillators

$n > 10^6$

Properties of the QM Harmonic Oscillator

Some Useful Integrals

$$\int_0^\infty e^{-\beta x^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{\beta}}$$

$$\int_0^\infty x e^{-\beta x^2} dx = \frac{1}{2\beta}$$

$$\int_0^\infty x^2 e^{-\beta x^2} dx = \frac{1}{4\beta}\sqrt{\frac{\pi}{\beta}}$$

$$\int_0^\infty x^3 e^{-\beta x^2} dx = \frac{1}{2\beta^2}$$

$$\int_0^\infty x^4 e^{-\beta x^2} dx = \frac{3}{8\beta^2}\sqrt{\frac{\pi}{\beta}}$$

Remember

$$\int_{-\infty}^\infty f(x)dx = 2\int_0^\infty f(x)dx$$

If f(-x) = f(x)

Even Integrand

$$\int_{-\infty}^\infty f(x)dx = 0$$

If f(-x) = -f(x)

Odd Integrand

Wavefunction Orthogonality

$$\psi_0 = N_0 e^{-\alpha x^2/2} \qquad \infty- < x < \infty$$

$$\psi_1 = N_1 (2\sqrt{\alpha}\, x) e^{-\alpha x^2/2} \qquad \infty- < x < \infty$$

$$\psi_2 = N_2 (4\alpha x^2 - 2) e^{-\alpha x^2/2} \qquad \infty- < x < \infty$$

$$<\psi_0|\psi_1>$$

$$\langle \psi_0 | \psi_1 \rangle = \int_{-\infty}^{\infty} \left(N_0 e^{-\alpha x^2/2} \right) \left(N_1 2\sqrt{\alpha}\, x e^{-\alpha x^2/2} \right) dx$$

$$\langle \psi_0 | \psi_1 \rangle = N_0 N_1 2\sqrt{\alpha} \int_{-\infty}^{\infty} x e^{-\alpha x^2} dx$$

Odd Integrand

$$\langle \psi_0 | \psi_1 \rangle = 0$$

Wavefunction Orthogonality

$$\psi_0 = N_0 e^{-\alpha x^2/2}$$

$$\psi_1 = N_1 (2\sqrt{\alpha}\, x) e^{-\alpha x^2/2}$$

$$\psi_2 = N_2 (4\alpha x^2 - 2) e^{-\alpha x^2/2}$$

$<\psi_0|\psi_2>$

$$\langle \psi_0 | \psi_2 \rangle = \int_{-\infty}^{\infty} \left(N_0 e^{-\alpha x^2/2} \right) \left(N_2 \left[4\alpha x^2 - 2 \right] e^{-\alpha x^2/2} \right) dx$$

$$\langle \psi_0 | \psi_2 \rangle = N_0 N_2 \left\{ 4\alpha \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx - 2 \int_{-\infty}^{\infty} e^{-\alpha x^2} dx \right\}$$

$$\int_0^{\infty} e^{-\beta x^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{\beta}}$$

$$\int_0^{\infty} x^2 e^{-\beta x^2} dx = \frac{1}{4\beta}\sqrt{\frac{\pi}{\beta}}$$

$$\langle \psi_0 | \psi_2 \rangle = N_0 N_2 \left\{ 4\alpha \bullet 2 \bullet \frac{1}{4\alpha}\sqrt{\frac{\pi}{\alpha}} - 2 \bullet 2 \bullet \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} \right\}$$

$$\langle \psi_0 | \psi_2 \rangle = 0$$

The Two Dimensional Harmonic Oscillator

The Schrödinger Equation

$$V(x,y) = \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2$$

$$\left\{-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right] + \left[\frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2\right]\right\}\psi(x,y) = E\psi(x,y)$$

$$\left\{\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2}k_x x^2\right] + \left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial y^2} + \frac{1}{2}k_y y^2\right]\right\}\psi(x,y) = E\psi(x,y)$$

The Solution: Separation of Variables

The Hamiltonian is of the form: $H(x,y) = H_x(x) + H_y(y)$

Therefore, assume that ψ is of the form: $\psi(x,y) = \psi_x(x) \bullet \psi_y(y)$

$$\left\{\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}+\frac{1}{2}k_x x^2\right]+\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial y^2}+\frac{1}{2}k_y y^2\right]\right\}\psi_x(x)\bullet\psi_y(y)=E\psi_x(x)\bullet\psi_y(y)$$

$$\downarrow$$

$$\psi_y\left[-\frac{\hbar^2}{2\mu}\frac{d^2\psi_x}{dx^2}+\frac{1}{2}k_x x^2\psi_x\right]+\psi_x\left[-\frac{\hbar^2}{2\mu}\frac{d^2\psi_y}{dy^2}+\frac{1}{2}k_y y^2\psi_y\right]=E\psi_x(x)\bullet\psi_y(y)$$

$$\downarrow$$

$$\underbrace{\frac{1}{\psi_x}\left[-\frac{\hbar^2}{2\mu}\frac{d^2\psi_x}{dx^2}+\frac{1}{2}k_x x^2\psi_x\right]}_{=\,E_x}+\underbrace{\frac{1}{\psi_y}\left[-\frac{\hbar^2}{2\mu}\frac{d^2\psi_y}{dy^2}+\frac{1}{2}k_y y^2\psi_y\right]}_{=\,E_y}=E$$

The above equation is of the form, f(x) + g(y) = constant.
Therefore, one can set each function equal to a constant.

$$E = E_x + E_y$$

$$\frac{1}{\psi_x}\left[-\frac{\hbar^2}{2\mu}\frac{d^2\psi_x}{dx^2}+\frac{1}{2}k_x x^2\psi_x\right]=E_x \qquad \frac{1}{\psi_y}\left[-\frac{\hbar^2}{2\mu}\frac{d^2\psi_y}{dx^2}+\frac{1}{2}k_y x^2\psi_y\right]=E_y$$

$$\downarrow \qquad\qquad \downarrow$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi_x}{dx^2}+\frac{1}{2}k_x x^2\psi_x=E_x\psi_x \qquad -\frac{\hbar^2}{2\mu}\frac{d^2\psi_y}{dx^2}+\frac{1}{2}k_y x^2\psi_y=E_y\psi_y$$

The above equations are just one dimensional HO Schrödinger equations. Therefore, one has:

$$\psi_{nx}=N_{nx}H_{nx}(\sqrt{\alpha}_x x)e^{-\alpha_x x^2/2} \qquad \psi_{ny}=N_{ny}H_{ny}(\sqrt{\alpha}_y y)e^{-\alpha_y y^2/2}$$

$$E_x=\left(n_x+\frac{1}{2}\right)\hbar\omega_x \qquad E_y=\left(n_y+\frac{1}{2}\right)\hbar\omega_y$$

$$\omega_x=\sqrt{\frac{k_x}{\mu}} \qquad \omega_y=\sqrt{\frac{k_y}{\mu}}$$

$$\alpha_x=\frac{\mu\omega_x}{\hbar} \qquad \alpha_y=\frac{\mu\omega_y}{\hbar}$$

Energies and Degeneracy

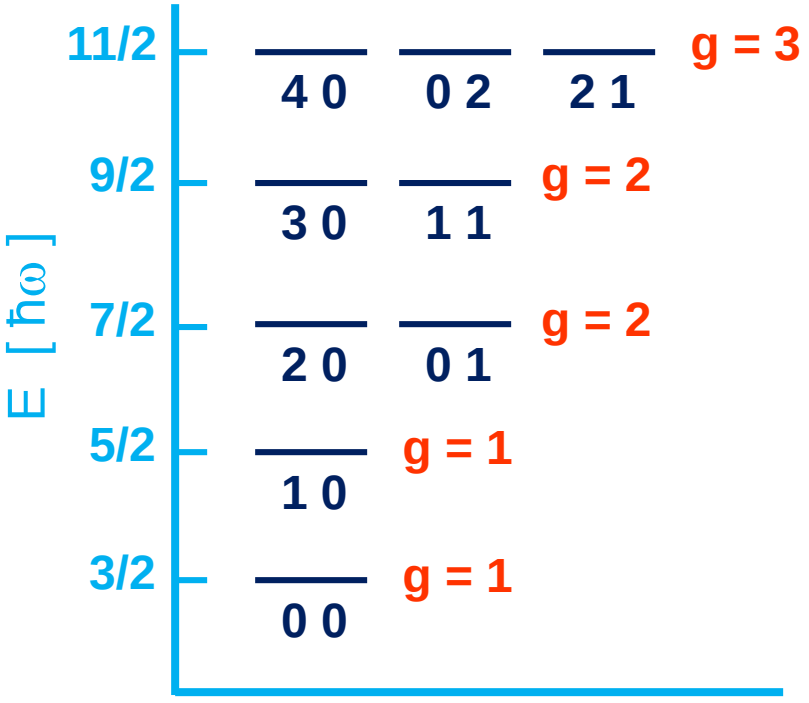
$$E = E_x + E_y = \left(n_x + \frac{1}{2}\right)\hbar\omega_x + \left(n_y + \frac{1}{2}\right)\hbar\omega_y \qquad \omega_x = \sqrt{\frac{k_x}{\mu}} \quad \omega_y = \sqrt{\frac{k_y}{\mu}}$$

Depending upon the relative values of k_x and k_y, one may have degenerate energy levels. For example, let's assume that $k_y = 4 \bullet k_x$.

$$\omega_y = 2\,\omega_x$$

$$E = \left(n_x + \frac{1}{2}\right)\hbar\omega_x + \left(2n_y + 1\right)\hbar\omega_x$$

$$E = \left(n_x + 2n_y + \frac{3}{2}\right)\hbar\omega_x$$

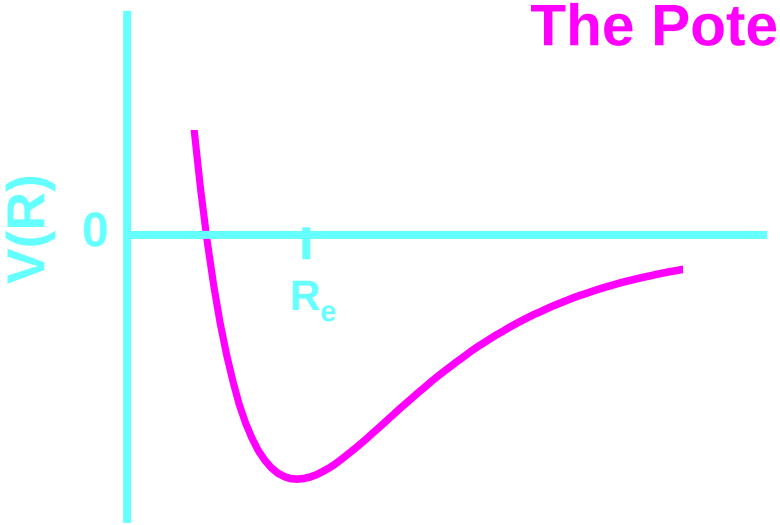


Application to spectroscopy

1. **The Vibrations of Diatomic Molecules**
2. **Vibrational Spectroscopy**
3. **Vibrational Anharmonicity**
4. **Vibrations of Polyatomic Molecules**

1. The Vibrations of Diatomic Molecules

The Potential Energy



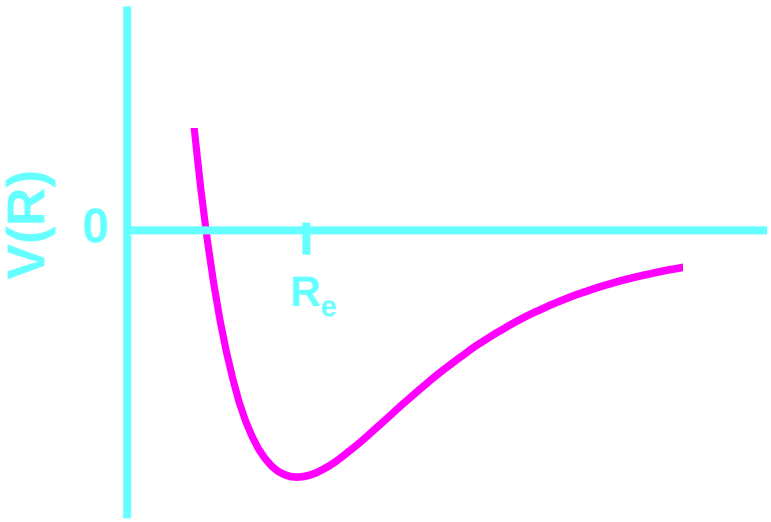
Define: $x = R - R_{eq}$

Expand V(x) in a Taylor series about x = 0 ($R = R_{eq}$)

$$V(x) = \sum_{n=0}^{\infty} \frac{1}{n!}\left(\frac{d^n V}{dx^n}\right)_{x=0} x^n$$

$$V(x) = \frac{1}{0!}(V)_{x=0} x^0 + \frac{1}{1!}\left(\frac{dV}{dx}\right)_{x=0} x^1 + \frac{1}{2!}\left(\frac{d^2V}{dx^2}\right)_{x=0} x^2 + \frac{1}{3!}\left(\frac{d^3V}{dx^3}\right)_{x=0} x^3 + \frac{1}{4!}\left(\frac{d^4V}{dx^4}\right)_{x=0} x^4 + \ldots$$

$$V(x) = (V)_{x=0} + \left(\frac{dV}{dx}\right)_{x=0} x + \frac{1}{2}\left(\frac{d^2V}{dx^2}\right)_{x=0} x^2 + \frac{1}{6}\left(\frac{d^3V}{dx^3}\right)_{x=0} x^3 + \frac{1}{24}\left(\frac{d^4V}{dx^4}\right)_{x=0} x^4 + \ldots$$



$$V(x) = \cancel{(V)_{x=0}} + \cancel{\left(\frac{dV}{dx}\right)_{x=0}} x + \frac{1}{2}\left(\frac{d^2V}{dx^2}\right)_{x=0} x^2 + \frac{1}{6}\left(\frac{d^3V}{dx^3}\right)_{x=0} x^3 + \frac{1}{24}\left(\frac{d^4V}{dx^4}\right)_{x=0} x^4 + \ldots$$

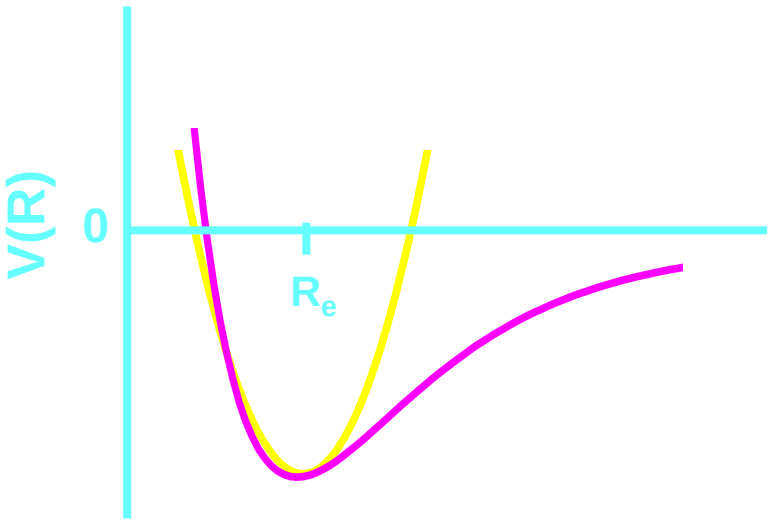
$$V(x) = \frac{1}{2}kx^2 + \gamma x^3 + \delta x^4 + \ldots$$

$(V)_{x=0} = 0$ By convention

$\left(\frac{dV}{dx}\right)_{x=0} = 0$ By definition of R_e as minimum

$$k = \left(\frac{d^2V}{dx^2}\right)_{x=0} \qquad \delta = \frac{1}{24}\left(\frac{d^4V}{dx^4}\right)_{x=0}$$

$$\gamma = \frac{1}{6}\left(\frac{d^3V}{dx^3}\right)_{x=0}$$



$$V(x) = \frac{1}{2}kx^2 + \gamma x^3 + \delta x^4 + \ldots$$

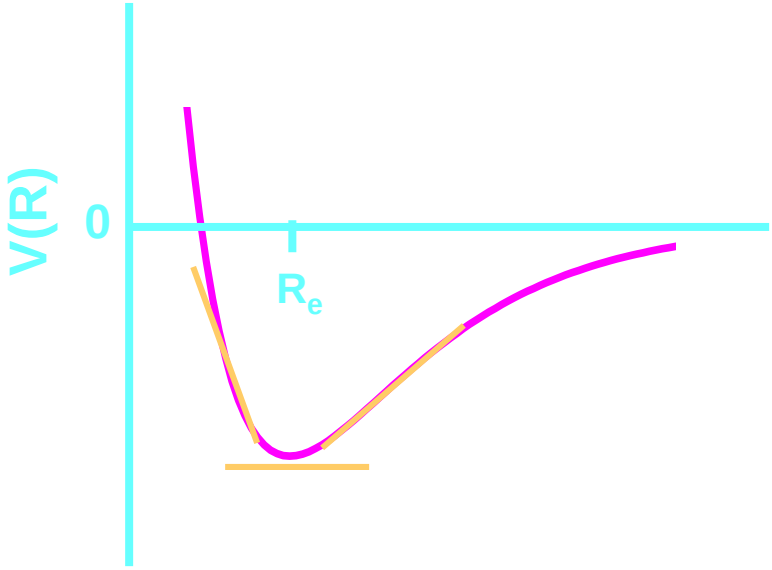
The Harmonic Oscillator Approximation

Ignore x^3 and higher order terms in V(x)

$$V(x) = \frac{1}{2}kx^2 \qquad \text{where} \qquad k = \left(\frac{d^2V}{dx^2}\right)_{x=0}$$

The Force Constant (k)

The Interpretation of k

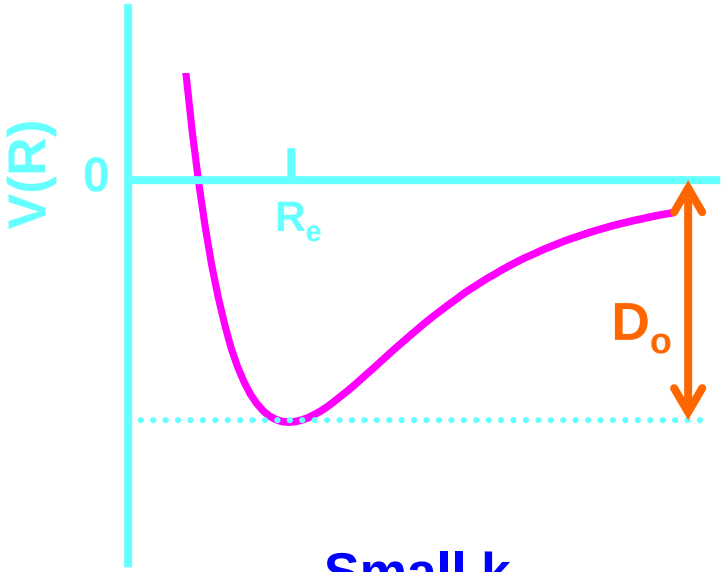


$$k = \left(\frac{d^2V}{dx^2}\right)_{x=0} = \frac{d}{dx}\left(\frac{dV}{dx}\right) = \frac{d}{dx}\left(Slope\right)$$

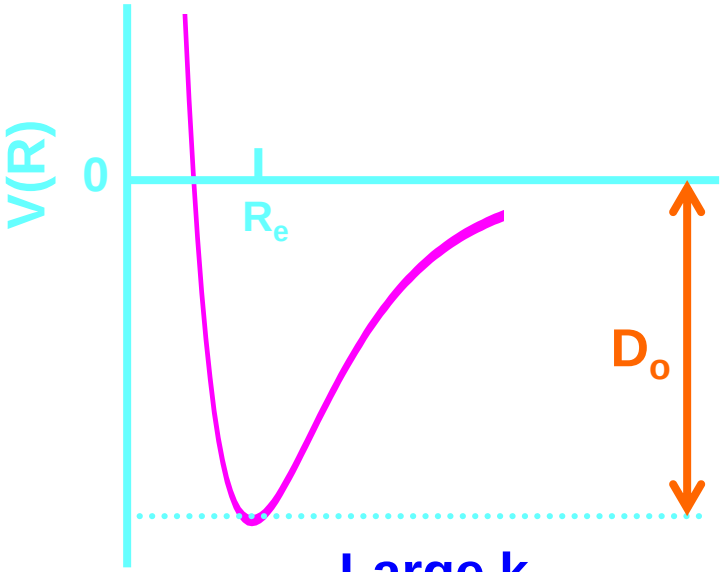
i.e. k is the “curvature” of the plot, and represents the “rapidity” with which the slope turns from negative to positive.

Another way of saying this is the k represents the “steepness” of the potential function at x=0 ($R=R_e$).

Correlation Between k and Bond Strength



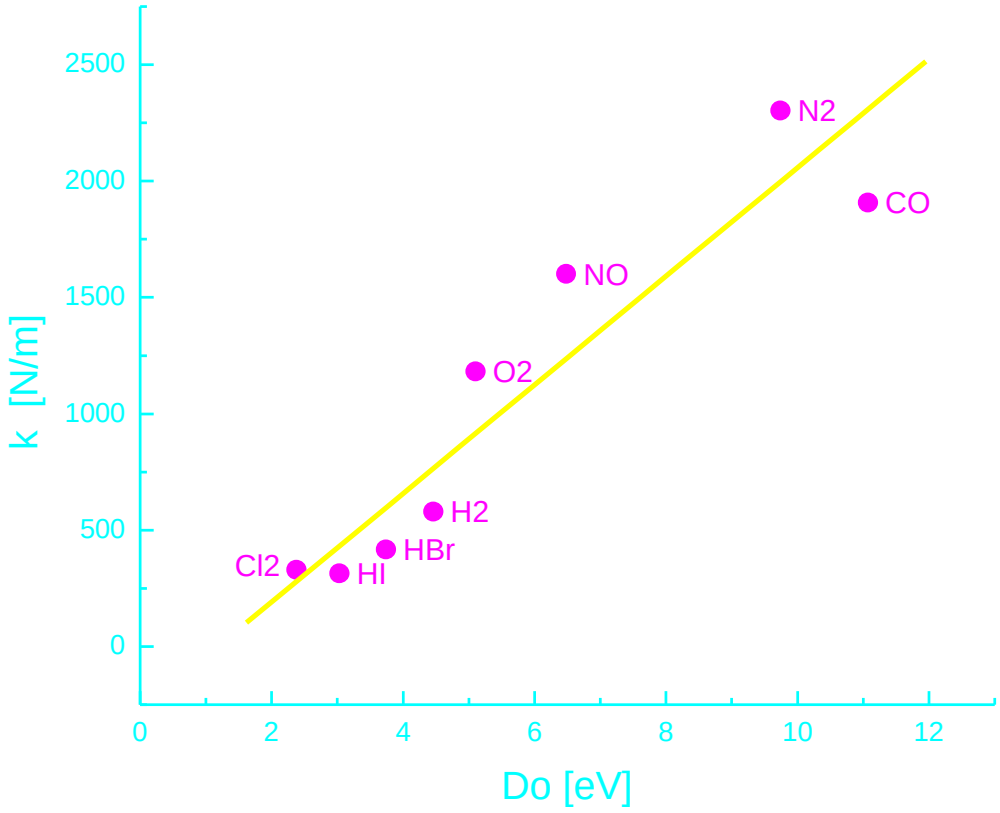
Small k
Small D_o



Large k
Large D_o

D_o is the Dissociation Energy of the molecule, and represents the chemical bond strength.

There is often a correlation between k and D_o.



Note the approximately linear correlation between Force Constant (k) and Bond Strength (D_o).

2. Vibrational Spectroscopy

Energy Levels and Transitions

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega = \left(n + \frac{1}{2}\right)h\nu \qquad \nu = \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Selection Rule

$\Delta n = \pm 1$ (+1 for absorption, -1 for emission)

IR Spectra: For a vibration to be IR active, the dipole moment must change during the course of the vibration.

Raman Spectra: For a vibration to be Raman active, the polarizability must change during the course of the vibration.

Transition Frequency

$n \rightarrow n+1$

$$\Delta E = \left[(n+1) + \frac{1}{2} \right] h\nu - \left[n + \frac{1}{2} \right] h\nu = h\nu$$

Wavenumbers: $\tilde{\nu} = \frac{\Delta E}{hc} = \frac{\nu}{c} \quad cm^{-1}$

Note: $\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

The Boltzmann Distribution

$$N_n \propto g_n e^{-E_n/kT} = e^{-E_n/kT}$$

The strongest transition corresponds to: $n=0 \rightarrow n=1$

Calculation of the Force Constant

Units of k

$$k = \left(\frac{d^2V}{dx^2} \right)_{x=0}$$

$$k = \frac{J}{m^2} = \frac{kg \bullet m^2 / s^2}{m^2} = \frac{kg}{s^2} = \frac{kg \bullet m / s^2}{m} = \frac{N}{m}$$

Calculation of k

$$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$\downarrow$$

$$k = \left(2\pi c\tilde{\nu}\right)^2 \mu$$

The IR spectrum of $^{79}Br^{19}F$ contains a single line at 380 cm^{-1}

Calculate the Br-F force constant, in N/m.

$h=6.63x10^{-34}$ J•s
$c=3.00x10^{8}$ m/s
$c=3.00x10^{10}$ cm/s
$k=1.38x10^{-23}$ J/K
1 amu = $1.66x10^{-27}$ kg
1 N = 1 kg•m/s^2

$$\mu = \frac{m_{Br} \cdot m_F}{m_{Br} + m_F} = \frac{(79\,amu)\cdot(19\,amu)}{79\,amu + 19\,amu}$$

$$\mu = 15.32\,amu \cdot 1.66x10^{-27}\,kg/amu = 2.54x10^{-26}\,kg$$

$$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \longrightarrow k = (2\pi c\tilde{\nu})^2\mu = \left[2(3.14)(3x10^{10}\,cm/s)(380\,cm^{-1})\right]^2(2.54x10^{-26}\,kg)$$

$$k = 130\,kg/s^2 = 130(kg\cdot m/s^2)/m = 130\,N/m$$

Calculate the intensity ratio, $R = \frac{I_{1\to 2}}{I_{0\to 1}}$,for the $^{79}Br^{19}F$ vibration at 25 ^{o}C.

$h=6.63x10^{-34}$ J•s
$c=3.00x10^{8}$ m/s
$c=3.00x10^{10}$ cm/s
$k=1.38x10^{-23}$ J/K

$\tilde{\nu}$ = 380 cm^{-1}

$$\frac{I_{1\to 2}}{I_{0\to 1}} = \frac{N_1}{N_0} = \frac{e^{-E_1/kT}}{e^{-E_0/kT}} = e^{-(E_1-E_0)/kT} = e^{-hc\tilde{\nu}/kT}$$

$$\frac{I_{1\to 2}}{I_{0\to 1}} = e^{-1.84} = 0.16$$

$$\boxed{\frac{hc\tilde{\nu}}{kT} = \frac{(6.63x10^{-34}\ J\cdot s)\left(3.00x10^{10}\ cm/s\right)\left(380\ cm^{-1}\right)}{\left(1.38x10^{-23}\ J/K\right)\left(298\ K\right)} = 1.84}$$

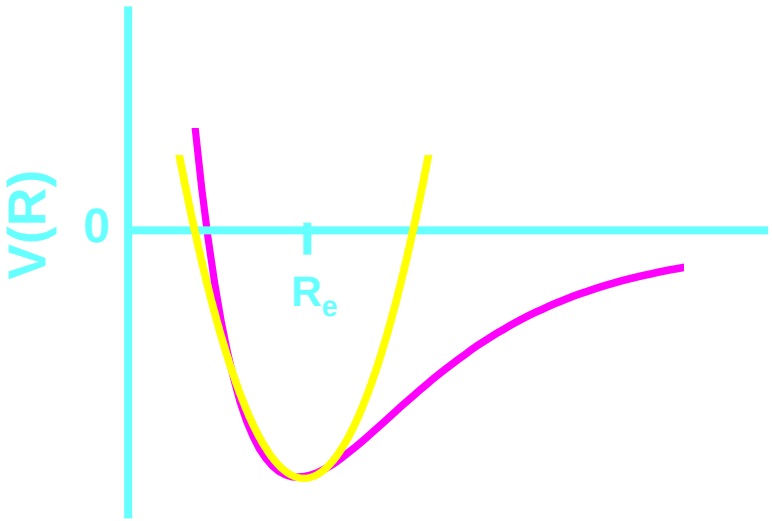
The n=1 $\rightarrow$ n=2 transition is called a ***hot band***, because its intensity increases at higher temperature

Dependence of hot band intensity on frequency and temperature

$$R = \frac{I_{1\rightarrow 2}}{I_{0\rightarrow 1}}$$

Molecule	$\tilde{\nu}$	T	R
$^{79}Br^{19}F$	380 cm^{-1}	25 ^{o}C	0.16
$^{79}Br^{19}F$	380	500	0.49
$^{79}Br^{19}F$	380	1000	0.65
$H^{35}Cl$	2880	25	9×10^{-7}
$H^{35}Cl$	2880	500	0.005
$H^{35}Cl$	2880	1000	0.04

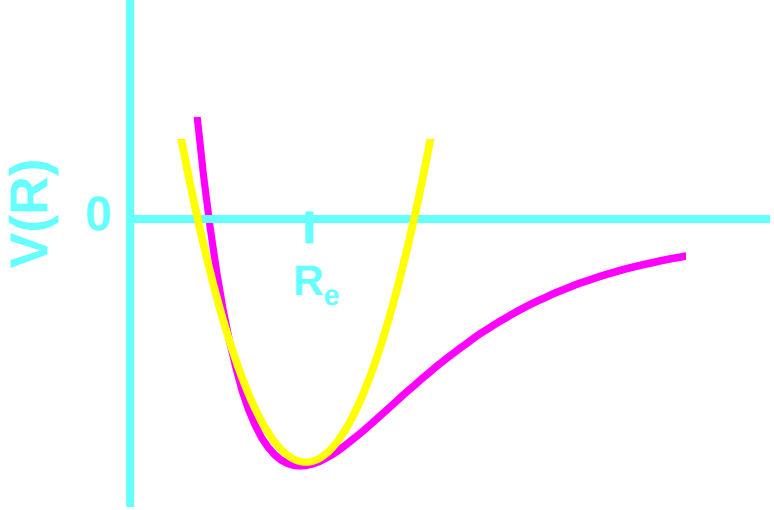
3. Vibrational Anharmonicity



$$V(x) = \frac{1}{2}kx^2 + \gamma x^3 + \delta x^4 + \ldots$$

Harmonic Oscillator Approximation: $V(x) \approx \frac{1}{2}kx^2$

The effect of including vibrational anharmonicity in treating the vibrations of diatomic molecules is to lower the energy levels and decrease the transition frequencies between successive levels.



$$V(x) = \frac{1}{2}kx^2 + \gamma x^3 + \delta x^4 + \ldots$$

A treatment of the vibrations of diatomic molecules which includes vibrational anharmonicity [includes higher order terms in V(x)] leads to an improved expression for the energy:

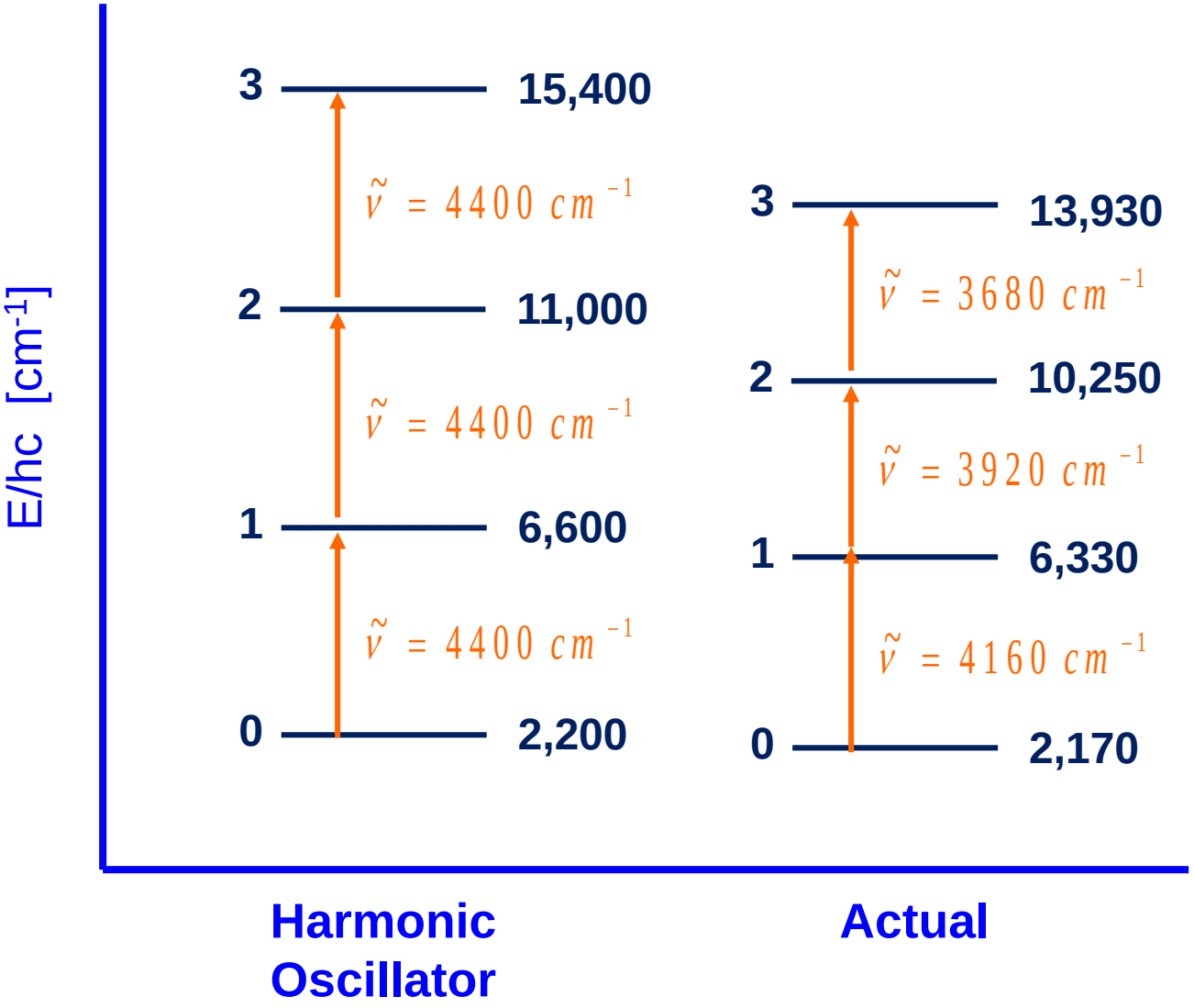
$$\frac{E_n}{hc} = \left(n + \frac{1}{2}\right)\bar{\nu} - \left(n + \frac{1}{2}\right)^2 x_e \bar{\nu}$$

$\tilde{\nu}$ is the harmonic frequency and x_e is the anharmonicity constant.

Measurement of the fundamental frequency (0→1) and first overtone (0→2) [or the "hot band" (1 →2)] permits determination of $\tilde{\upsilon}$ and x_e.

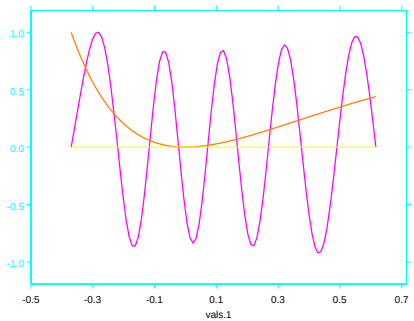
See HW Problem

Energy Levels and Transition Frequencies in H_2



Anharmonic Oscillator Wavefunctions

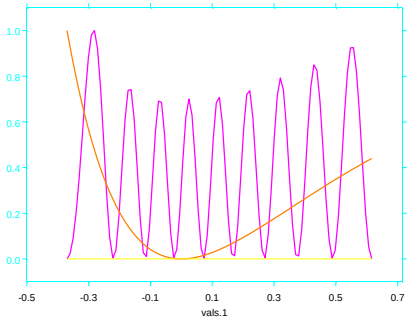
ψ



(xang ψ V zero)

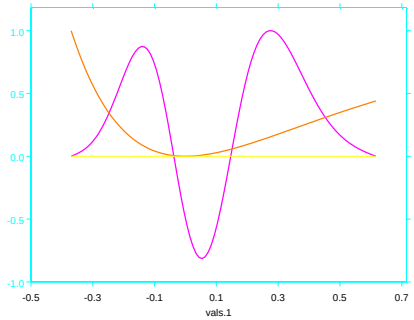
n = 10

ψ^2



(xang ψ2 V zero)

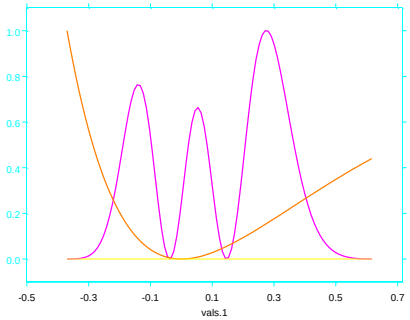
ψ



(xang ψ V zero)

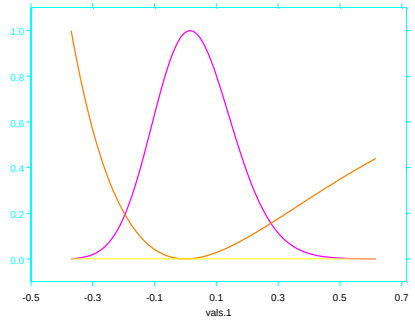
n = 2

ψ^2



(xang ψ2 V zero)

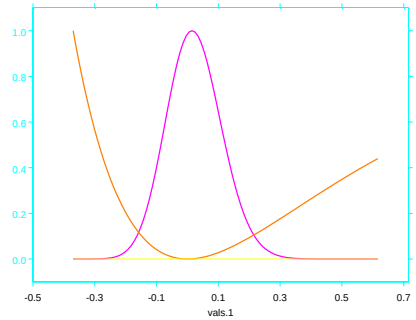
ψ



(xang ψ V zero)

n = 0

ψ^2



(xang ψ2 V zero)

Examples for HO

Example. For the ψ_1 of the HO : $\psi_1 = Axe^{-\alpha x^2/2}$ $\infty - < x < \infty$

1- Find the normalization factor

2. Find **<x>** **<p>** **<x²>** $< T > = \left\langle \frac{p^2}{2\mu} \right\rangle = \frac{1}{2\mu} \left\langle p^2 \right\rangle$

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

Example. For the ψ_1 of the HO : $\psi_1 = Axe^{-\alpha x^2/2}$ $\infty - < x < \infty$

1- Find the normalization factor
2. Find **<x>**

Normalization

$$\langle \psi_1 | \psi_1 \rangle = \int_{-\infty}^{\infty} \left[A_1 x e^{-\alpha x^2/2} \right]^2 dx = 1$$

from HW Solns.

$$A = \sqrt{2\alpha} \cdot \left(\frac{\alpha}{\pi} \right)^{1/4}$$

Positional Averages

<x>

$$< x > = \langle \psi_1 | x | \psi_1 \rangle = \int_{-\infty}^{\infty} x \left[A_1 x e^{-\alpha x^2/2} \right]^2 dx$$

from
HW Solns.

$$< x > = 0$$

<x²>

$$< x^2 > = \langle \psi_1 | x^2 | \psi_1 \rangle = \int_{-\infty}^{\infty} x^2 \left[A_1 x e^{-\alpha x^2/2} \right]^2 dx$$

from
HW Solns.

$$< x^2 > = \frac{3}{2\alpha}$$

Momentum Averages

<p>

$$< p >= \langle \psi_1 | \hat{p} | \psi_1 \rangle = \int_{-\infty}^{\infty} \left[A_1 x e^{-\alpha x^2/2} \right] \left[\frac{\hbar}{i} \frac{d\left(A_1 x e^{-\alpha x^2/2} \right)}{dx} \right] dx$$

from HW Solns.

$$< p > = 0$$

<p²>

$$< p^2 >= \langle \psi_1 | p^2 | \psi_1 \rangle = \int_{-\infty}^{\infty} \left[A_1 x e^{-\alpha x^2/2} \right] \left[-\hbar^2 \frac{d^2\left(A_1 x e^{-\alpha x^2/2} \right)}{dx^2} \right] dx$$

from HW Solns.

$$< p^2 > = \frac{3}{2} \hbar^2 \alpha$$

Energy Averages

Kinetic Energy

$$< T > = \left\langle \frac{p^2}{2\mu} \right\rangle = \frac{1}{2\mu} \left\langle p^2 \right\rangle$$

$$< T > = \frac{1}{2\mu} \left(\frac{3}{2} \hbar^2 \alpha \right)$$

from
HW Solns.

$$< T > = \frac{3}{4} \hbar \omega$$

Potential Energy

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

$$< V > = \frac{1}{2} k \left(\frac{3}{2\alpha} \right)$$

from
HW Solns.

$$< V > = \frac{3}{4} \hbar \omega$$

Total Energy

$$E = \left(n + \frac{1}{2} \right) \hbar \omega = \frac{3}{2} \hbar \omega \quad = < T > + < V >$$

In spectroscopy, we commonly refer to the “energy in wavenumbers”, which is actually E/hc:

$$\frac{E(n_1 n_2 n_3 \ldots)}{hc} = \sum_{i=1}^{3N-1} \left(n_i + \frac{1}{2} \right) \tilde{\nu}_i$$

The water molecule has three normal modes, with fundamental frequencies: $\tilde{\nu}_1$ = 3833 cm^{-1}, $\tilde{\nu}_2$ = 1649 cm^{-1}, $\tilde{\nu}_3$ = 3943 cm^{-1}.

What is the energy, in cm^{-1}, of the (112) state (i.e. n_1=1, n_2=1, n_3=2)?

$$\frac{E(112)}{hc} = \left(1 + \frac{1}{2}\right)\tilde{\nu}_1 + \left(1 + \frac{1}{2}\right)\tilde{\nu}_2 + \left(2 + \frac{1}{2}\right)\tilde{\nu}_3$$

$$= \frac{3}{2}\left(3833\,cm^{-1}\right) + \frac{3}{2}\left(1649\,cm^{-1}\right) + \frac{5}{2}\left(3943\,cm^{-1}\right)$$

$$= 18{,}081\,cm^{-1}$$

The water molecule has three normal modes, with fundamental frequencies: $\tilde{\nu}_1$ = 3833 cm^{-1}, $\tilde{\nu}_2$ = 1649 cm^{-1}, $\tilde{\nu}_3$ = 3943 cm^{-1}.

What is the energy difference, in cm^{-1}, between (112) and (100), i.e. E(112)/hc – E(100)/hc ?

$$\frac{E(112)}{hc} = 18,081\ cm^{-1}$$

$$\frac{E(100)}{hc} = \left(1+\frac{1}{2}\right)\tilde{\nu}_1 + \left(0+\frac{1}{2}\right)\tilde{\nu}_2 + \left(0+\frac{1}{2}\right)\tilde{\nu}_3$$

$$= \frac{3}{2}\left(3833\ cm^{-1}\right) + \frac{1}{2}\left(1649\ cm^{-1}\right) + \frac{1}{2}\left(3943\ cm^{-1}\right) = 8,546\ cm^{-1}$$

$$\frac{E(112)}{hc} - \frac{E(100)}{hc} = 18,081\ cm^{-1} - 8,546\ cm^{-1} = 9,535\ cm^{-1}$$

This corresponds to the frequency of the combination band in which the molecule's vibrations are excited from $n_2=0 \rightarrow n_2=1$ and $n_3=0 \rightarrow n_3=2$.