Use the result for $\psi^{(1)}$ to derive an expression for $E_q^{(2)}$

$$E_q^{(2)} = \left\langle \psi_q^{(0)} \mid \hat{H}^{(1)} \mid \psi_q^{(1)} \right\rangle = \sum_k \left\langle \psi_q^{(0)} \mid \hat{H}^{(1)} \mid a_k \psi_k^{(0)} \right\rangle$$

$$= \sum_k a_k \left\langle \psi_q^{(0)} \mid \hat{H}^{(1)} \mid \psi_k^{(0)} \right\rangle = \sum_k a_k H_{qk}^{(1)}$$

But

$$\therefore a_k = -\frac{H_{kq}^{(1)}}{E_k^{(0)} - E_q^{(0)}}$$

$$\therefore E_q^{(2)} = -\sum_k \frac{H_{kq}^{(1)} \cdot H_{qk}^{(1)}}{E_k^{(0)} - E_q^{(0)}}$$

$$H_{kq}^{(1)} = \left(H_{qk}^{(1)}\right)^{*}$$ since $\mathbf{H}^{(1)}$ is self-adjoint

$$\therefore E_q^{(2)} = -\sum_{k \neq q} \frac{\left|H_{kq}^{(1)}\right|^2}{E_k^{(0)} - E_q^{(0)}}$$

Note: if q is the ground state then $E_q^{(2)} < 0$ always.

Review: the Classical Harmonic Oscillator

- It is the simplest model for *molecular vibration*

  - The simplest case to consider is a diatomic molecule with two atomic masses, m_1 and m_2.

  - At low vibrational energies, the potential energy of the molecular bond is approximately symmetric with respect to the bond length at rest and the vibration of such a molecule obeys the equations of *simple harmonic motion*.
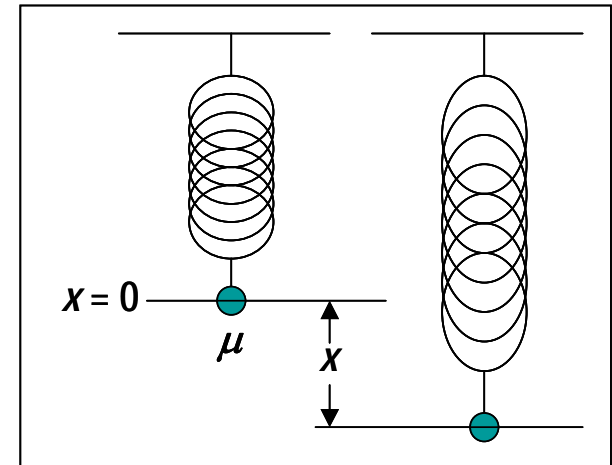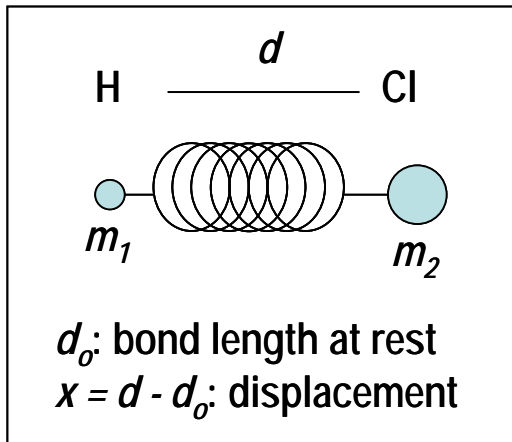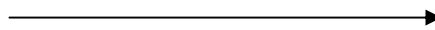
$$\frac{d^2x}{dt^2} = -\omega^2 x$$

The equation for simple harmonic motion:

For a system with more than one mass, we must replace the mass m in the spring equation with a **reduced mass** μ, given by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \qquad \text{or} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

H $\overset{d}{\rule{3cm}{0.4pt}}$ Cl

m_1 m_2

d_o: bond length at rest
$x = d - d_o$: displacement

Mathematically equivalent, but simpler

$\longrightarrow$

$x = 0$

μ

x

Review: QM Harmonic Oscillator

energy

V(x)

- The potential energy of an Harmonic oscillator

$$V(x) = -\int_0^x F(x) \cdot dx = -\int_0^x (-k_h x)dx = \tfrac{1}{2} k_h x^2$$

- The Schrodinger equation for the system is therefore

$$\left(-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + \frac{1}{2} k_h x^2 \right) \cdot \psi(x) = E \cdot \psi(x)$$

$E_k + V(x)$

$\leftarrow\ \mathbf{d}\ \rightarrow$

- The eigenfunctions are Hermite polynomials, $H_n(\alpha^{1/2}x)$

$$\psi_n(x) = A_n \cdot H_n(\alpha^{1/2}x) \cdot exp(-\alpha x^2/2)$$

$-x \qquad x=0 \qquad x$
$\mathbf{d = d_o\text{-}x} \quad \mathbf{d = d_o} \quad \mathbf{d = d_o\text{+}x}$

e.g.,

$$\psi_0(x) = \left(\frac{\alpha}{\pi} \right)^{1/4} \cdot exp\left(-\tfrac{1}{2}\alpha x^2 \right) \qquad \psi_2(x) = \left(\frac{\alpha}{4\pi} \right)^{1/4} \cdot \left(2\alpha x^2 - 1 \right) \cdot exp\left(-\tfrac{1}{2}\alpha x^2 \right)$$

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi} \right)^{1/4} \cdot x \cdot exp\left(-\tfrac{1}{2}\alpha x^2 \right)$$

$$E_v = \hbar \sqrt{\frac{k_h}{\mu}} \cdot \left(v + \frac{1}{2} \right) = h\nu_o \cdot \left(v + \frac{1}{2} \right)$$

- The eigenvalues, or the total energy E
  - v is the vibrational quantum number
  - ν_o is the frequency of oscillator or the vibrational frequency
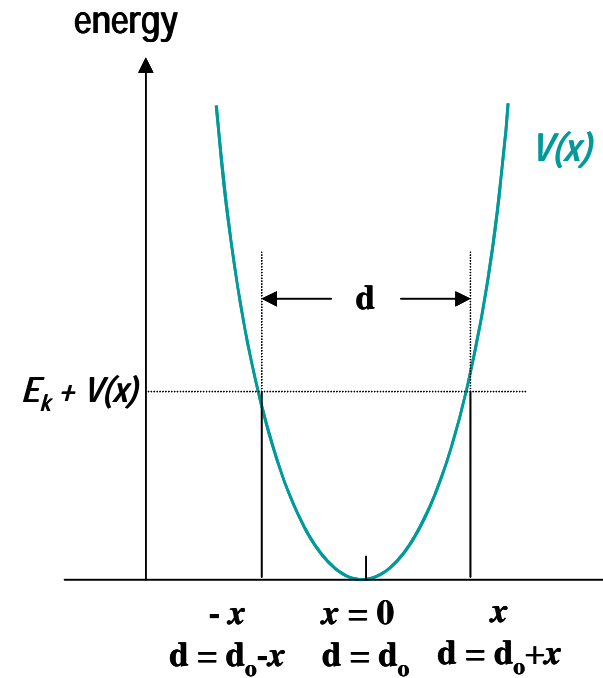
$$v = 0,1,2,3,\ldots$$

$$\nu_o = \frac{1}{2\pi} \sqrt{\frac{k_h}{m}}$$

$$E_v = h\nu_o \cdot \left(v + \frac{1}{2} \right)$$ where v = 0,1,2,3,… and $$\nu_o = \frac{1}{2\pi} \sqrt{\frac{k_h}{m}}$$

- The quantized energy levels for the harmonic oscillator are *equidistant* from one another.

- The lowest possible energy, corresponding v = 0, $E_0 = 0.5\ h\nu_o$
  - In classical theory a molecule could be undergoing no vibration, but in quantum mechanics, this is not allowed
  - Even at 0 K, vibration still occurs with energy ½ $h\nu_o$. This is the *zero-point energy*.
  - Consistent with Heisenberg Uncertainty principle; if no vibration occurred, the position and momentum of the atoms would both have precise values and this is not allowed!

$\psi_n(x)$
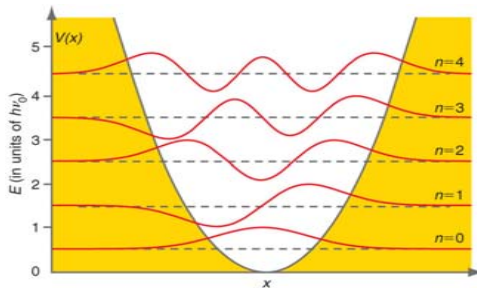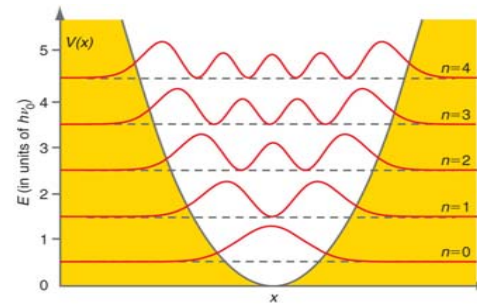
$\psi_n{}^\star(x)\ \psi_n(x)$

- The quantum oscillator can penetrate into classically forbidden regions - tunneling.
- The relative percentages of ψ in the classical forbidden regions suggests that the tunneling probability decreases as the total vibrational energy increases.

We defined two operators:

$$\hat{a} = \frac{1}{\sqrt{2}}(q + i\hat{p}) \qquad \hat{a}^+ = \frac{1}{\sqrt{2}}(q - i\hat{p})$$

Note: $\quad q = \sqrt{\alpha}x \qquad \hat{p} = \frac{1}{\hbar\sqrt{\alpha}}\hat{p}_x \qquad \alpha = \frac{\omega m}{\hbar} = \frac{\sqrt{km}}{\hbar}$

Some relationships between **a**, **a**$^+$ and **H**.

$$[\hat{a}, \hat{a}^+] = 1 \qquad [\hat{a}, \hat{H}] = \hat{a} \qquad [\hat{a}^+, \hat{H}] = -\hat{a}^+$$

$$\hat{a}\hat{a}^+ = \hat{H} + \frac{1}{2} \qquad \hat{a}^+\hat{a} = \hat{H} - \frac{1}{2}$$

$$\hat{H} = \frac{1}{2}(\hat{a}\hat{a}^+ + \hat{a}^+\hat{a})$$

Most relevant operations for nth wave function

$$\hat{a} \mid n \; >= \sqrt{n} \mid n-1 >$$

$$\hat{a}^{+} \mid n \; >= \sqrt{n+1} \mid n+1 >$$

Example: Use the spectral results for time–independent perturbation theory to find the first and second order corrections to the energy and the first order correction to the wave function for the first excited state of a harmonic oscillator, $|n = 1\rangle$, (frequency = $\vee$ and α =0.5) in their simplest forms if the perturbation operator is $\mathbf{H}^{(1)} = x$, where x is the displacement coordinate of the vibrator.

Answer:

First order correction: $E_{n=1}^{(1)} = <n=1|\hat{H}^{(1)}|n=1> = <n=1|x|n=1>$

$$\therefore \hat{H}^{(1)} = \frac{1}{2}\left(\frac{2}{\alpha}\right)^{\frac{1}{2}}\left(\hat{a}+\hat{a}^{+}\right)$$ Since α = 0.5 $\Rightarrow \hat{H}^{(1)} = \frac{1}{2}\left(\frac{2}{0.5}\right)^{\frac{1}{2}}\left(\hat{a}+\hat{a}^{+}\right) = \left(\hat{a}+\hat{a}^{+}\right)$

$$\therefore E_{n=1}^{(1)} = <1|\left(\hat{a}+\hat{a}^{+}\right)|1>$$

$$= <1|\hat{a}|1> + <1|\hat{a}^{+}|1>$$

$$= <1|\sqrt{1}|0> + <1|\sqrt{2}|2>$$

$$= \delta_{1,0} + \sqrt{2}\delta_{1,2} = 0$$ since the HO wave functions are orthonormal

$$\therefore E_{n=1}^{(1)} = 0$$

Next: $\psi_q^{(1)} = \sum_{k \neq q} a_k \psi_k^{(0)}$ where $a_k = \dfrac{H_{kq}^{(1)}}{\left(E_q^{(0)} - E_k^{(0)}\right)}$

In this problem, q =1

$$\therefore H_{k,1}^{(1)} = <k | \hat{H}^{(1)} | 1> = <k | \left(\hat{a} + \hat{a}^+\right) | 1>$$

$$= \delta_{k,0} + \sqrt{2}\delta_{k,2}$$

Therefore: $H_{k,1}^{(1)} = 0$ unless k = 0 or 2

$$\therefore \psi^{(1)} = a_0 \psi_0^{(0)} + a_2 \psi_2^{(0)} = a_0 | 0 > + a_2 | 2 >$$

$$a_0 = \frac{1}{E_1^{(0)} - E_0^{(0)}} \quad ; \quad a_2 = \frac{\sqrt{2}}{E_1^{(0)} - E_2^{(0)}}$$

$$\because E_n^{(0)} = h\nu(n + \frac{1}{2}) \Rightarrow E_1^{(0)} - E_0^{(0)} = h\nu\left(\frac{3}{2} - \frac{1}{2}\right) = h\nu$$

$$\Rightarrow E_1^{(0)} - E_2^{(0)} = h\nu\left(\frac{3}{2} - \frac{5}{2}\right) = -h\nu$$

$$\therefore \psi_1^{(1)} = \frac{1}{h\nu}|0> - \frac{\sqrt{2}}{h\nu}|2>$$

Lastly: $E_q^{(2)} = \sum_{k \neq q} \frac{\left|H_{kq}^{(1)}\right|^2}{E_q^{(0)} - E_k^{(0)}}$

Like the first order correction to the wave function $E_q^{(2)}$ is non-zero for k = 0 and 2

$$\therefore E_1^{(2)} = \frac{\left|H_{0,1}^{(1)}\right|^2}{E_1^{(0)} - E_0^{(0)}} + \frac{\left|H_{2,1}^{(1)}\right|^2}{E_1^{(0)} - E_2^{(0)}}$$

$$= \frac{1}{h\nu} - \frac{\left(\sqrt{2}\right)^2}{h\nu} = \frac{1}{h\nu} - \frac{2}{h\nu}$$

$$= -\frac{1}{h\nu}$$

Summary:

$$E_1 = E_1^{(0)} + E_1^{(1)} + E_1^{(2)} = \frac{3}{2}h\nu + 0 - \frac{1}{h\nu} = \frac{3}{2}h\nu - \frac{1}{h\nu}$$

$$\psi_1 = |1> - \frac{1}{h\nu}|0> - \frac{\sqrt{2}}{h\nu}|2>$$