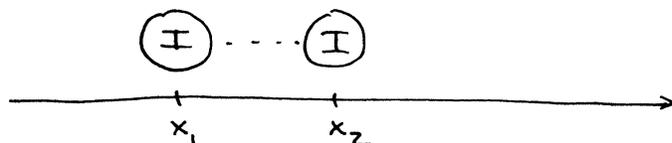


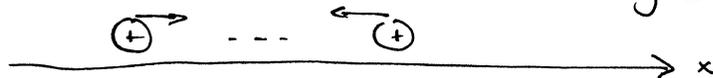
The Harmonic Oscillator

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This is one of the most important model problems in chemistry. Diatomics (and any bonded species) look enormously like harmonic oscillators



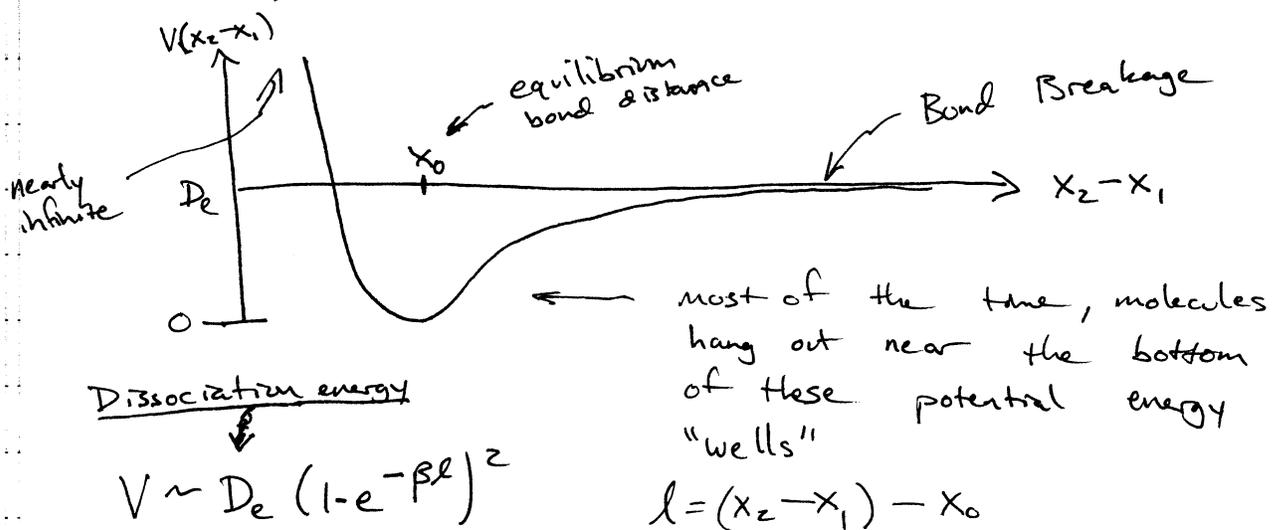
If we pull the two atoms apart there's a restoring force due to negative charges in the central bonded region and positive nuclear charges.



If we push them together, the core electrons overlap and there's an outward restoring force



We can plot what this looks like:



Dissociation energy

$$V \sim D_e (1 - e^{-\beta l})^2$$

$$l = (x_2 - x_1) - x_0$$

This is called a Morse potential, it is a very good mimic

of the behavior of real bonded atoms.

Find the minimum:

$$\frac{\partial V}{\partial l} = 0$$

$$\frac{\partial V}{\partial l} = 2D_e(1 - e^{-\beta l})(+\beta e^{-\beta l}) = 2\beta D_e(e^{-\beta l} - e^{-2\beta l})$$

At the minimum

$$2\beta D_e(e^{-\beta l} - e^{-2\beta l}) = 0$$

$$\Rightarrow l = 0 \text{ or } (x_2 - x_1 = x_0)$$

Curvature: $\left(\frac{\partial^2 V}{\partial l^2}\right) = 2\beta D_e(-\beta e^{-\beta l} + 2\beta e^{-2\beta l}) = 2\beta^2 D_e(2e^{-2\beta l} - e^{-\beta l})$

At $l=0$,

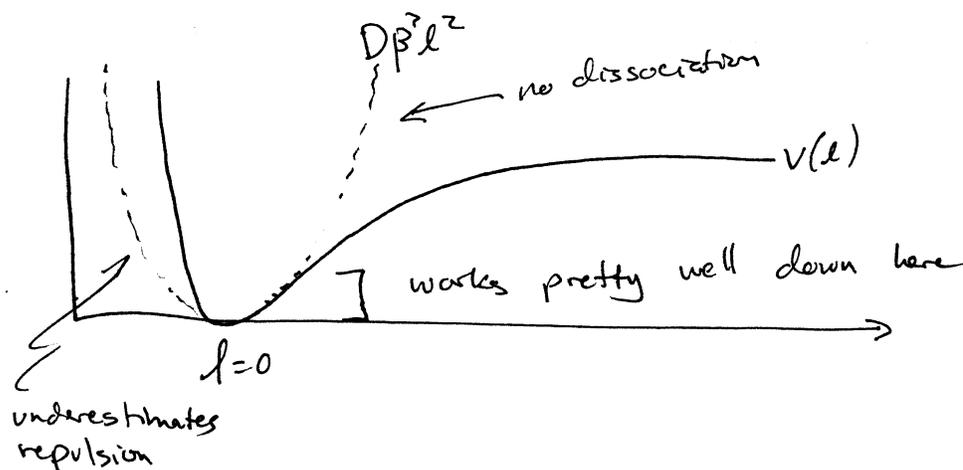
$$\frac{\partial^2 V}{\partial l^2} = 2\beta^2 D_e$$

So in a Maclaurin series:

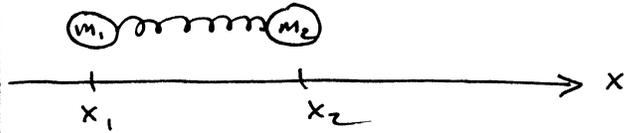
$$V(l) = \underbrace{V(0)}_0 + \underbrace{V'(0)}_0 l + \underbrace{\frac{V''(0)}{2!} l^2}_{\text{first surviving term}} + \dots$$

$$V(l) \approx D\beta^2 l^2$$

← this is a harmonic potential



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two atoms connected by a bond.

$$V = \frac{1}{2} k (x_2 - x_1 - x_0)^2$$

deviation from equilibrium bond distance \$x_0\$

Force on atom 1: $F_1 = -\frac{dV}{dx_1} = +k(x_2 - x_1 - x_0)$

Force on atom 2: $F_2 = -\frac{dV}{dx_2} = -k(x_2 - x_1 - x_0)$ $F_2 = -F_1$

Newton's equations give us coupled 2nd order diff eqs which are hard.

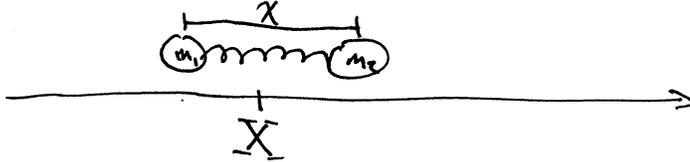
$$m_1 \frac{d^2 x_1}{dt^2} = k(x_2 - x_1 - x_0)$$

$$m_2 \frac{d^2 x_2}{dt^2} = -k(x_2 - x_1 - x_0)$$

A trick:

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} = \text{center-of-mass position}$$

$$x = x_2 - x_1 = \text{relative coordinate}$$



$$\frac{dX}{dt} = \frac{1}{m_1 + m_2} \left[m_1 \frac{dx_1}{dt} + m_2 \frac{dx_2}{dt} \right] \leftarrow \text{simple derivative definition of } X'$$

$$\frac{d^2 X}{dt^2} = \frac{1}{m_1 + m_2} \left[m_1 \frac{d^2 x_1}{dt^2} + m_2 \frac{d^2 x_2}{dt^2} \right]$$

$$= \frac{1}{m_1 + m_2} \left[k(x_2 - x_1 - x_0) - k(x_2 - x_1 - x_0) \right]$$

$$\boxed{M \frac{d^2 X}{dt^2} = 0}$$

center of mass is not accelerating (but it may still be moving)

Similar treatment for x :

$$x = x_2 - x_1$$

$$\frac{dx}{dt} = \frac{dx_2}{dt} - \frac{dx_1}{dt}$$

$$\frac{d^2x}{dt^2} = \frac{d^2x_2}{dt^2} - \frac{d^2x_1}{dt^2}$$

$$= -\frac{1}{m_2} k(x_2 - x_1 - x_0) - \frac{1}{m_1} k(x_2 - x_1 - x_0)$$

$$= -\frac{m_1}{m_2 m_1} k(x - x_0) - \frac{m_2}{m_1 m_2} k(x - x_0)$$

$$\frac{d^2x}{dt^2} = -\frac{(m_1 + m_2)}{m_1 m_2} k(x - x_0)$$

$$\left(\frac{m_1 m_2}{m_1 + m_2} \right) \frac{d^2x}{dt^2} = -k(x - x_0)$$

$\mu = \frac{m_1 m_2}{m_1 + m_2}$ = "reduced" mass

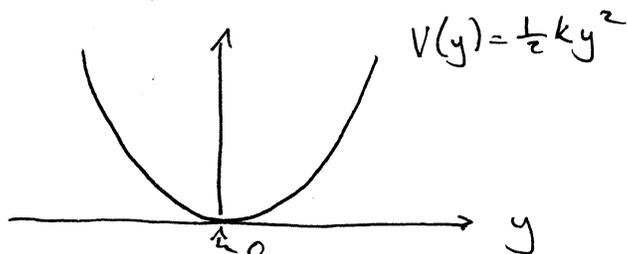
If $m_1 = m_2 = m$, what is μ ?

If $m_1 = 1000m_2$, what is μ ?

Let's shift our coordinate to 0 using:

$$y = x - x_0$$
$$\frac{dy}{dt} = \frac{dx}{dt}$$
$$\frac{d^2y}{dt^2} = \frac{d^2x}{dt^2}$$

$$\mu \frac{d^2y}{dt^2} = -ky$$



$y=0$ corresponds to equilibrium bond length
 k = spring constant or how stiff is the bond

$$\frac{d^2 y}{dt^2} = -\frac{k}{m} y$$

$$\frac{d^2 y}{dt^2} + \frac{k}{m} y = 0$$

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

$$y'(t) = -A\omega \sin \omega t + B\omega \cos \omega t$$

$$y''(t) = -A\omega^2 \cos \omega t - B\omega^2 \sin \omega t = -\omega^2 y(t)$$

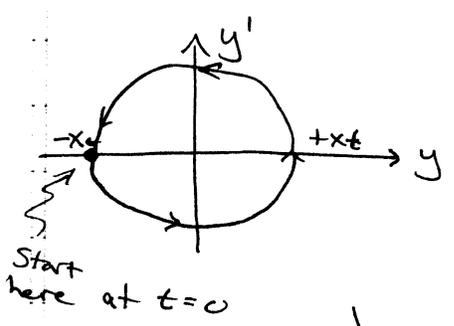
$$-\omega^2 y(t) + \frac{k}{m} y(t) = 0 \implies \text{true when } \omega = \sqrt{\frac{k}{m}}$$

Consider what happens when we pull back on the spring:

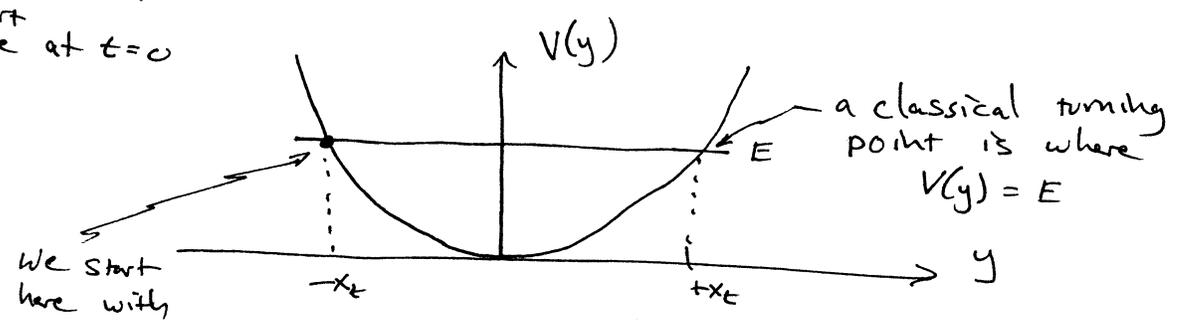
$$y(0) = -x_e \implies A = -x_e$$
$$y'(0) = 0 \implies B = 0$$

$$y(t) = -x_e \cos \omega t$$

$$y'(t) = x_e \omega \sin \omega t$$

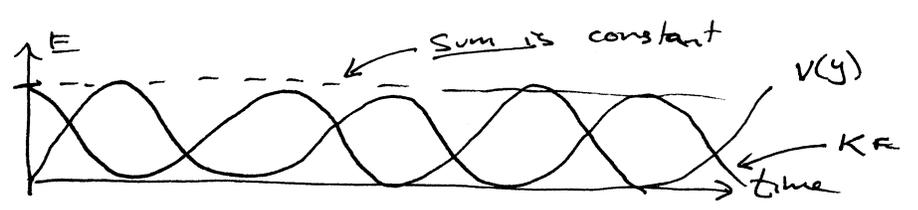


← path we take in position/velocity space is called an orbit.



$$E = \frac{1}{2} k x_e^2$$

(no kinetic energy)



The total energy $KE + V = \frac{1}{2} \mu v_y^2 + \frac{1}{2} k y^2 = E$

$$= \frac{p^2}{2\mu} + \frac{k}{2} y^2$$

What's a good guess at a Hamiltonian operator in QM?

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial y^2} + \frac{k}{2} y^2$$

The Schrödinger equation we must solve is

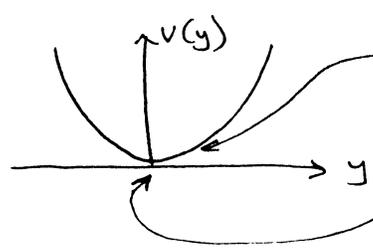
$$\hat{H}\psi = E\psi$$

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi(y)}{\partial y^2} + \frac{k}{2} y^2 \psi(y) = E \psi(y)$$

Last time we solved the classical motion for a harmonic oscillator

$$V(y) = \frac{1}{2}ky^2$$

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



We choose the zero of energy such that $V(0) = 0$

We also adjust the coordinate y so that $y=0$ is the equilibrium bond length

Hamiltonian to solve:

$$\left[\underbrace{-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial y^2}}_{\text{kinetic}} + \underbrace{\frac{1}{2}ky^2}_{\text{potential}} \right] \psi(y) = E\psi(y)$$

Classically, we got this equation for $y(t)$:

$$y(t) = A \sin\left(\sqrt{\frac{k}{\mu}} t\right) + B \cos\left(\sqrt{\frac{k}{\mu}} t\right) = A \sin(\omega t) + B \cos(\omega t)$$

$$\omega = \sqrt{\frac{k}{\mu}} \quad k = \mu\omega^2$$

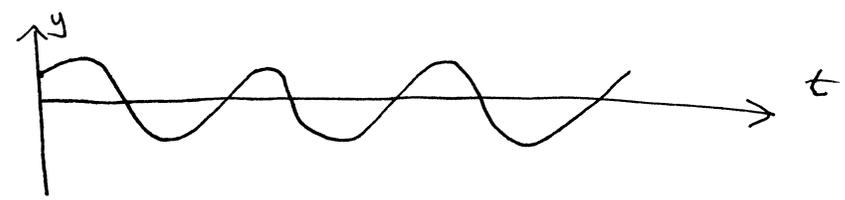
$$\left. \begin{aligned} y(0) &= y_0 \\ \dot{y}(0) &= v_0 \end{aligned} \right\} \text{initial conditions}$$

$$y(0) = B = y_0$$

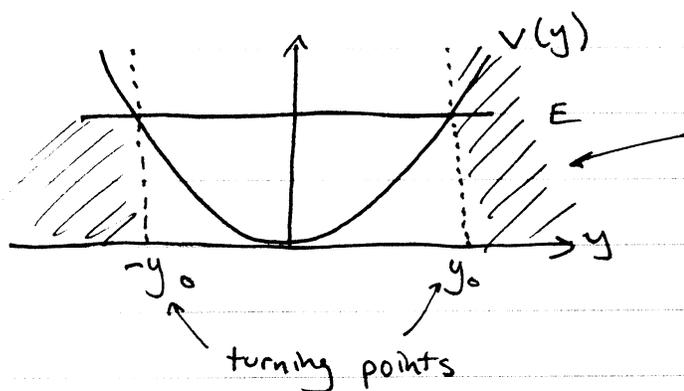
$$\dot{y}(t) = A\omega \cos \omega t - y_0 \omega \sin(\omega t)$$

$$\dot{y}(0) = A\omega = v_0 \quad \longrightarrow \quad A = \frac{v_0}{\omega}$$

$$y(t) = y_0 \cos \omega t + \frac{v_0}{\omega} \sin \omega t$$



$$E = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 y^2$$



classically forbidden region

the coordinate will never be found outside these turning points, at least according to classical mechanics!

At the turning points

$$E = V(y) = \frac{1}{2} m \omega^2 y_0^2$$

$$y_0 = \pm \sqrt{\frac{2E}{m\omega^2}}$$

Now, back to Quantum

Consider these two situations.

$$\left[\frac{d^2}{dy^2} + c^2 \right] \psi(y) = 0$$

$$(\alpha^2 + c^2) e^{\alpha y} = 0$$

$$(\alpha + ic)(\alpha - ic) e^{\alpha y} = 0$$

$$\psi(y) = A e^{-icy} + B e^{+icy}$$

$$\text{or } \cos(ky) + \sin(ky)$$

When the c^2 term is positive

the wave function is

Oscillatory

$$\left[\frac{d^2}{dy^2} - c^2 \right] \psi(y) = 0$$

$$(\alpha^2 - c^2) e^{\alpha y} = 0$$

$$(\alpha + c)(\alpha - c) e^{\alpha y} = 0$$

$$\psi(y) = \underbrace{A e^{-cy}}_{\text{exponential decay}} + \underbrace{B e^{+cy}}_{\text{exponential growth}}$$

When the c^2 term is

negative, the wave function

decays exponentially

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dy^2} + \frac{1}{2} m \omega^2 y^2 \right] \psi(y) = E \psi(y) \leftarrow \text{Schrodinger}$$

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$$\left[\frac{d^2}{dy^2} - \frac{2m}{\hbar^2} \left(\frac{1}{2} m \omega^2 y^2 - E \right) \right] \psi(y) = 0$$

$$\left[\frac{d^2}{dy^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2} m \omega^2 y^2 \right) \right] \psi(y) = 0$$

what's the sign of this term?

* In the classically allowed region

$$E > \frac{1}{2} m \omega^2 y^2$$

(C^2 is positive)

So the solutions to $\psi(y)$ will oscillate

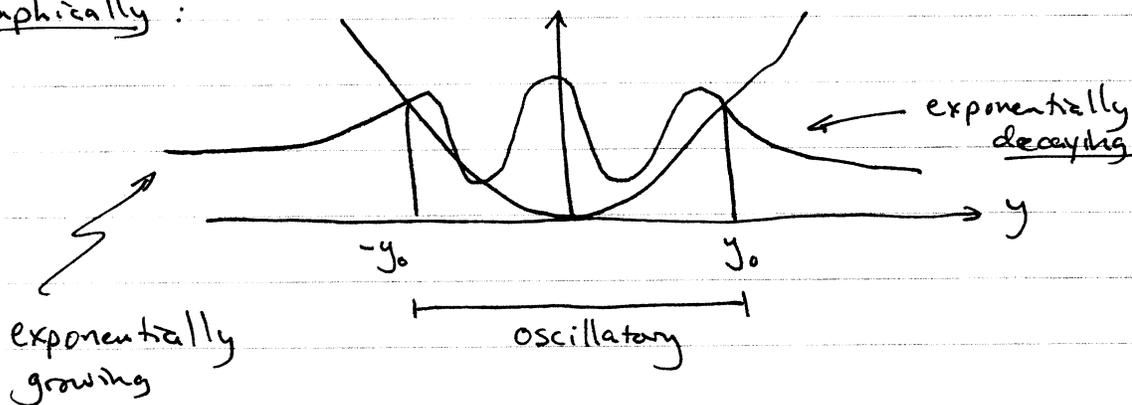
* In the classically forbidden region

$$E < \frac{1}{2} m \omega^2 y^2$$

(C^2 is negative)

So the solutions to $\psi(y)$ will be decaying.

Graphically:



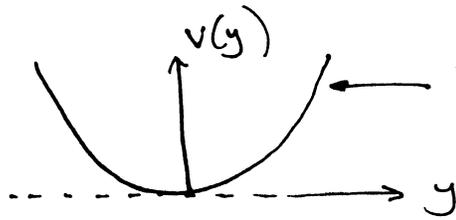
The asymptotic solutions $|y| \rightarrow \infty$ or $\frac{1}{2} m \omega^2 y^2 \gg E$

$$\frac{d^2}{dy^2} \psi(y) = -\frac{2m}{\hbar^2} \left(E - \frac{1}{2} m \omega^2 y^2 \right) \psi(y)$$

$$\approx -\frac{2m}{\hbar^2} \left(-\frac{1}{2} m \omega^2 y^2 \right) \psi(y)$$

$$\frac{d^2}{dy^2} \psi(y) = \frac{m^2 \omega^2}{\hbar^2} y^2 \psi(y)$$

Last time:



$$V(y) = \frac{1}{2} \mu \omega^2 y^2$$

↑
reduced mass

frequency of classical oscillator

9.5

$$\hat{H} \psi(y) = E \psi(y)$$

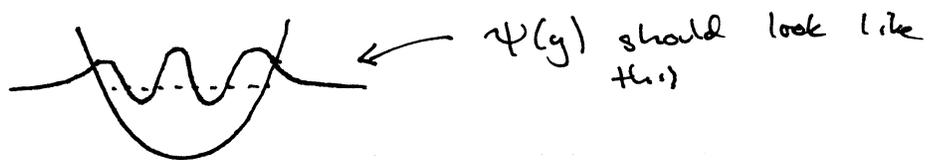
Solving a QM problem: knowing ψ , being able to use this to get $\langle x \rangle$, $\langle p \rangle$, ...

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dy^2} + \frac{1}{2} \mu \omega^2 y^2 \right] \psi(y) = E \psi(y)$$

equivalent ↷

$$\left[\frac{d^2}{dy^2} + \frac{2\mu}{\hbar^2} \left(E - \frac{1}{2} \mu \omega^2 y^2 \right) \right] \psi(y) = 0$$

We argued that the wavefunctions that solve this must decay or grow in the classically forbidden region where $E < \frac{1}{2} \mu \omega^2 y^2$ and oscillate in the allowed region, $E > \frac{1}{2} \mu \omega^2 y^2$



We started to solve it in the asymptotic region:

$$\frac{d^2}{dy^2} \psi(y) = \frac{\mu^2 \omega^2}{\hbar^2} y^2 \psi(y) \quad \leftarrow E \text{ is small compared to } y^2$$

$$\beta^2 = \frac{\mu \omega}{\hbar} \rightarrow \frac{d^2}{dy^2} \psi(y) = \beta^4 y^2 \psi(y)$$

define $q = \beta y$

$$\frac{d\psi}{dy} = \frac{d\psi}{dq} \frac{dq}{dy} \quad \leftarrow \text{chain rule}$$

$$\frac{d^2\psi}{dy^2} = \frac{d}{dq} \left(\frac{d\psi}{dq} \frac{dq}{dy} \right) \frac{dq}{dy} \quad \leftarrow \text{chain rule again}$$

Since $q = \beta y$
 $\frac{dq}{dy} = \beta$, so

$$\frac{d^2 \psi}{dy^2} = \frac{d^2 \psi}{dq^2} \beta^2$$

\therefore

$$\frac{d^2 \psi}{dq^2} \beta^2 = \beta^4 \left(\frac{q}{\beta}\right)^2 \psi(q)$$

$$\frac{d^2 \psi}{dq^2} = q^2 \psi(q)$$

This has general solutions: $\psi(q) = A e^{\pm q^2/2}$

One of these, $A e^{+q^2/2}$ can't be a valid wave function because it can't be normalized ($\psi(q) \rightarrow \infty$ as $q \rightarrow \infty$).

Let's test the other one $\psi(q) = A e^{-q^2/2}$

$$\frac{d\psi}{dq} = -A q e^{-q^2/2}$$

$$\frac{d^2 \psi}{dq^2} = \underbrace{A q^2 e^{-q^2/2}} - A e^{-q^2/2}$$

Since $q \gg 1$, this term dominates

$$\approx A q^2 e^{-q^2/2} = q^2 \psi(q) \quad \checkmark$$

$$\therefore \psi = A e^{-q^2/2} = A e^{-\beta^2 y^2/2} = A e^{-u w y^2/2t}$$

This is the solution in the asymptotic region, now we need solutions in the middle.

$$\frac{d^2}{dy^2} \psi(y) = \left(-\frac{2mE}{\hbar^2} + \frac{m^2 \omega^2}{\hbar^2} y^2 \right) \psi(y)$$

$$q = \beta y$$

$$\frac{d^2}{dq^2} \psi(q) = \left(q^2 - \frac{2E}{\hbar\omega} \right) \psi(q)$$

$$\psi(q) = A e^{-q^2/2} f(q)$$

← we'll assume this form

↑ asymptotic behavior

↖ oscillatory behavior (polynomials)

$$\frac{d^2 \psi(q)}{dq^2} = \left(f'' e^{-q^2/2} - q f' e^{-q^2/2} - f e^{-q^2/2} - q e^{-q^2/2} f' + q^2 f e^{-q^2/2} \right) A$$

$$= A e^{-q^2/2} (f'' - 2q f' - f + q^2 f)$$

$$\underbrace{A e^{-q^2/2}} \left(f'' - 2q f' - f + q^2 f \right) = \left(q^2 - \frac{2E}{\hbar\omega} \right) \underbrace{A e^{-q^2/2}} f$$

cancel

$$f'' - 2q f' + \left(\frac{2E}{\hbar\omega} - 1 \right) f = 0$$

↳ We can look up solutions to this diff EQ.

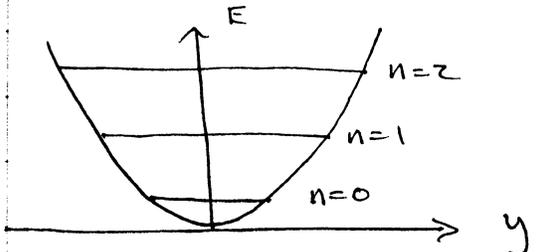
← Solved in 1864 by Charles Hermite

$$f'' - 2q f' + 2n f = 0$$

Hermite's equation
 $n = 0, 1, 2, \dots$ otherwise there's no solution!

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

$E_n = (n + \frac{1}{2})\hbar\omega \quad n = 0, 1, 2, \dots$



$$E_2 = \frac{5}{2} \hbar \omega$$

$$E_1 = \frac{3}{2} \hbar \omega$$

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

evenly-spaced energy levels

$$f_n(q) = H_n(q)$$

$H_n(q)$ = Hermite Polynomials!

$$\psi_n(q) = A_n e^{-q^2/2} H_n(q)$$

$$H_0(q) = 1$$

$$H_1(q) = 2q$$

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

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

$$\psi_n(y) = A_n e^{-\beta^2 y^2/2} H_n(\beta y)$$

$$\beta = \sqrt{\frac{\mu \omega}{\hbar}}$$

$$A_n = \frac{1}{(2^n n!)^{1/2}} \left(\frac{\beta^2}{\pi} \right)^{1/4}$$

Normalization Constant

Things to note:

① power of (q) is = index of polynomial

$$H_0(q) = 1$$

$$H_1(q) = 2q$$

② The wavefunctions form an orthonormal set.

$$\langle n | m \rangle = \delta_{nm}$$

③ The wavefunctions with $n = \text{even}$ are even around $y = 0$

Those with $n = \text{odd}$ are odd around $y = 0$

$$\int_{-\infty}^{\infty} \underbrace{\psi_0(x)}_{\text{even}} \times \underbrace{\psi_1(x)}_{\text{odd}} \times \underbrace{\psi_0(x)}_{\text{even}} dx = ?$$

What's the derivative of an odd function? even or odd?

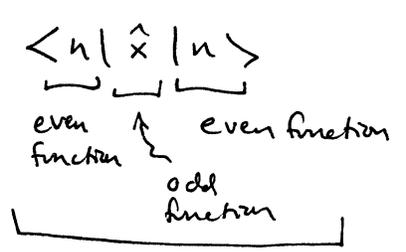
- ④ Higher energy = more nodes = higher n
- ⑤ The lowest energy is not zero $\frac{\hbar\omega}{2}$ is called the zero point energy. Even at 0K, the oscillator will still be vibrating with this amount of energy
- ⑥ The lobes of the wavefunction near the classical turning points are larger than in the center.

You should be able to solve $\langle x \rangle_n$ and $\langle p \rangle_n$ without doing any work! Here's how:

$$\langle x \rangle_n = \int_{-\infty}^{\infty} \psi_n^*(x) \hat{x} \psi_n(x) dx = \langle n | \hat{x} | n \rangle$$

$$= A_n^* A_n \int_{-\infty}^{\infty} \underbrace{H_n(\beta^{1/2}x)}_{\text{polynomial}} \underbrace{H_n(\beta^{1/2}x)}_{\text{polynomial}} \underbrace{x e^{-\alpha x^2}}_{\text{gaussian}} dx$$

$|n\rangle \begin{cases} \text{if } n = \text{even,} & |n\rangle \text{ is even around } x=0 \\ \text{if } n = \text{odd,} & |n\rangle \text{ is odd around } x=0 \end{cases}$



even: $\psi(x) = \psi(x)$ $\cos(x)$

odd: $\psi(-x) = -\psi(x)$ $\sin(x)$

$$\int_{-a}^a \psi_{\text{odd}} = 0$$

The integrals of odd functions over symmetric limits are 0!

What about $\langle P \rangle_n$

Remember that $\hat{p} = -i\hbar \frac{\partial}{\partial x}$

What does $\frac{\partial}{\partial x}$ do to an even polynomial like

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

$$\frac{\partial}{\partial x} H_2(x) = 8x - 0 \rightarrow \text{odd}$$

What does $\frac{\partial}{\partial x}$ do to an odd polynomial like

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

$$\frac{\partial}{\partial x} H_3(x) = 24x^2 - 12 \leftarrow \text{even!}$$

The first derivative will switch the "even-odd"ness of a function so:

$$\langle P \rangle_n = \langle n | \hat{p} | n \rangle = \int_{-\infty}^{\infty} \underbrace{\psi_n^*(x)}_{\text{even}} \underbrace{\left(-i\hbar \frac{\partial}{\partial x} \right)}_{\text{odd}} \underbrace{\psi_n(x)}_{\text{even}} dx$$

$$\underbrace{\text{odd}}_{\text{even}}$$

Either way, we're left with an odd function over symmetric limits!

$$\therefore \langle P \rangle_n = 0$$

Suppose we want the uncertainty in x : $\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$

Harder: $\langle x^2 \rangle_n$ & $\langle p^2 \rangle_n$

$$\langle x^2 \rangle_n = A_n^* A_n \int \underbrace{H_n(\beta^{1/2} x)}_{\text{polynomial of degree } n} \underbrace{H_n(\beta^{1/2} x)}_{\text{of degree } n} x^2 e^{-\beta x^2} dx$$

polynomial of degree $2n+2$ \leftarrow painful and tedious

An algebraic ~~approach~~ to the Harmonic oscillator

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$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2 \hat{x}^2}{2}$$

← simplest form of the Hamiltonian

We'll define 2 new operators called "raising & lowering" operators.

$$\hat{a} = \frac{\beta}{\sqrt{2}} \left(\hat{x} + \frac{i\hat{p}}{m\omega} \right)$$

Note $\hat{a} \neq \hat{a}^\dagger$ so these are Not Hermitian operators and don't correspond to a physical observable.

$$\hat{a}^\dagger = \frac{\beta}{\sqrt{2}} \left(\hat{x} - \frac{i\hat{p}}{m\omega} \right)$$

One useful property: $[\hat{a}, \hat{a}^\dagger] = 1$

Proof: $\frac{\beta^2}{2} \left(\hat{x} + \frac{i\hat{p}}{m\omega} \right) \left(\hat{x} - \frac{i\hat{p}}{m\omega} \right) - \frac{\beta^2}{2} \left(\hat{x} - \frac{i\hat{p}}{m\omega} \right) \left(\hat{x} + \frac{i\hat{p}}{m\omega} \right)$

$$= \frac{\beta^2}{2} \left(\hat{x}^2 - \frac{i}{m\omega} \hat{x} \hat{p} + \frac{i}{m\omega} \hat{p} \hat{x} + \frac{\hat{p}^2}{m^2 \omega^2} - \hat{x}^2 - \frac{i}{m\omega} \hat{x} \hat{p} + \frac{i}{m\omega} \hat{p} \hat{x} - \frac{\hat{p}^2}{m^2 \omega^2} \right)$$

$$= \frac{\beta^2}{2} \left[\frac{2i}{m\omega} [\hat{p}\hat{x} - \hat{x}\hat{p}] \right]$$

$$= \frac{i\beta^2}{m\omega} [\hat{p}, \hat{x}] = \frac{i\beta^2}{m\omega} (-i\hbar) = \frac{\hbar}{m\omega} \beta^2 = \frac{\hbar}{m\omega} \frac{m\omega}{\hbar} = 1$$

Why is that useful?

We can solve for \hat{x} & \hat{p} in

terms of \hat{a} & \hat{a}^\dagger

$$\hat{a} + \hat{a}^\dagger = \frac{2\beta}{\sqrt{2}} \hat{x}$$

$$\hat{a} - \hat{a}^\dagger = \frac{\beta}{\sqrt{2}} \left(\frac{2i}{m\omega} \hat{p} \right)$$

$$\hat{x} = \frac{\hat{a} + \hat{a}^\dagger}{\sqrt{2} \beta}$$

$$\hat{p} = \frac{m\omega}{i} \frac{\hat{a} - \hat{a}^\dagger}{\sqrt{2} \beta}$$

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2$$

← we'll need \hat{x}^2 & \hat{p}^2

$$\hat{p}^2 = \frac{-m^2 \omega^2}{2\beta^2} (\hat{a} - \hat{a}^\dagger)^2 = \frac{-m^2 \omega^2}{2\beta^2} (\hat{a} - \hat{a}^\dagger)(\hat{a} - \hat{a}^\dagger)$$

$$\hat{p}^2 = -\frac{\mu \omega^2}{2\beta^2} (\hat{a}^2 - \hat{a}^\dagger \hat{a} - \hat{a} \hat{a}^\dagger + \hat{a}^{\dagger 2})$$

$$\begin{aligned} \hat{x}^2 &= \frac{1}{2\beta^2} (\hat{a} + \hat{a}^\dagger)(\hat{a} + \hat{a}^\dagger) \\ &= \frac{1}{2\beta^2} (\hat{a}^2 + \hat{a}^\dagger \hat{a} + \hat{a} \hat{a}^\dagger + \hat{a}^{\dagger 2}) \end{aligned}$$

← If we know what \hat{a} & \hat{a}^\dagger do to a state, we know what \hat{x}^2 & \hat{p}^2 do also!

$$\begin{aligned} \hat{H} &= -\frac{\mu \omega^2}{4\mu} \left(\frac{\hbar}{\mu \omega}\right) (\hat{a}^2 - \hat{a}^\dagger \hat{a} - \hat{a} \hat{a}^\dagger + \hat{a}^{\dagger 2}) + \frac{1}{2} \mu \omega^2 \frac{\hbar}{2\mu \omega} (\hat{a}^2 + \hat{a}^\dagger \hat{a} + \hat{a} \hat{a}^\dagger + \hat{a}^{\dagger 2}) \\ &= -\frac{\hbar \omega}{4} (\hat{a}^2 - \hat{a}^\dagger \hat{a} - \hat{a} \hat{a}^\dagger + \hat{a}^{\dagger 2}) + \frac{\hbar \omega}{4} (\hat{a}^2 + \hat{a}^\dagger \hat{a} + \hat{a} \hat{a}^\dagger + \hat{a}^{\dagger 2}) \\ &= \frac{\hbar \omega}{4} (2\hat{a}^\dagger \hat{a} + 2\hat{a} \hat{a}^\dagger) = \frac{\hbar \omega}{2} (\hat{a}^\dagger \hat{a} + \hat{a} \hat{a}^\dagger) \end{aligned}$$

Remember that $[\hat{a}, \hat{a}^\dagger] = 1 \rightarrow \hat{a} \hat{a}^\dagger - \hat{a}^\dagger \hat{a} = 1 \rightarrow \hat{a} \hat{a}^\dagger = 1 + \hat{a}^\dagger \hat{a}$

$$\begin{aligned} \therefore \hat{H} &= \frac{\hbar \omega}{2} (\hat{a}^\dagger \hat{a} + 1 + \hat{a}^\dagger \hat{a}) \\ &= \frac{\hbar \omega}{2} (2\hat{a}^\dagger \hat{a} + 1) = \hbar \omega (\hat{a}^\dagger \hat{a} + \frac{1}{2}) \end{aligned}$$

\hat{H} is very simple in terms of \hat{a} & \hat{a}^\dagger

$$\hat{N} = \hat{a}^\dagger \hat{a} \quad (\hat{N} \text{ is hermitian})$$

$\hat{N} |n\rangle = n |n\rangle$ ← same eigenstates of \hat{H} that we find before
 ↗ eigenvalue of \hat{N} (no assumption that n is an integer)

We can use \hat{N} to find expressions for \hat{a} & \hat{a}^\dagger operating on $|n\rangle$

Last time, we started an algebraic approach:

$$\hat{H} = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}$$

creation: $\hat{a}^\dagger = \frac{\beta}{\sqrt{2}} \left(\hat{x} - \frac{i\hat{p}}{m\omega} \right)$

$$\beta = \sqrt{\frac{m\omega}{\hbar}}$$

annihilation: $\hat{a} = \frac{\beta}{\sqrt{2}} \left(\hat{x} + \frac{i\hat{p}}{m\omega} \right)$

number: $\hat{N} = \hat{a}^\dagger \hat{a}$

Things we proved:

$$[\hat{a}, \hat{a}^\dagger] = 1$$

$$\hat{p}^2 = \frac{-m^2\omega^2}{2\beta^2} (\hat{a}^2 - \hat{a}^\dagger \hat{a} - \hat{a} \hat{a}^\dagger + \hat{a}^{\dagger 2})$$

$$\hat{x}^2 = \frac{1}{2\beta^2} (\hat{a}^2 + \hat{a}^\dagger \hat{a} + \hat{a} \hat{a}^\dagger + \hat{a}^{\dagger 2})$$

$$\hat{H} = \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) = \hbar\omega \left(\hat{N} + \frac{1}{2} \right)$$

Why are we doing this?

$$\langle x^2 \rangle_n = \langle n | \hat{x}^2 | n \rangle$$

= Integral of a 2n+2 degree polynomial. Yuck!

Today: what do $\hat{a}|n\rangle$ & $\hat{a}^\dagger|n\rangle$ do to a state $|n\rangle$

What we know:

$\hat{N}|n\rangle = n|n\rangle$ ← eigenvalues of \hat{N}
 $\hat{H}|n\rangle = \hbar\omega \left(\hat{N} + \frac{1}{2} \right) |n\rangle = \hbar\omega \left(n + \frac{1}{2} \right) |n\rangle$ ↑ eigenstates of \hat{H} (dH)

$$\hat{H}|n\rangle = \hbar\omega \left(\hat{N} + \frac{1}{2} \right) |n\rangle = \hbar\omega \left(n + \frac{1}{2} \right) |n\rangle$$

Consider: $\hat{N} \hat{a} |n\rangle = (\hat{a}^\dagger \hat{a}) \hat{a} |n\rangle$

The commutator tells us that $\hat{a} \hat{a}^\dagger - \hat{a}^\dagger \hat{a} = 1$

so: $\hat{a}^\dagger \hat{a} = \hat{a} \hat{a}^\dagger - 1$

Some operator gymnastics:

$$\hat{N} \hat{a} |n\rangle = (\hat{a} \hat{a}^\dagger - 1) \hat{a} |n\rangle$$

$$= (\hat{a} \hat{a}^\dagger \hat{a} - \hat{a}) |n\rangle$$

$$= \hat{a} (\hat{a}^\dagger \hat{a} - 1) |n\rangle$$

$$= \hat{a} (\hat{N} - 1) |n\rangle = \hat{a} (n-1) |n\rangle$$

$$= (n-1) \hat{a} |n\rangle$$

$$\hat{N} \hat{a} |n\rangle = \hat{a} (\hat{N}-1) |n\rangle = \hat{a} (n-1) |n\rangle$$

$$\left. \begin{aligned} \hat{N} [\hat{a} |n\rangle] &= (n-1) [\hat{a} |n\rangle] \\ \hat{N} [|n-1\rangle] &= (n-1) [|n-1\rangle] \end{aligned} \right\} \therefore \hat{a} |n\rangle \propto |n-1\rangle$$

Similarly:

$$\hat{N} (\hat{a}^+ |n\rangle) = \hat{a}^+ \hat{a} \hat{a}^+ |n\rangle = \hat{a}^+ (1 + \hat{a}^+ \hat{a}) |n\rangle = \hat{a}^+ (1 + \hat{N}) |n\rangle = \hat{a}^+ (n+1) |n\rangle$$

$$\left. \begin{aligned} \hat{N} [\hat{a}^+ |n\rangle] &= (n+1) [\hat{a}^+ |n\rangle] \\ \hat{N} [|n+1\rangle] &= (n+1) [|n+1\rangle] \end{aligned} \right\} \therefore \hat{a}^+ |n\rangle \propto |n+1\rangle$$

\hat{a} is the annihilation operator
 \hat{a}^+ is the creation operator

(These annihilate or create quanta (or particles!) in advanced treatments of QM)

A few limits:

$$\langle \hat{H} \rangle_n = \langle n | \hat{H} |n\rangle \geq 0 \quad (\text{because } \hat{H} \text{ is a sum of squared quantities})$$

$$\langle n | \hbar \omega (n + \frac{1}{2}) |n\rangle \geq 0$$

$$\hbar \omega (n + \frac{1}{2}) \geq 0 \xrightarrow{\text{require}} n \geq -\frac{1}{2}$$

We can meet this condition if we require:

$$\hat{a} |0\rangle = 0 \quad (\text{boundary condition})$$

$$\hat{a} |0\rangle \sim |-1\rangle = 0$$

and since $|-1\rangle = 0$, $\hat{a} |-1\rangle = \hat{a} 0 = 0$

$$\text{All } |n\rangle = 0 \text{ for } n \leq -1$$

$$\hat{N}(\hat{a}^+|0\rangle) = \hat{a}^+\hat{a}\hat{a}^+|0\rangle = \hat{a}^+(\hat{a}^+\hat{a}+1)|0\rangle = \hat{a}^+|0\rangle$$

$$\hat{N}(\hat{a}^+|0\rangle) = 1(\hat{a}^+|0\rangle) \quad \leftarrow$$

Likewise $\hat{N}(\hat{a}^+\hat{a}^+|0\rangle) = 2(\hat{a}^+\hat{a}^+|0\rangle)$

$$N(\hat{a}^+\hat{a}^+\hat{a}^+|0\rangle) = 3(\hat{a}^+\hat{a}^+\hat{a}^+|0\rangle)$$

⋮

$n = 0, 1, 2, 3, \dots$ is an integer

We've essentially proven that harmonic oscillator is quantized.

$$\hat{H}|n\rangle = \hbar\omega(\hat{N} + \frac{1}{2})|n\rangle = \hbar\omega(n + \frac{1}{2})|n\rangle$$

$$E_n = \hbar\omega(n + \frac{1}{2}) \quad n = 0, 1, 2, \dots$$

To preserve normalization we need one modification:

$$\begin{aligned} \hat{a}|n\rangle &= \sqrt{n}|n-1\rangle \\ \hat{a}^+|n\rangle &= \sqrt{n+1}|n+1\rangle \end{aligned}$$

} could you prove this?
 $\langle n|\hat{a}^+\hat{a}|n\rangle$

Now, think about \hat{x}^2 : $\frac{1}{2\beta^2}(\hat{a}^2 + \hat{a}^+\hat{a} + \hat{a}\hat{a}^+ + \hat{a}^+{}^2)$

$$\hat{x}^2|n\rangle = \frac{1}{2\beta^2}(\hat{a}\hat{a}|n\rangle + \hat{a}^+\hat{a}|n\rangle + \hat{a}\hat{a}^+|n\rangle + \hat{a}^+\hat{a}^+|n\rangle)$$

$$= \frac{1}{2\beta^2}(\sqrt{n}\hat{a}|n-1\rangle + \sqrt{n}\hat{a}^+|n-1\rangle + \sqrt{n+1}\hat{a}|n+1\rangle + \sqrt{n+1}\hat{a}^+|n+1\rangle)$$

$$= \frac{1}{2\beta^2}(\sqrt{n}\sqrt{n-1}|n-2\rangle + \sqrt{n}\sqrt{n}|n\rangle + \sqrt{n+1}\sqrt{n+1}|n\rangle + \sqrt{n+1}\sqrt{n+2}|n+2\rangle)$$

$$= \frac{1}{2\beta^2}(\sqrt{n}\sqrt{n-1}|n-2\rangle + (2n+1)|n\rangle + \sqrt{n+1}\sqrt{n+2}|n+2\rangle)$$

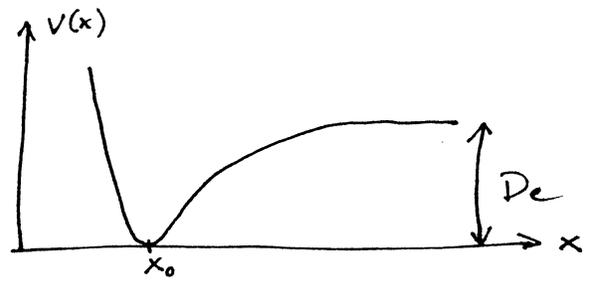
$$\langle n|\hat{x}^2|n\rangle = \frac{1}{2\beta^2}(\cancel{\sqrt{n}\sqrt{n-1}\langle n|n-2\rangle} + (2n+1)\langle n|n\rangle + \cancel{\sqrt{n+1}\sqrt{n+2}\langle n|n+2\rangle})$$

$$\langle n|\hat{x}^2|n\rangle = \frac{2n+1}{2\beta^2} = \frac{(2n+1)\hbar}{2\mu\omega} \quad \leftarrow \text{No integrals at all}$$

A diversion into spectroscopy

Consider again the Morse oscillator:

$$V(x) = D_e (1 - e^{-\alpha(x-x_0)})^2$$

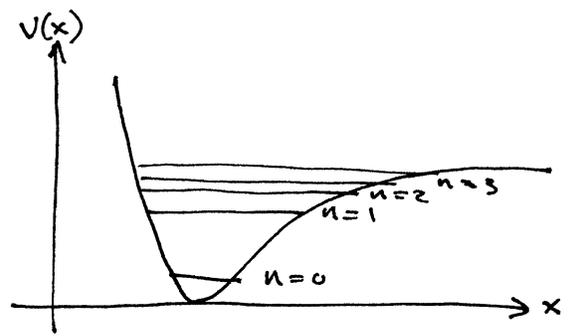


- The Morse oscillator is a much better approximation to actual molecular surfaces because it dissociates.
- It is an anharmonic model
- It is analytically solvable, but very difficult.

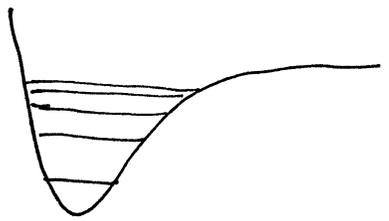
$$E_n = D_e B (n + \frac{1}{2}) [2 - B(n + \frac{1}{2})] \quad n = 0, 1, 2, \dots$$

where $B^2 = \frac{\hbar^2 \alpha^2}{2\mu D_e}$ ← unitless

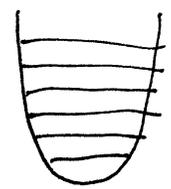
The levels get closer together as n increases



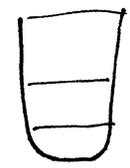
(There's also an n_{max} which has an energy just below the dissociation threshold.)



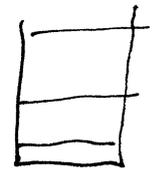
$V(x) = \text{Morse}$
DE decreases



$V(x) = \text{harmonic}$
DE constant



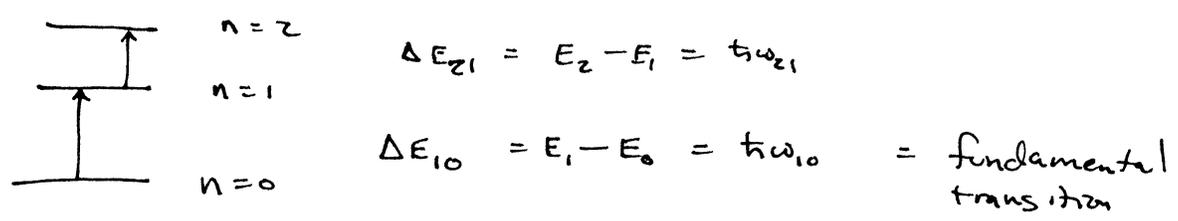
$V(x) = x^4$



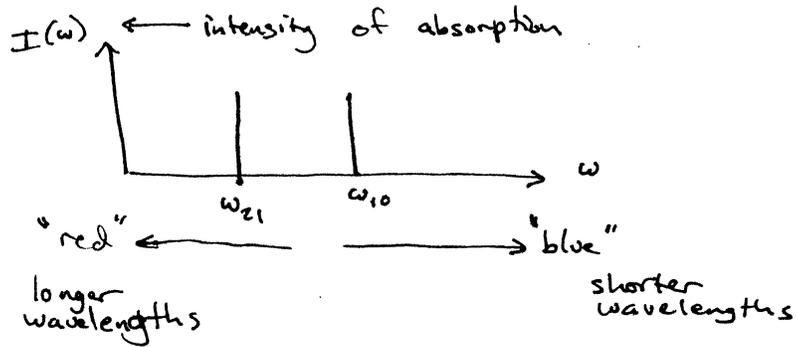
$V(x) = \text{particle in a box}$

DE increases

Vibrational Spectroscopy



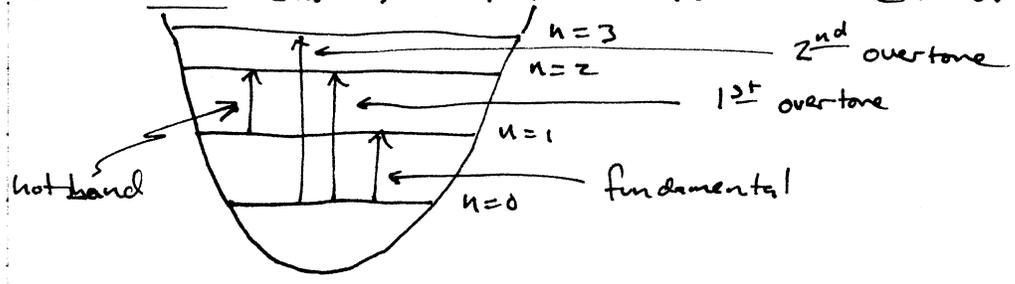
$\Delta E_{21} < \Delta E_{10} \quad \therefore \quad \omega_{21} < \omega_{10}$



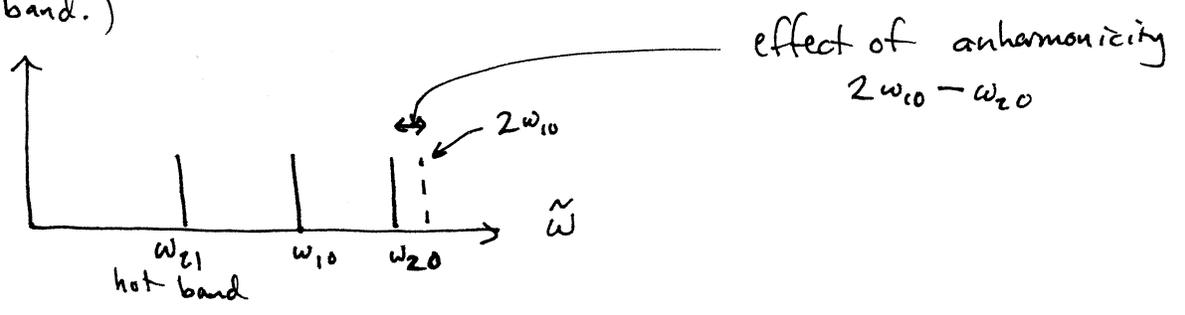
remember: $c = \lambda \nu$
 $\nu = \frac{\omega}{2\pi}$
 $\lambda = \frac{2\pi c}{\omega}$

$\frac{1}{\lambda} = \frac{\omega}{2\pi c} = \tilde{\omega}$ units of $\frac{1}{\text{length}}$ (usually cm^{-1})

The basic principle of spectroscopy is that light induces transitions in molecules from their initial state to a final state. Think about the ^{nearly} harmonic oscillator



In a hot band the molecules starts in $n=1$ (the warmer the sample, the ~~bigger~~ ^{bigger} the population in $n=1$ to begin with, which is why this is called the "hot" band.)



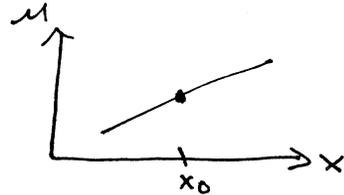
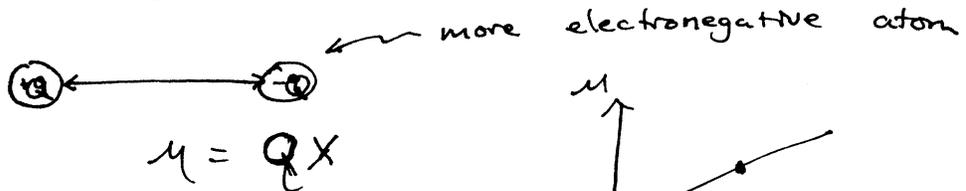
The basics:

$I_{nm} \sim |M_{nm}|^2$ Dipole moment integral
↑ Intensity of the $n \rightarrow m$ transition The dipole moment is what interacts with the light.

$M_{nm} = \langle n | \hat{\mu} | m \rangle$ ↖ final vibrational state
↑ ↑ Dipole moment operator
↑ Initial vibrational state

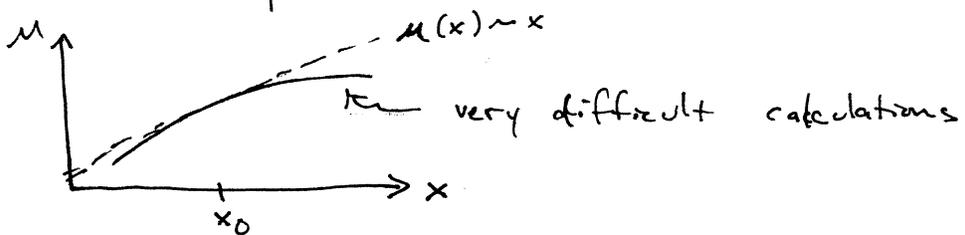
$$= \int_{-\infty}^{\infty} \psi_n^*(x) \hat{\mu}(x) \psi_m(x) dx$$

The Dipole Depends on bond extension:



For homonuclear diatomics $\mu = 0 \therefore$ no IR transitions are possible in the gas phase, but a different kind of scattering (Raman) is possible.

A more realistic picture:



$$\mu(x) = \underbrace{\mu(x_0)}_{\substack{\text{equilibrium} \\ \text{dipole moment} \\ \mu_0}} + \underbrace{\frac{\partial \mu}{\partial x} \Big|_{x=x_0}}_{\substack{\text{transition} \\ \text{dipole moment} \\ = \mu'}} (x-x_0) + \frac{1}{2} \frac{\partial^2 \mu}{\partial x^2} \Big|_{x=x_0} (x-x_0)^2 + \dots$$

$$\mu(x) \approx \mu_0 + \mu'(x-x_0)$$

Define $q \equiv x - x_0$ ← displacement from equilibrium

← equilibrium dipole moment.

$$\mu(q) = \mu_0 + \mu'q$$

$$M_{nm} = \int_{-\infty}^{\infty} \psi_n^*(q) (\mu_0 + \mu'q) \psi_m(q) dq$$

$$= \langle n | \mu_0 + \mu'q | m \rangle$$

$$= \langle n | \mu_0 | m \rangle + \mu' \langle n | q | m \rangle$$

$$= \mu_0 \underbrace{\langle n | m \rangle} + \mu' \langle n | q | m \rangle$$

= 0 because we don't consider the $n=m$ case for spectroscopy

$$M_{nm} = \mu' \langle n | q | m \rangle$$

$$I_{nm} \approx |M_{nm}|^2 = (\mu')^2 |\langle n | q | m \rangle|^2$$

Dominant factor in determining the intensity

Determines the "selection rules"

$\langle n | q | m \rangle$ for a harmonic oscillator

$$q = \frac{1}{\sqrt{2}\beta} (\hat{a} + \hat{a}^{\dagger})$$

$$\beta = \left(\frac{\mu\omega}{\hbar} \right)^{1/2}$$

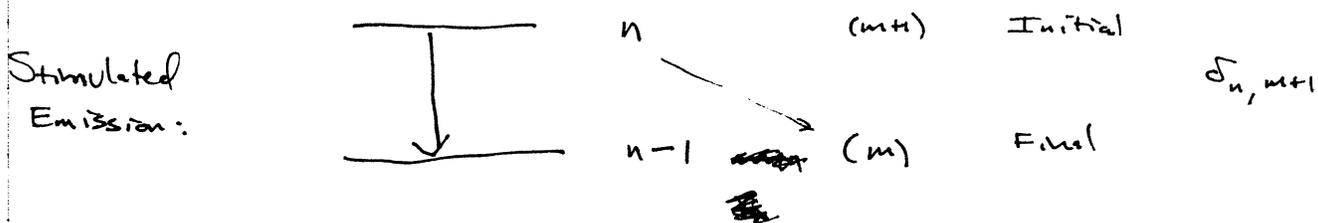
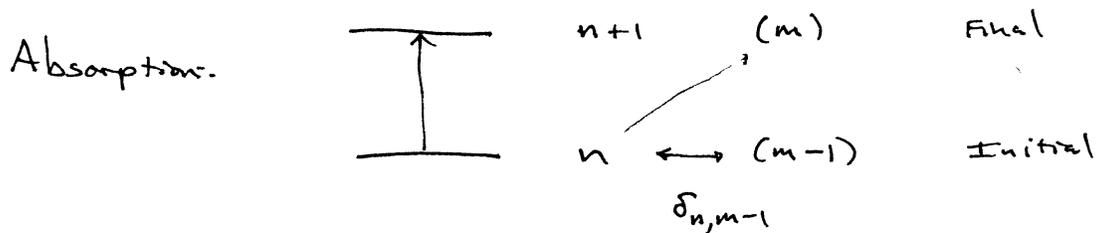
$$\hat{a} |n\rangle = \sqrt{n} |n-1\rangle$$

$$\hat{a}^{\dagger} |n\rangle = \sqrt{n+1} |n+1\rangle$$

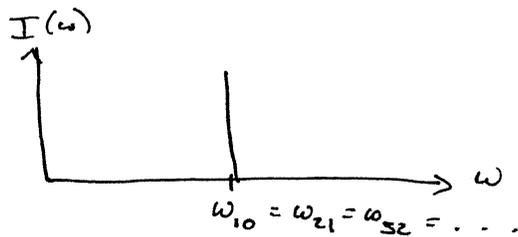
$$\langle n | \frac{1}{\sqrt{2}\beta} (\hat{a} + \hat{a}^{\dagger}) | m \rangle = \frac{1}{\sqrt{2}\beta} \left\{ \underbrace{\langle n | \hat{a} | m \rangle}_{\sqrt{m} |m-1\rangle} + \underbrace{\langle n | \hat{a}^{\dagger} | m \rangle}_{\sqrt{m+1} |m+1\rangle} \right\}$$

$$\langle n|q|m\rangle = \frac{1}{\sqrt{2}\beta} \left\{ \sqrt{m} \langle n|m-1\rangle_{\delta_{n,m-1}} + \sqrt{m+1} \langle n|m+1\rangle_{\delta_{n,m+1}} \right\}$$

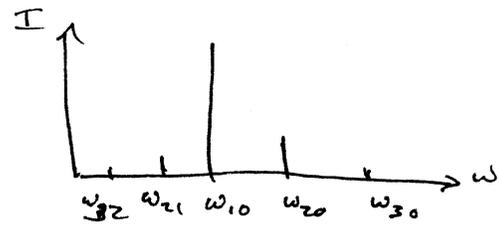
This tells us that the initial state "n" is ± 1 from the final state m. For the harmonic oscillator there are only 2 vibrational transitions we can see spectroscopically:



Selection Rule: final = initial ± 1



Harmonic



Anharmonic

$$\langle n \pm 2 | q | n \rangle \ll \langle n \pm 1 | q | n \rangle$$

Next time Raman scattering!

In IR:



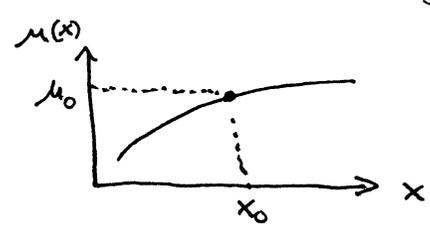
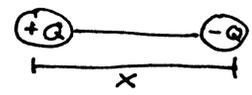
$I_1 < I_0$ if absorbed

Last time we talked about spectroscopy:

$$I_{mn} \approx |M_{mn}|^2$$

$$M_{mn} = \langle m | \hat{\mu} | n \rangle = \int \psi_m^*(x) \hat{\mu} \psi_n(x) dx$$

$\hat{\mu}$ measures the molecular dipole as a function of the bond stretching coordinate:



$$\mu(x) = \mu(x_0) + \left. \frac{\partial \mu}{\partial x} \right|_{x=x_0} (x-x_0) + \frac{1}{2} \left. \frac{\partial^2 \mu}{\partial x^2} \right|_{x=x_0} (x-x_0)^2$$

$$\approx \mu_0 + \mu'(x-x_0)$$

$$I_{mn} \sim |M_{mn}|^2 = \underbrace{\mu'}^2 \underbrace{|\langle m | q | n \rangle|}^2$$

↑
dominant factor in determining intensity

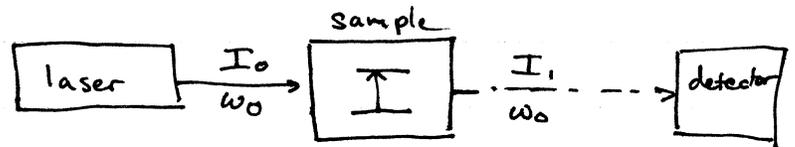
↑ determines the "selection rules" for HO:

$$\langle m | q | n \rangle = \frac{1}{\sqrt{2}} \left(\sqrt{n} \langle m | n-1 \rangle + \sqrt{n+1} \langle m | n \rangle \right)$$

Only ± 1 transitions are allowed for HO!

Raman Scattering:

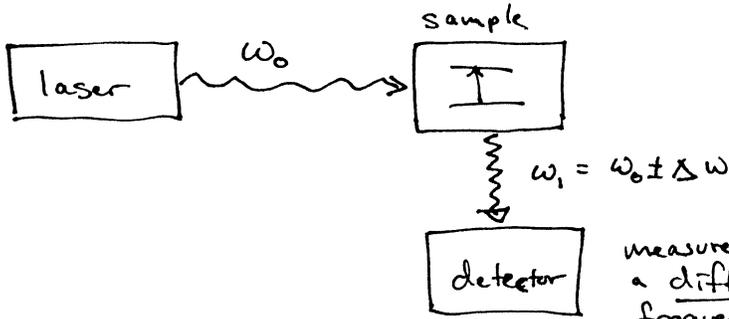
In a typical IR experiment:



$I_1 < I_0$ if light was absorbed at ω_0

measure intensity along beam path at same frequency

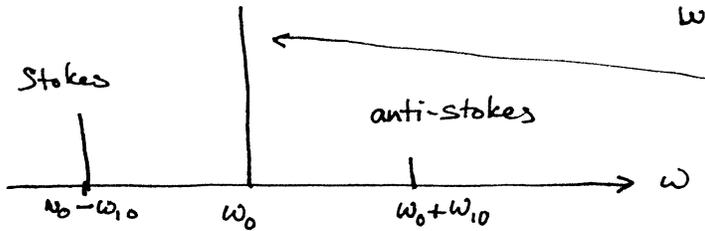
In a Raman experiment



$$\Delta\omega = |\omega_{10}|$$

some of the light is frequency shifted due to the elastic scattering

measure at a different frequency than we came in with



Rayleigh scattering leaves the frequency of the light alone, but changes its direction

$$I_{\text{Rayleigh}} \propto \frac{d^6}{\lambda^4}$$

light lost energy to molecules

elastic or "Rayleigh" scattering

light gained energy from molecules (like a hot band)

Blue light scatters much more than red, or green... (which is why the sky is blue.)

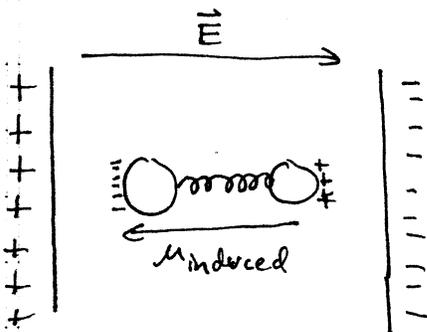
$$I_{\text{Raman}} \sim |M_{\text{induced}}|^2$$

$$M_{\text{induced}} \approx \alpha E$$

← electric field of the light

polarizability of the molecule (how easy is it to push electrons around)

$M_{\text{induced}} \neq 0$ (even for homonuclear diatomics and He) so even if there's no IR signal, there can be a Raman signal



$$\alpha(q) = \alpha(0) + \frac{\partial \alpha}{\partial q} \bigg|_{q=0} q + \frac{1}{2} \frac{\partial^2 \alpha}{\partial q^2} \bigg|_{q=0} q^2 + \dots$$

$$\approx \alpha_0 + \alpha' q$$

The molecules are vibrating in time:

$$q(t) = \cos(\omega t) \quad (\omega = \sqrt{\frac{k}{\mu}})$$

$$E(t) = E_0 \cos(\omega t) \quad \leftarrow \text{The light oscillates also!}$$

$$M_{\text{induced}} = \alpha E = (\alpha_0 + \alpha' \cos(\omega t)) [E_0 \cos(\omega t)]$$

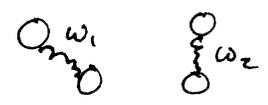
$$= \alpha_0 E_0 \cos \omega t + E_0 \alpha' \cos(\omega t) \cos(\omega t)$$

$$\cos A \cos B = \frac{1}{2} [\cos(A+B) + \cos(A-B)]$$

$$M_{\text{induced}} = \alpha_0 E_0 \cos \omega t + \frac{\alpha' E_0}{2} \left\{ \cos[(\omega_0 + \omega)t] + \cos[(\omega_0 - \omega)t] \right\}$$

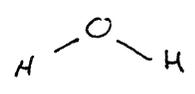
↑
↑
↑
 Rayleigh anti-stokes Stokes

Vibrational & Raman spectroscopy are both still very active areas of chemistry because ω , μ' , α' are all very sensitive to the environment surrounding the molecule, and if we hold 2 molecules near each other



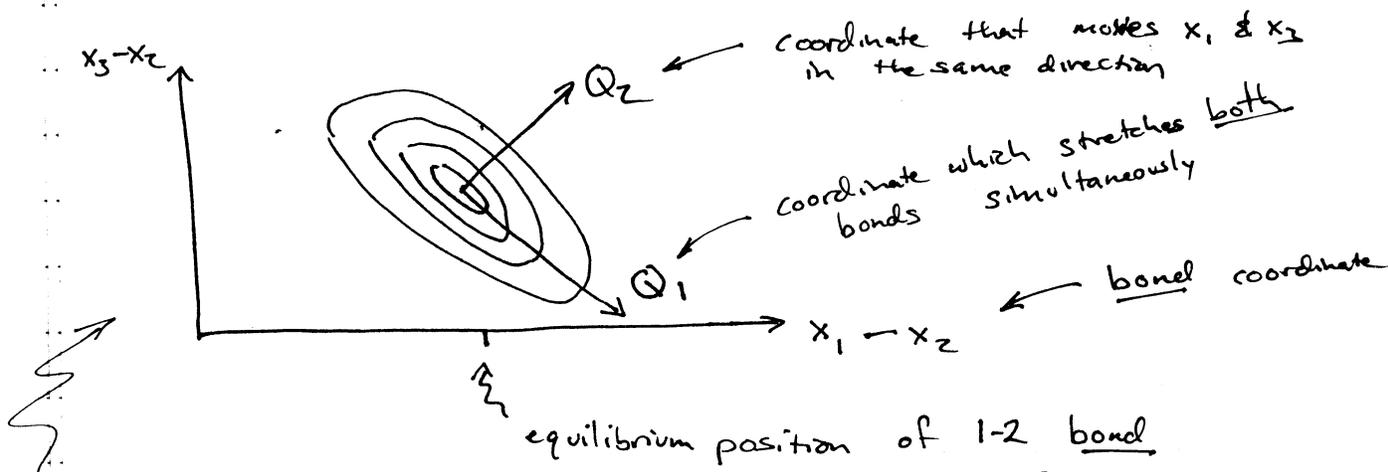
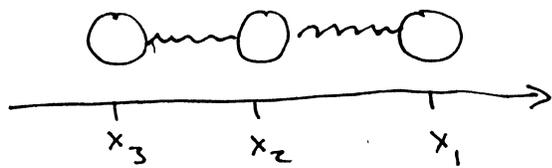
the vibrations are "coupled" and we can use 2 lasers to infer orientational information!

What about polyatomics?



→ N-atoms: $T = \frac{1}{2} \sum_{i=1}^N m_i (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2)$
 → We tackle these with Normal Mode vibrations (bending, symmetric stretch, asymmetric stretch).

Where do these normal modes come from?



Contour plot of the potential energy surface.

Q_1 is a symmetric stretch coordinate

Q_2 is an asymmetric stretch coordinate

These are the normal modes of the molecule and they are linear combinations of the atomic coordinates

Step 1: We introduce mass-weighted displacements:
↙ x position of atom 1 at equilibrium

$$\begin{aligned}
 q_1 &= \sqrt{m_1} (x_1 - x_1^0) \\
 q_2 &= \sqrt{m_1} (y_1 - y_1^0) \\
 q_3 &= \sqrt{m_1} (z_1 - z_1^0) \\
 q_4 &= \sqrt{m_2} (x_2 - x_2^0) \\
 &\vdots \\
 q_{3N} &= \sqrt{m_N} (z_N - z_N^0)
 \end{aligned}$$

The kinetic energy is then: $T = \frac{1}{2} \sum_{i=1}^{3N} \dot{q}_i^2$

$$V = \underbrace{V(0)}_{=0} + \underbrace{\sum_{i=1}^{3N} \left. \frac{\partial V}{\partial q_i} \right|_{q_i=0}}_{=0 \text{ at equilibrium}} q_i + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} \underbrace{\left. \frac{\partial^2 V}{\partial q_i \partial q_j} \right|_{q_i=q_j=0}}_{K_{ij} = \text{force constants}} q_i q_j$$

$$V = \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} K_{ij} q_i q_j$$

Step 2: We set up a force constant matrix

$$K = \begin{pmatrix}
 k_{11} & k_{12} & \dots & k_{1,3N} \\
 k_{21} & k_{22} & \dots & k_{2,3N} \\
 \vdots & \vdots & \ddots & \vdots \\
 k_{3N,1} & k_{3N,2} & \dots & k_{3N,3N}
 \end{pmatrix}$$

Step 3: Diagonalize the force constant matrix

$$\begin{pmatrix}
 k_{11} & k_{12} & \dots \\
 k_{21} & k_{22} & \dots \\
 \vdots & \ddots & \ddots
 \end{pmatrix} \rightarrow \begin{pmatrix}
 \lambda_1 & 0 & 0 & \dots \\
 0 & \lambda_2 & 0 & \dots \\
 0 & 0 & \lambda_3 & \dots \\
 \vdots & \vdots & \vdots & \ddots
 \end{pmatrix} \quad \underline{u^T K u = \lambda^2}$$

$\lambda_1 \leftarrow 3N$ eigenvalues

$Q_i = \sum_j c_{ij} q_j$ ↙ eigenvector for λ_i
↖ old coords

$\{Q_i\}$ are a new set of coordinates or normal modes that tell us about the inherent vibrational structure of a molecule

nonlinear molecules \rightarrow 6 of the λ_i are 0 (3 translations)
 linear molecules \rightarrow 5 of the λ_i are 0 (3 or 2 rotations)

$$T = \frac{1}{2} \sum_{i=1}^{3N} \dot{Q}_i^2 \qquad V = \sum_{i=1}^{3N-6 \text{ or } 5} \lambda_i Q_i^2$$

each mode is a harmonic oscillator and all of the modes are decoupled from each other

$$H = \sum_{i=1}^{3N-6} \left[\frac{1}{2} \dot{Q}_i^2 + \lambda_i Q_i^2 \right] + \sum_{i=1}^6 \frac{1}{2} \dot{Q}_i^2$$

$$= \sum_{i=1}^{3N-6} \left[\frac{-\hbar^2}{2} \frac{\partial^2}{\partial Q_i^2} + \lambda_i \hat{Q}_i^2 \right] = \sum_i \hat{H}_i$$

\hat{H}_i sum of 1D harmonic oscillators

For each mode i :

$$\hat{H}_i \psi_i(Q_i) = E_i \psi_i(Q_i)$$

$$\omega_i^2 = \lambda_i \qquad \text{or} \qquad \omega_i = \sqrt{\lambda_i}$$

$$E_i = \hbar \omega_i \left(n_i + \frac{1}{2} \right) \qquad n_i = 0, 1, 2, \dots$$

$$E = \sum_{i=1}^{3N} \hbar \omega_i \left(n_i + \frac{1}{2} \right)$$

$$\Psi(Q_1, Q_2, Q_3, \dots, Q_{3N}) = \psi_{n_1}(Q_1) \psi_{n_2}(Q_2) \psi_{n_3}(Q_3) \dots$$

$$\psi_{n_i}(Q_i) = A_{n_i} H_{n_i}(y_i) e^{-y_i^2/2} \qquad y_i = Q_i \left(\frac{\lambda_i^{3/2}}{\hbar} \right)^{1/2}$$

Normal modes & Spectroscopy

(30)

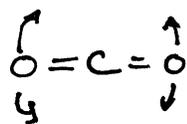
Vibrational modes of a molecule can be either IR "active" or Raman "active" (or both!).

I^{IR} depends on $\left. \frac{\partial \mu}{\partial Q} \right|_{Q=0}$ ← does the vibrational mode change the molecular dipole

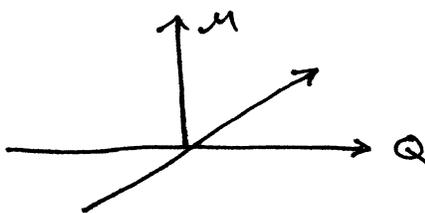
I^{Raman} depends on $\left. \frac{\partial \alpha}{\partial Q} \right|_{Q=0}$ ← does the vibrational mode change the polarizability of the molecule

In molecules with a center of symmetry these are mutually exclusive:

Consider these modes of CO_2 :

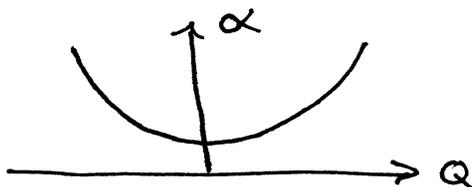


i.e. the bending mode @ 526 cm^{-1}



$$\left. \frac{\partial \mu}{\partial Q} \right|_{Q=0} \neq 0$$

so this mode is IR active



$$\left. \frac{\partial \alpha}{\partial Q} \right|_{Q=0} = 0$$

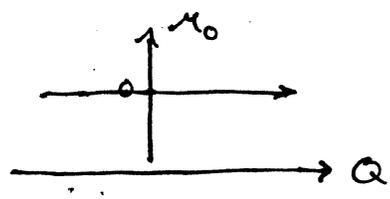
so it is Raman inactive

Another mode:

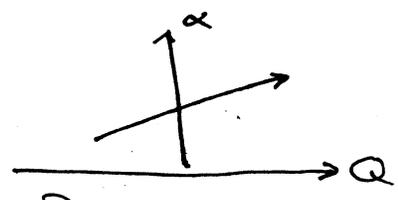


i.e. the symmetric stretch at 1480 cm^{-1}

This mode doesn't change the molecular dipole: but it does change the polarizability



IR inactive $(\frac{\partial \mu}{\partial Q}) = 0$



Raman active $(\frac{\partial \alpha}{\partial Q}) \neq 0$

The rule of mutual exclusion:

If a molecule has a center of symmetry then no transition is allowed in both Raman scattering & IR spectroscopy, but only in one or the other.

Water (not centrosymmetric)

all 3 modes are IR active

symmetric stretch is Raman active

bend & asymmetric stretch are only weakly Raman active