The Simple Harmonic Oscillator
CHEM 361B: Introduction to Physical Chemistry

Dr. Michael Groves

Department of Chemistry and Biochemistry
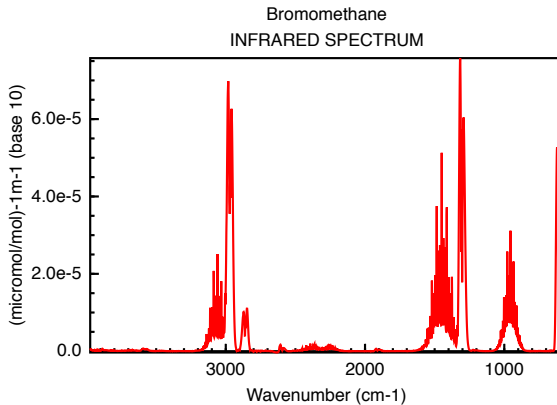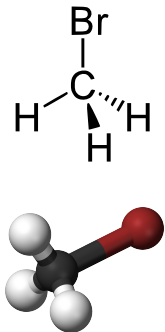California State University, Fullerton

Lecture 9

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Learning Objective: Develop a model for the simple harmonic oscillator and apply it to diatomic molecules to predict their vibrational spectra.

References:

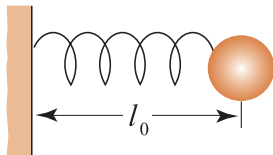- McQuarrie Chapter 5

Bromomethane Example

Classical Simple Harmonic Oscillator

Applying Newton's second law with Hooke's law describing the only force:

$$-k(x - \ell_0) = m\frac{d^2x}{dt^2}$$

Let $z = (x - \ell_0)$. It can be shown that the solution to the differential equation is

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

where the angular frequency is

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

Quantum Simple Harmonic Oscillator

The potential energy of a SHO is

$$U(x) = \frac{1}{2}m\omega^2 x^2$$

which means that the Schrödinger equation looks like

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

Recall that the momentum operator and the position operator are

$$\hat{P} = -i\hbar\frac{d}{dx} \quad \text{and} \quad \hat{X} = x$$

So the Schrödinger Equation can be expressed as

$$\frac{1}{2m}\left(\hat{P}^2 + (m\omega\hat{X})^2\right)\psi = E\psi \quad \text{or} \quad \hat{H}\psi = E\psi$$

$a_\pm$

To solve the Schrödinger Equation with the harmonic potential, we will use an algebraic method involving the promotion/demotion ladder operators

$$a_+ = \frac{1}{\sqrt{2\hbar m\omega}}(-i\hat{P} + m\omega\hat{X})$$

$$a_- = \frac{1}{\sqrt{2\hbar m\omega}}(i\hat{P} + m\omega\hat{X})$$

Do a_+ and a_- Commute?

To find if these operators commute we starting with

$$a_- a_+ = \frac{1}{\sqrt{2\hbar m\omega}}(i\hat{P} + m\omega\hat{X})\frac{1}{\sqrt{2\hbar m\omega}}(-i\hat{P} + m\omega\hat{X}) = \frac{1}{\hbar\omega}\hat{H} + \frac{1}{2}$$

and then finding

$$a_+ a_- = \frac{1}{\sqrt{2\hbar m\omega}}(-i\hat{P} + m\omega\hat{X})\frac{1}{\sqrt{2\hbar m\omega}}(i\hat{P} + m\omega\hat{X}) = \frac{1}{\hbar\omega}\hat{H} - \frac{1}{2}$$

This means that

$$[a_+, a_-] = a_+ a_- - a_- a_+ = -1 \quad \text{(does not commute)}$$

Using a_+ and a_- as the Hamiltonian

Regardless of this result, the Hamiltonian can be written as both

$$\hat{H} = \hbar\omega(a_- a_+ - \frac{1}{2})$$
$$\hat{H} = \hbar\omega(a_+ a_- + \frac{1}{2})$$

so the Schrödinger equation can be expressed as

$$\hbar\omega \left(a_\pm a_\mp \pm \frac{1}{2} \right) \psi = E\psi$$

What is $a_\pm$?

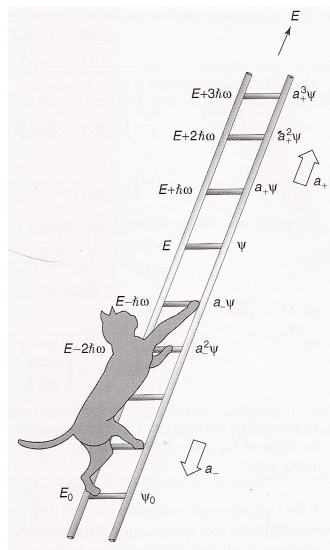If ψ satisfies the Schrödinger equation with energy E, then show that a_+ satisfies the Schrödinger equation with energy $E + \hbar\omega$

$$\hat{H}(a_+\psi) = \hbar\omega(a_+a_- + \frac{1}{2})(a_+\psi)$$
$$= (E + \hbar\omega)(a_+\psi)$$

Similarly for a_-

$$\hat{H}(a_-\psi) = \hbar\omega(a_-a_+ - \frac{1}{2})(a_-\psi)$$
$$= (E - \hbar\omega)(a_-\psi)$$

These two operators allow the generation of new solutions with higher and lower energies respectively.

SHO - Finding the First Solution

If the lowering operator a_- is used repeatedly then eventually the ground state will be reached. This means that

$$a_- \psi_0 = 0$$

This can be used to determine ψ_0:

$$\frac{1}{\sqrt{2\hbar m \omega}} \left(\hbar \frac{d}{dx} + m\omega x \right) \psi_0 = 0$$

Solving this differential equation gives:

$$\psi_0(x) = A e^{-\frac{m\omega}{2\hbar} x^2}$$

SHO - Finding the First Solution (cont.)

Normalizing ψ_0 gives

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2}$$

When this solution is evaluated using the Schrödinger equation the energy of the ground state is

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

Now that the ground state is found, any excited state can be determined by

$$\psi_n(x) = A_n(a_+)^n\psi_0(x), \quad \text{with } E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

The First Excited State of the SHO

For example, to find the first excited state, apply the raising operator to ψ_0:
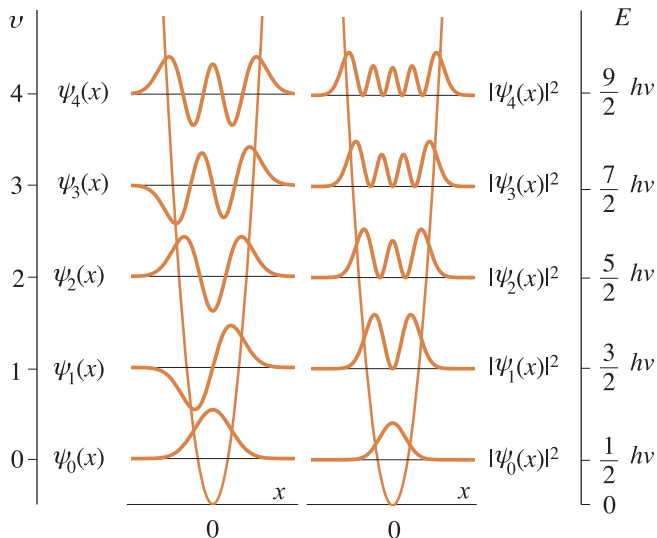
$$\psi_1 = A_1 a_+ \psi_0$$

which gives

$$\psi_1 = A_1 \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \left(\frac{2m\omega}{\hbar}\right)^{\frac{1}{2}} x e^{-\frac{m\omega}{2\hbar}x^2}$$

Normalizing using

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2} = 2 \int_0^{\infty} x^2 e^{-ax^2} = \frac{1}{2}\sqrt{\frac{\pi}{a^3}}$$
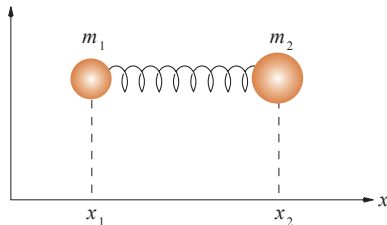
gives $A_1 = 1$.

SHO States

SHO - Diatomic Molecules

For a vibrating diatomic molecule the mass in the angular frequency ($\omega = \sqrt{\frac{k}{m}}$) must instead be

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

which is the reduced mass. To find the energy of a vibrating diatomic molecule, the only additional thing we need its spring constant k since
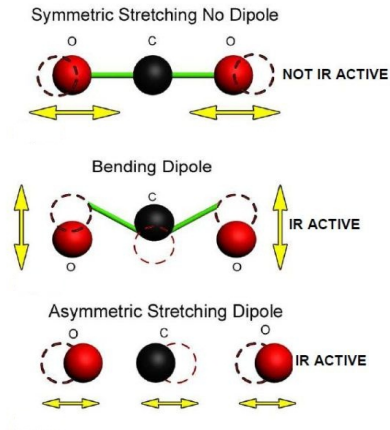
$$E_n = \hbar \left(\frac{k}{\mu} \right)^{1/2} \left(n + \frac{1}{2} \right)$$

SHO - Diatomic Molecules Examples

1. The infrared spectrum of $^{75}Br^{19}F$ consists of an intense line at 380 cm^{-1}. Calculate the force constant (k) of $^{75}Br^{19}F$.

2. The force constant of $^{35}Cl^{35}Cl$ is 319 N m^{-1}. Calculate the fundamental vibrational frequency and the zero-point energy of $^{35}Cl^{35}Cl$.
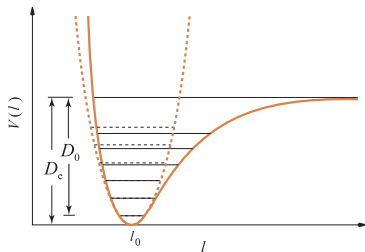
Infrared Active Modes

Not all vibrations are visible to light. Only the ones where the dipole moment changes. For instance, the symmetric stretch in CO_2 is not infrared active, however the bending and asymmetric stretch are.

Symmetric Stretching No Dipole

O   C   O

NOT IR ACTIVE

Bending Dipole

C

IR ACTIVE

O   O

Asymmetric Stretching Dipole

O   C   O

IR ACTIVE

Anharmonic Potential

A better representation of reality is the anharmonic potential

- Possible to break the bond

The energy levels in the bottom of the anharmonic potential are very similar to the harmonic (parabolic) potential.

- Only at higher energy levels do the two models differ.

Summary

- The simple harmonic oscillator uses a parabolic potential to trap the particle in a well
- Instead of solving the Schrödinger equation directly, we used the raising and lowering operators to define and solve a first order differential equation
- Quantization of the energy, again, naturally occurred in the solution.
- Infrared active modes are vibrations which modify the dipole moment of the particle
- The anharmonic potential is a more accurate picture of reality. However, when the particle is close to the ground state, both models are typically very close