Chemistry 2
Lecture 5
The Simple Harmonic Oscillator

Assumed knowledge
The wavefunctions for the particle in a box are zero at the box edges, leading to quantization of the energy levels and the appearance of zero point energy. For a particle in a box, the energy levels depend on $n^2$.

Learning outcomes
- Be able to draw the wavefunctions for the first few solutions to the Schrödinger equation for the harmonic oscillator
- Be able to calculate the energy separation between the vibrational levels for the harmonic oscillator
- Be able to explain the dependence of this separation on the masses of the atoms and the strength of the bond
- Be aware of and be able to calculate the zero point energy of a vibrating molecule
- Be able to draw the potential energy curve for a real molecule and explain why it is different to the harmonic potential

Classical Harmonic Oscillator
- A vibrating molecule behaves like 2 masses joined by a spring
- If the bond is stretch or compressed, there is a restoring force which is proportional to the distortion

\[ F = -kx \]

- $F = 0$ when $x = 0$
- $F = kx$ when $x < 0$
- $F = -kx$ when $x > 0$

As $dV/dx = -F$, $V = \frac{1}{2} kx^2$
- $k$ is the force constant: stiff springs = strong bonds = large $k$
Reduced Mass

- A vibrating molecule behaves like 2 masses joined by a spring.
- The motion is described in terms of the movement of the effective or reduced mass, $\mu$, from the centre of mass.

\[
\mu = \frac{m_1 \times m_2}{m_1 + m_2}
\]

Classical Harmonic Oscillator

- The energy changes between potential energy, $V$, and kinetic energy, $T$:
  - $x < 0 \quad V = \frac{1}{2} k x^2 \quad T = 0$
  - $x = 0 \quad V = 0 \quad T = \frac{1}{2} \mu v^2$
  - $x > 0 \quad V = \frac{1}{2} k x^2 \quad T = 0$

- The bond vibrates with characteristic frequency, $\nu$:
  - $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$
    - strong bonds = large $k$ = high $\nu$
    - light atoms = small $\mu$ = high $\nu$

\[

\text{Classical Harmonic Oscillator}

\[E = T + V = \frac{1}{2} \mu v^2 + \frac{1}{2} k x^2\]
Amplitude

- The 'turning points' are the maximum displacements and have $T=0$ and $E=V$
- These occur at $x=-L/2$ and $+L/2$
- $\varepsilon = V = \frac{\hbar^2}{2m} k x^2 = \frac{1}{2} k (L/2)^2$
- $L^2 = \frac{8\varepsilon}{k}$
- $L = \frac{8\varepsilon}{k}^{1/2}$
- Length varies with $\varepsilon^{1/2}$

The Schrödinger equation

- The Hamiltonian has parts corresponding to Kinetic Energy and Potential Energy. In terms of the displacement:

$$\hat{H}\Psi(x) = \left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + V(x)\right)\Psi(x)$$

Recap: The particle in a box

- Wavefunction is zero at edge as potential is infinite
- Confining the particle leads to quantization of energy levels
- Energy depends on $n^2$
- Lowest energy possible has $n = 1$
The particle in a box vs Harmonic Oscillator

The Box:
- The box is a 1d well, with sides of infinite potential
- \( E_n \) is proportional to \( n^2/L^2 \)
- Energies decrease as \( L \) increases

The harmonic oscillator:
- \( V = \frac{1}{2}kx^2 \)
- Like a box with \( L \) increasing with \( n^{1/2} \)
- \( E \propto L^2 \):
- From above, \( E_n \propto n^2/L^2 \):
  - \( E_n \propto n^2 \)
  - \( E_n \propto n \)
  - Energy depends on \( n \) NOT \( n^2 \)

Quantum Harmonic Oscillator

- Solving the Schrödinger equation gives the energy levels as:
  \[ E_n = \frac{\hbar}{2\pi} \sqrt{\frac{k}{\mu}} \left( n + \frac{1}{2} \right) \]
  where \( n \) is the quantum number and can be 0, 1, 2, 3...
  \[ E_n = \left( n + \frac{1}{2} \right) \mu \nu \]
  where \( \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \)
- Energy depends linearly on quantum number (as predicted)
Quantum Harmonic Oscillator

- Zero point energy: lowest energy corresponds to \( n = 0 \)
  \[
  \epsilon_0 = \left(0 + \frac{1}{2}\right) \hbar \nu = \frac{1}{2} \hbar \nu
  \]

- Just as for the particle in a box, confining the oscillator leads to quantization of energy and non zero minimum energy
- The molecule has vibrational energy even in the lowest possible energy level (and even at \( T = 0 \) K)

The particle in a box vs Harmonic Oscillator

**The Box:**
- Energy levels depend on \( n^2 \)
- Lowest energy has \( n = 1 \):
  - ZPE: \( \epsilon_1 = \frac{1}{2} \hbar \nu \)

**The harmonic oscillator:**
- Energy levels depend on \( n \)
- Lowest energy has \( n = 0 \):
  - ZPE: \( \epsilon_0 = \frac{1}{2} \hbar \nu \)

Quantum Harmonic Oscillator

\[
\epsilon_n = \left(n + \frac{1}{2}\right) \hbar \nu
\]
The particle in a box vs Harmonic Oscillator

The Box:
- wavefunctions are zero at the edge of the box as \( V = \infty \)

The harmonic oscillator:
- at edges, \( V \neq \infty \) but it is increasing sharply
- wavefunction "leaks" outside classically allowed potential region

Harmonic Oscillator Wavefunctions

- wavefunctions are not simple sine waves (but resemble them)
- at low energies, \( \psi^2 \) is largest in the centre (as for particle in the box) akin to classical non-vibrating ground state
- at high energies, \( \psi^2 \) has increasing value at classical turning points
- wavefunction "leaks" outside classically allowed potential region.
  Here \( V > E \) and as \( E = T + V \), the kinetic energy is negative!

Problems with the Harmonic Oscillator

Harmonic oscillator:
- \( V \) keeps increasing as bond is stretched but it never breaks!
- \( V \) keeps increasing as bond compressed but allows nuclei to run into one another
**Anharmonic Oscillator (AHO)**
- The lowest possible energy is the ZPE = $\frac{1}{2} \hbar \nu$
- $D_a = D_n + \frac{1}{2} \hbar \nu$

**Harmonic oscillator:**
- $V$ keeps increasing as bond is stretched but it never breaks!
- $V$ keeps increasing as bond compressed but allows nuclei to run into one another

**Real molecule**
- At large $x$, bond will break
- At small $x$, energy must increase more sharply

**Near dissociation, energy levels become continuous**
Morse Potential

- The simplest approximation to the real potential energy curve is the Morse Potential

\[ V(r) = D_e \left[ 1 - e^{-\alpha r} \right]^2 \]

where \( \alpha = \left( \frac{k}{2D_e} \right)^{1/2} \)

- The solutions are:

\[ \epsilon_n = \left( n + \frac{1}{2} \right) \hbar \nu_e = \left( n + \frac{1}{2} \right)^2 \hbar^2 \nu_e x_e \]

where \( x_e = \frac{\nu_e}{4D_e} \)

- The energy levels get closer and closer together with increasing \( \nu \)

Summary

- The wavefunctions for the harmonic oscillator resemble those of the particle in a box but spill outside the classically allowed region
- The energy levels for the harmonic oscillator increase linearly with the quantum number \( \nu \): they are equally spaced on the energy ladder
- There is a minimum energy, called the zero point energy, associated with the vibrations of a molecule
- The potential energy curve for a real molecule rises more steeply for compressed bonds than for the harmonic oscillator and leads to dissociation for large separations
- The vibrational energy levels of a real molecule get closer together as the energy increases.

Next lecture

- The vibrational spectrum of the harmonic and anharmonic oscillator

Week 11 homework

- Work through the units worksheet and the practice problems at the end of the lectures and check your answers with those available online
- Play with the “IR Tutor” in the 3rd floor computer lab and with the online simulations:
  
**Practice Questions**

1. The bonding in H₂ and D₂ is identical as they only differ in the number of neutrons.
   (a) What is the ratio of the reduced masses for the H₂ and D₂?
   (b) Assuming that H₂ and D₂ have identical force constants, what is the ratio of their vibrational frequencies?

2. Calculate the reduced mass for HF, HCl, HBr and HI (in atomic mass units).

3. Using your answer to question 2, what does the reduced mass of a molecule HX tend to as X becomes very heavy?

4. Using your answer to question 3, describe the vibrational motion of the molecule HX as X becomes very heavy.