

Lecture 18

Particle In a Box

- The particle in a box model describes a particle free to move in a small space surrounded by impenetrable barriers.
- For example, in classical systems, a particle trapped in a large box can move at any speed within the box and it is no more likely to be found at one position than another.
- The particle may only occupy certain positive energy levels
- The particle can never have zero energy, meaning that the particle can never “sit still.”
- Depending on the particle’s energy level, it is more likely to be found at certain positions than at others.

The energy difference between two levels in the particle in a box equation:

$$\Delta E = \frac{h^2}{8ma^2} (2N + 1)$$

For a particle in a 2D/3D box of sides a, b, and c , the wavefunctions are:

$$\psi(x, y, z) = \sqrt{\frac{8}{abc}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c}$$

Translational Partition Function from a 2-D/3-D particle-in-a-box equation:

$$E = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

Harmonic Oscillator

- A harmonic oscillator is a good approximation for the vibration of diatomic molecules and the vibration of bonds in polyatomic molecules.
- Vibrational frequencies are characteristic of a particular type of bond such as C—H, C—C, C=C, and C—N, but they can also be used to determine force constants k for the particular vibration.
- When the force constant, k, for a double-bond vibration decreases (the frequency decreases), it means that the bond has become weaker; the double-bond character has decreased. These differences in bond strength for the same type of bond in different molecules are a useful clue to the distribution of electrons in the molecules.
- As you may or may not recall, bond strength is influenced by factors such as electronegativity, molecular geometry, and the presence of lone pairs or multiple bonds.
 - If atoms forming a bond have different **electronegativities**, the more electronegative atom tends to attract electrons more strongly, leading to an uneven distribution of electron density and a polar bond.
 - The **molecular geometry** (a.k.a. arrangement of atoms in a molecule) affects how electron pairs are distributed. For example, in a double bond, the electrons are

more localized between the two bonded atoms compared to a single bond, impacting bond strength.

- **Lone pairs** can create regions of higher electron density, affecting the overall electron distribution in the molecule.
- **Multiple bonds** involve stronger interactions than single bonds due to the increased electron density between the bonded atoms.
- Take a mass, m , connected to an infinitely heavy wall by a spring. Assume there's no gravity.
- The equilibrium length of the spring is referred to as l_0 .
- When we pull on the mass and extend the spring to length L , there's going to be a restoring force to bring the spring back to its original position; same would happen if you were to compress the spring.
- The displacement is positive if the spring is extended and the displacement is negative if the spring is compressed.
- NOTE: The force constant is the measure of the stiffness or strength of the electronic bond holding the nuclei together. It's not affected by any changes in the reduced mass, thus making the force constant independent of the reduced mass.

Simple Harmonic Oscillator

- Each oscillator has a fundamental vibration frequency, ν_0 ; ν_0 depends on the strength of the bond and the masses.

Harmonic Potential Energy equation: $U = \frac{1}{2}kx^2$

- k = force constant for the bond
- x = the displacement from an equilibrium position

Harmonic Oscillator Schrödinger equation: $-\frac{\hbar^2}{2\mu} \frac{d^2\psi_v}{dx^2} + \frac{1}{2}kx^2\psi_v = E_v\psi_v$

- ψ_v : wavefunction

Quantum Oscillator Energy equation: $E_v = (v + \frac{1}{2})h\nu_0$

Vibration Frequency of the oscillator: $\nu_0 = \frac{1}{2\pi} \left(\frac{k}{\mu}\right)^{1/2}$

- μ = reduced mass of the oscillator
- k = force constant for the bond

Wavenumber of a light wave: $\bar{\nu}_0 = \frac{\nu_0}{c}$; c = velocity of light (3.00×10^8 m/s)

Ratio of New Mass 1 to Original Mass 1 Equation: $\frac{\nu_0(m_{1x}, m_2)}{\nu_0(m_1, m_2)} = \left[\frac{\mu(m_1, m_2)}{\mu(m_{1x}, m_2)}\right]^{1/2}$

m_1 = original first mass

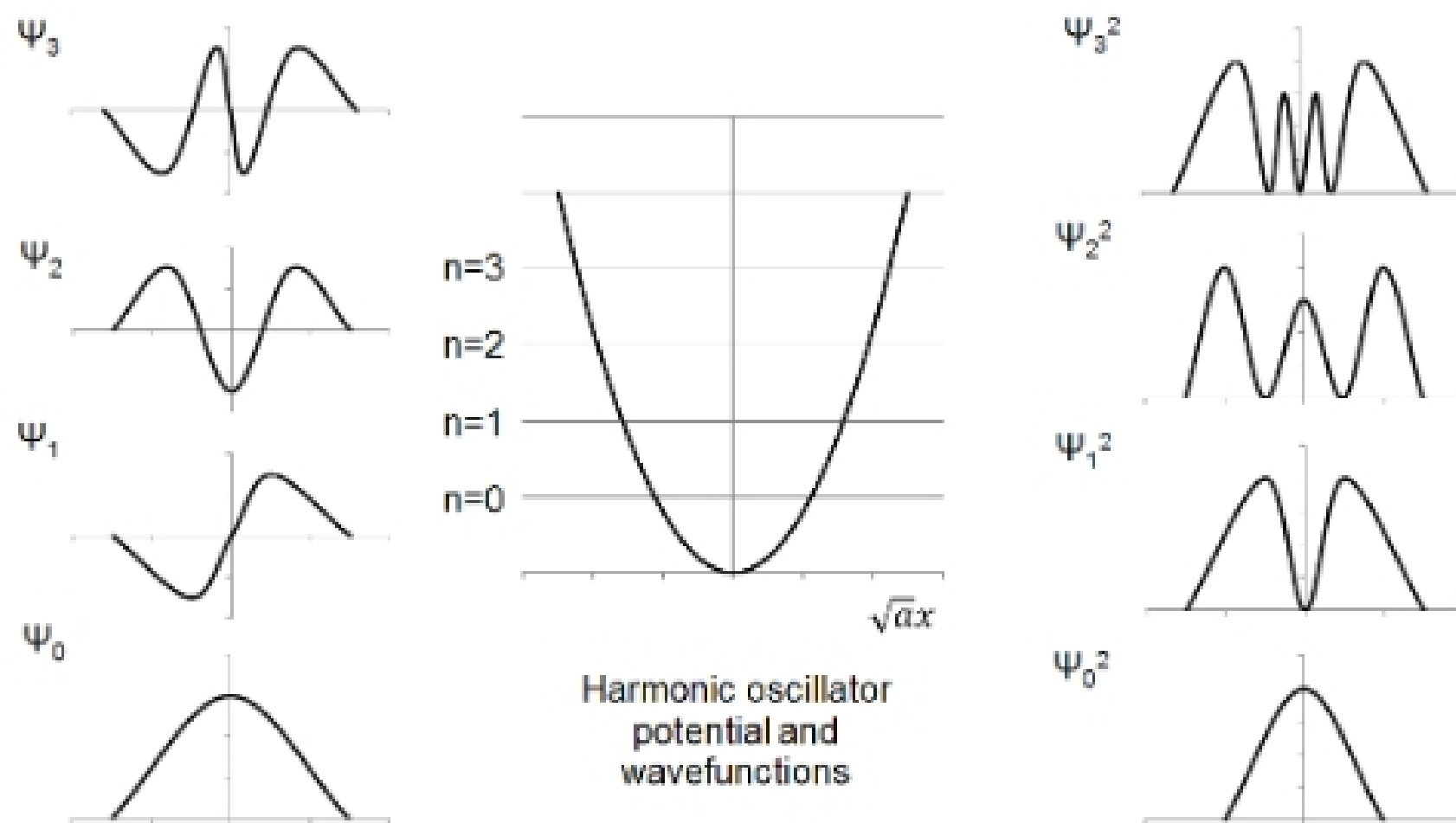
m_{1x} = new first mass

Ratio of New Mass 2 to Original Mass 2 Equation: $\frac{\nu_0(m_1, m_{2x})}{\nu_0(m_1, m_2)} = \left[\frac{\mu(m_1, m_2)}{\mu(m_1, m_{2x})} \right]^{1/2}$

m_2 = original second mass

m_{2x} = new second mass

Simple Harmonic Oscillator Eigenfunctions and Eigenvalues



ψ_v	E_v
$\psi_2 = \left(\frac{2a}{\pi}\right)^{1/4} (4ax^2 - 1)e^{-ax^2}$	$E_2 = \frac{5}{2} h\nu_0$
$\psi_1 = \left(\frac{2a}{\pi}\right)^{1/4} 2a^{1/2} x e^{-ax^2}$	$E_1 = \frac{3}{2} h\nu_0$
$\psi_0 = \left(\frac{2a}{\pi}\right)^{1/4} e^{-ax^2}$	$E_0 = \frac{1}{2} h\nu_0$

NOTE: According to quantum mechanics, the lowest energy level is $\frac{1}{2} h\nu_0$, called the **zero-point energy**.

Reduced Mass