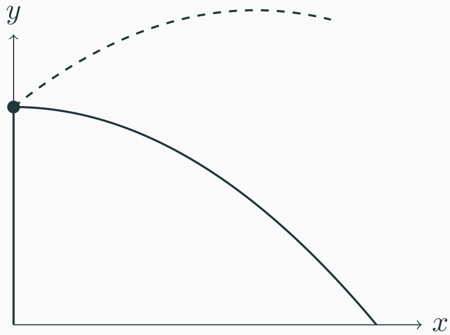
Lecture 2: Quantum Mechanics Overview, Probability

Summary of Quantum Mechanics, Average Value, Permutations, Combinations

Recall: Classical Mechanics

In classical mechanics, a system is described by a function, the trajectory $x(t)$

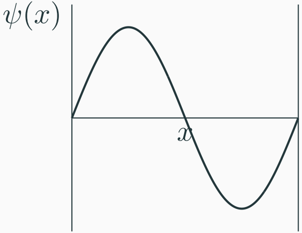
- At time t, the particle is located at position $x(t)$
- If you know the $x(t)$, can calculate velocity and acceleration

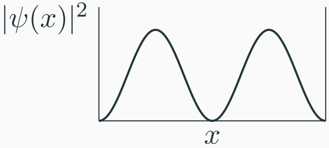


Wavefunction

In quantum mechanics, a system is described by a wavefunction $\psi(x)$

- $\psi(x)$ contains all information about the state of the system
- $|\psi(x)|^2$ is the probability density of finding a particle at position x
- In this class, only concerned with the spatial wavefunction $\psi(x)$, not the full time dependent wavefunction $\psi(x,t)$



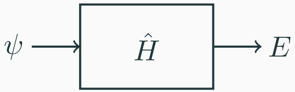


Schrödinger Equation

Hamiltonian Operator $\hat{H}$

An operator corresponding to the total energy of a system

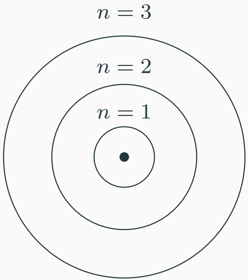
Think of it as a magical black box:



Schrödinger Equation

$$\hat{H}\psi_n = E_n\psi_n$$

- E_n : Allowed energy eigenvalue
- Only certain E_n allowed: quantum mechanical energies are quantized



Quantum vs Classical

Quantum

- Energies are quantized
- Probabilistic
- Uses summations $\sum_i$
- Statistical Mechanics is a Quantum Theory
- Quantum numbers label the allowed energy levels

Classical

- Energies are continuous
- Deterministic
- Uses integrals $\int$
- Thermodynamics is a Classical theory

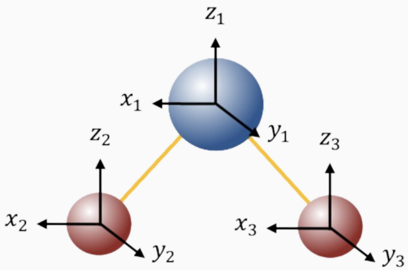
Molecular Motion: Translational, Rotational, Vibrational

Types of Molecular Motion

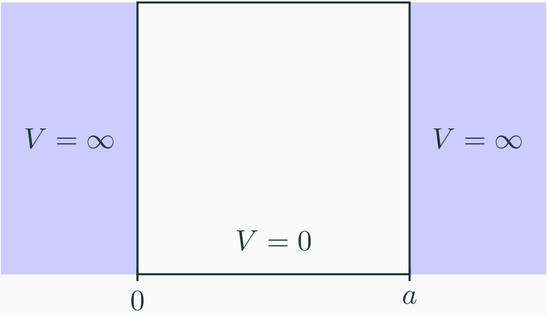
- **Translational:** movement in 3D space
- **Rotational:** rotation around an axis
- **Vibrational:** stretching and bending of bonds

Degrees of Freedom (DOF)

- Total DOF: 3N for N atoms
- Translational DOF: 3
- Rotational DOF: 2 (linear) or 3 (nonlinear)
- Vibrational DOF: $3N - 5$ (linear) or $3N - 6$ (nonlinear)



Translational: Particle in a Box



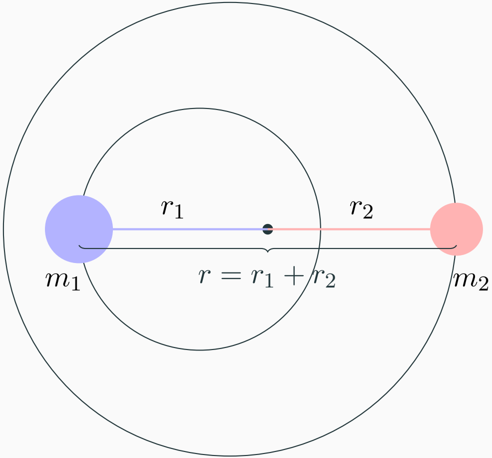
Allowed Energy Levels

$$E_n = \frac{n^2 h^2}{8ma^2} \qquad n = 1, 2, 3, \ldots$$

Potential Energy

$$V(x) = \begin{cases} 0, & 0 < x < a, \\ \infty, & x \leq 0 \text{ or } x \geq a \end{cases}$$

Rotational: Rigid Rotor



Allowed Energy Levels

$$E_J = \frac{\hbar^2}{2I} J(J+1) \qquad J = 0, 1, 2, \ldots$$

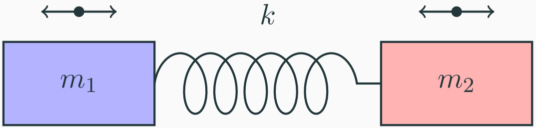
Moment of Inertia (I)

$$I = \mu r^2$$

Reduced Mass (μ)

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

Vibrational: Harmonic Oscillator



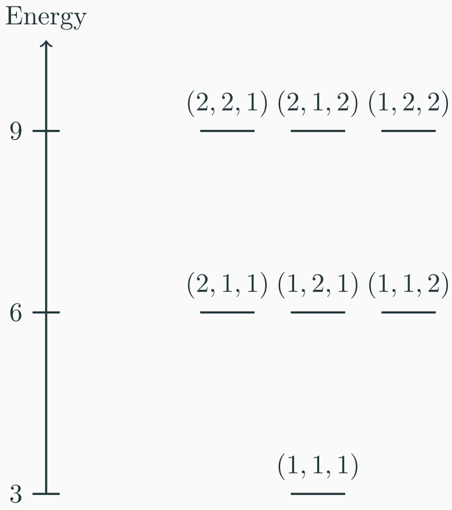
Allowed Energy Levels

$$E_n = h\nu\left(n + \frac{1}{2}\right) \qquad n = 0, 1, 2, \ldots$$

Vibrational Frequency (ν)

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Degeneracy



Degeneracy

When different quantum states have the same energy

1D Particle in a Box

$$E_n = \frac{n^2 h^2}{8ma^2} \qquad n = 1, 2, 3, \ldots$$

3D Particle in a Box

$$E_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} \left(n_x^2 + n_y^2 + n_z^2 \right)$$

Probability Distribution

Discrete variable x with allowed values x_i with probabilities p_i:

$$P(a \leq x \leq b) = \sum_{x_i \in [a,b]} p_i$$

$$\sum_i p_i = 1 \qquad \text{(normalization)}$$

Continuous variable x with probability density $p(x)$:

$$P(a \leq x \leq b) = \int_a^b p(x)\,dx$$

$$\int_{-\infty}^{\infty} p(x)\,dx = 1 \qquad \text{(normalization)}$$

Average Value

Average Value (Expectation Value)

Sum over all possible values, weighted by their probability

$$\begin{aligned}\langle f(x)\rangle &= \sum_i f(x_i)p_i \quad \text{(discrete)}\\ &= \int_{-\infty}^{\infty} f(x)\,p(x)\,dx \quad \text{(continuous)}\end{aligned}$$

Example: Average value of rolling a fair die

$$\sum_{i=0}^{n} f(x_i)p_i = \frac{1}{6}\cdot 1 + \frac{1}{6}\cdot 2 + \frac{1}{6}\cdot 3 + \frac{1}{6}\cdot 4 + \frac{1}{6}\cdot 5 + \frac{1}{6}\cdot 6 = 3.5$$

Counting Principle

Counting Principle

If one event can occur m ways an a second independent event can occur n ways, then the total number of outcomes is given by the product

$$W = m \times n$$

Example: Number of outfits

Shirts: Red, White, Blue
Pants: Black, Gray, Navy, Olive

$$\_\_\_\_ \times \_\_\_\_ = 3 \times 4 = 12$$

Permutations

Permutations (order matters, no repetition)

The number of ways to arrange k objects out of n is:

$$P(n,k) = \frac{n!}{(n-k)!}$$

Example: Arranging 3 letters out of ABCDE

A B C D E

$$\_\_\_\_ \times \_\_\_\_ \times \_\_\_\_ = 5 \times 4 \times 3 = 60$$

Combinations

Combinations (order does not matter, no repetition)

The number of ways to choose k objects out of n is:

$$\binom{n}{k} = \frac{n!}{k!(n-k)!} = \frac{P(n,k)}{k!}$$

Example: Choosing 3 letters out of ABCDE

- There are $5 \times 4 \times 3 = 60$ ways to arrange three letters
- This overcounts, because each *combination* can be arranged in multiple orders:

$$\{\text{ABC}\} \to \text{ABC, ACB, BAC, BCA, CAB, CBA}$$

- The number of orderings of 3 letters is 3!, so we divide:

$$\binom{5}{3} = \frac{60}{3!} = 10$$

Stars and Bars

Stars and Bars (order does not matter, yes repetition)

The number of ways to distribute k identical objects into n distinct bins (bins can be empty) is:

$$\binom{n+k-1}{k} = \frac{(n+k-1)!}{k!(n-1)!}$$

Example: 3 scoops of ice cream from 5 flavors

- Vanilla, Chocolate, Strawberry, Cookies and Cream, Mint

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  V C S CC M

- Number of arrangements = Number of ways to choose positions for the stars:

$$\binom{3+5-1}{3} = \binom{7}{3} = 35$$