Week 2 - Light, Matter & The Schroedinger Equation

1. Wave - particle Duality of Light & Matter

2. Schroedinger Eqn.

3. State Functions / Wavefunction
   a. What is it? What does it mean?
   b. Probability and Probability density
   c. Normalization
   d. Orthogonal & orthonormal
   e. Averages

4. Operators
   a. Linearity
   b. Hermiticity
   c. Commutator
   d. Eigenvalues & eigenvectors

Wave - particle Duality of Light & Matter

Einstein showed that light has both particle & wave properties with the following relation, and De Broglie extended this concept to matter:

\[ \lambda = \frac{h}{p} = \frac{h}{mv} \quad \text{particle-like} \]

(Wave - particle duality -)

Recall for a wave we have the following:

Ordinary frequency - \( \nu \) (Hz = s\(^{-1}\))

Angular frequency - \( \omega = 2\pi \nu \) (rad\(s\)^{-1}\))

Period of oscillation - \( T = \frac{1}{\nu} \) or \( T = \frac{2\pi}{\omega} \)

Wavelength - \( \lambda \)

Wavenumber - \( \vec{k} = \frac{1}{\lambda} \)
Since matter is wave-like, there must be some sort of wave function that describes the system, we find that function with

The Schrödinger Eq

\[ \hat{H} \Psi_n(x) = E_n \Psi_n(x) \]

\[ \uparrow \quad \text{Energy operator} \quad \uparrow \text{Energy Eigenvalue} \]

\[ \downarrow \]

\[ \hat{H} = K.E. + P.E. = \hat{T} + \hat{V} = \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \]

What is the potential, \( V(x) \)?

Depends on the system. Some systems we will look at:

1. Particle in a box
2. Harmonic Oscillator
3. Rigid Rotor
4. Hydrogen atom

State functions, \( \Psi \)

(3.a) State function is a function that describes the state of a particle. On its own, \( \Psi \) makes no sense physically (It's just math).

However, \( |\Psi|^2 \) does have a physical meaning. It's the probability distribution function or probability density.

(3.b) Probability distribution density

\[ |\Psi|^2 = \Psi^*(x) \Psi(x) \]

\[ \text{Complex conjugate of } \Psi(x) \]

\[ \int_a^b |\Psi(x)|^2 dx = \int_a^b \Psi^*(x) \Psi(x) dx \quad \text{Probability of finding a particle between } a \text{ and } b \]
(3.9) Normalization

Usually, we want to specify our probabilities in terms of X%, out of 100%, (or something along those lines) to do that we must first normalize our wave function.

How to Normalize a wave function:

\[ |Y(x)|^2 \quad \text{(probability distribution)} \quad \Rightarrow \quad |A|^2 \int_a^b |\Psi(x)|^2 dx = 1 \]

Example: Suppose \( \Psi = \cos\left(\frac{nx}{a}\right) \) is a wave function for a particle between \( 0 \leq x \leq a \). Find a normalized wave function where \( n \geq a \) are integers.

\[ \int_0^a |A\cos\left(\frac{nx}{a}\right)|^2 dx = 1 \]

Let \( U = \frac{nx}{a} \), \( du = \frac{nan}{a} dx \)

If \( x=0 \), \( U=0 \)
\( x=a \), \( U=n\pi \)

\[ |A|^2 \int_0^{n\pi} \cos^2\left(\frac{nx}{a}\right) dx = 1 \]

\[ \frac{n\pi}{(n\pi)} |A|^2 \left[ \frac{1}{2} \cos(2U) + \frac{1}{2} dU = 1 \right] \]

\[ \frac{1}{2} \left( \frac{a}{n\pi}\right) |A|^2 \left[ \frac{1}{2} \sin(2U) + U \right]_{0}^{n\pi} = 1 \]

\[ \frac{1}{2} \left( \frac{a}{n\pi}\right) |A|^2 \left[ \frac{1}{2} \sin(2U) + U \right]_{0}^{n\pi} = 1 \]

\[ \frac{1}{2} \left( \frac{a}{n\pi}\right) |A|^2 \left[ \frac{1}{2} \sin(n\pi) + n\pi - \left( \frac{1}{2} \sin(0) + 0 \right) \right] = 1 \]
\[ \frac{1}{2} \left( \frac{a}{\pi} \right) |A|^2 \left( \frac{1}{\sqrt{\pi}} \right) = 1 \implies A = \sqrt{\frac{2}{a}} \]

\[ \therefore \text{ Normalized Wavefunction is } \psi(x) = \sqrt{\frac{2}{a}} \cos \left( \frac{\pi x}{a} \right) \]

3.2. Orthogonal & Orthonormal Wavefunctions

Consider two wavefunctions \( \psi_a \) \& \( \psi_b \), \( a \neq b \)

These functions are orthogonal if

\[ \int_{-\infty}^{\infty} \psi_a^*(x) \psi_b(x) dx = 0 \]

Then the two functions represent mutually exclusive states for the particle.

example)

\[ \begin{array}{c}
\psi_a \\
\hline
x_1 \\
\hline
x_2 \\
\hline
x_3 \\
\hline
x_4 \\
\hline
\psi_b
\end{array} \]

Mutually exclusive if there is no overlap such that if the particle is in \( \psi_a \) then it cannot be in \( \psi_b \), therefore it can never be in \( \psi_a \psi_b \) described in math...

Orthogonal functions satisfy:

\[ \int \psi_a^*(x) \psi_b(x) dx = \begin{cases} 0 & \text{if } a \neq b \\ \text{non-zero} & \text{if } a = b \end{cases} \]

Orthonormal functions satisfy:

\[ \int \psi_a^*(x) \psi_b(x) dx = \begin{cases} 0 & \text{if } a \neq b \\ 1 & \text{if } a = b \end{cases} \]
3. e) Averages

Discrete: \( \langle x \rangle = \sum_{j=1}^{n} x_j P(x_j) \)  
\( X_j = \) property/outcome  
\( P(x_j) = \) probability of \( X_j \) happening

\( \text{e.g., card game, dice} \)

Continuous: \( \langle x \rangle = \int_{-\infty}^{\infty} x P(x) dx \)

\( \text{In Q.M.:} \ P(x) = \psi^*(x) \psi(x) = |\psi(x)|^2 \)  
\( \text{Probability distribution function} \)

\( \text{e.g.} \langle E \rangle = \int \psi^*(x) \hat{\mathcal{A}} \psi(x) dx \)

\( \text{Average Energy} \)

\( \text{Energy operator} \)

\( \text{Applied to find observable (property/outcome)} \)

4) Operators

An operator is a symbol that corresponds to a certain mathematical operation

\( \text{e.g.} \ \frac{d^2}{dx^2} \ |_x \ \text{SQR} \sqrt{\text{rotate } 90^\circ \text{ etc.}} \)

Important Q.M. operators:

- Position: \( \hat{\mathbf{x}} = x \)
- Potential Energy: \( \hat{\mathbf{V}} = V \)
- Linear momentum: \( \hat{\mathbf{p}}_x = -i \hbar \frac{d}{dx} \)
- Kinetic Energy: \( \hat{\mathbf{f}}_x = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \)
- Total Energy operator (Hamiltonian): \( \hat{\mathbf{H}} = \hat{\mathbf{\mathcal{A}}} + \hat{\mathbf{V}} \)

\( = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V \)
4. a) **Linearity**

An operator is linear if it satisfies two properties:

1. **Additive** (Adds Linearity)
   \[ \hat{A}(f(x) + g(x)) = \hat{A}(f(x)) + \hat{A}(g(x)) \]

2. **Homogeneity** (Scales linearly)
   \[ c\hat{A}(f(x)) = \hat{A}(cf(x)) \]

E.g.) Are the following linear?

1. \( \hat{A}(f(x)) = (f(x))^2 \)
   \[ \hat{A}(f(x) + g(x)) = (f(x) + g(x))^2 = f^2(x) + 2f(x)g(x) + g^2(x) \]
   \[ \hat{A}(f(x)) + \hat{A}(g(x)) = f^2(x) + g^2(x) \]
   This operator is not linear because it fails additivity

2. \( \hat{A}(f(x)) = f^*(x) \)
   \[ c\hat{A}(f(x)) = cf^*(x) \]
   \[ \hat{A}(cf(x)) = c^*f^*(x) \]
   Only when \( c \) is real is this operator linear. If \( c \) is complex then \( \hat{A} \) is non-linear because it fails homogeneity

4. b) **Hermitian Operators**

Operators that are equal to their conjugate transpose.

To prove an operator is Hermitian: Let \( f_m(x), f_n(x) \) be state functions

\[ \hat{\psi} \text{ is an operator} \]

\[ \int_{-\infty}^{\infty} f_m^*(x) \hat{\psi} f_n(x) \, dx = \int_{-\infty}^{\infty} f_n(x) \hat{\psi}^* f_m(x) \, dx \]

If the above is true then \( \hat{\psi} \) is a Hermitian operator.
Commutator

Two operators \( \hat{A}, \hat{B} \) commute

\[
[\hat{A}, \hat{B}] = (\hat{A}\hat{B} - \hat{B}\hat{A})f(x) = \hat{A}\hat{B}f(x) - \hat{B}\hat{A}f(x) = 0
\]

Then \( \hat{A} \not\equiv \hat{B} \) commute

Example:

Consider the two operators

\( \hat{A} = \hat{p}_x = -i\hbar \frac{d}{dx} \) and \( \hat{B} = \hat{x} = x \)

Do these two operators commute with an arbitrary function \( f(x) \)?

\[
[\hat{p}_x, \hat{x}]f(x) = (\hat{p}_x \hat{x} - \hat{x} \hat{p}_x)f(x) = \hat{p}_x \hat{x} f(x) - \hat{x} \hat{p}_x f(x)
\]

\[
= -i\hbar \frac{d}{dx} f(x) - x(-i\hbar \frac{d}{dx} f(x))
\]

\[
= -i\hbar f(x) - i\hbar x \frac{df(x)}{dx} + i\hbar x \frac{df(x)}{dx}
\]

\[
= -i\hbar f(x)
\]

\( \Rightarrow [\hat{p}_x, \hat{x}] = -i\hbar \neq 0 \)

So \( \hat{p}_x \not\equiv \hat{x} \) do not commute

Physically, this means we cannot simultaneously observe position & momentum

(Heisenberg Uncertainty Principle)

4d: Eigenvalues and Eigenvectors

Suppose \( \hat{A} \) is a linear operator \( \hat{v} \) is a vector and \( \lambda \) is a scalar.

If \( \hat{A}\hat{v} = \lambda \hat{v} \) then \( \lambda \) is an eigenvalue and \( \hat{v} \) is an eigenvector.

The Schrödinger Eq. is an Eigenvalue/Eigenvector expression.

\[ \hat{H} \psi = E \psi \quad \text{Eigenfunction} \]

\[ \Lambda \quad \text{Eigenvalue} \]

\[ \text{operator} \]

\[ \text{operator} \]