Lecture 4

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- Wave Equation for Unidimensional Particle
  - In classical mechanics, we have the energy problem, with E as the total energy, T as the kinetic energy, and V as the potential energy:

    $$E = T + V = \frac{p^2}{2m} + V(x)$$

  - In quantum mechanics, we may define the Hamiltonian as:

    $$\hat{H} = \frac{\hat{p}}{2m} + V(\hat{x})$$

    * Where $\hat{p}$ is the momentum operator and $\hat{x}$ is the position
  - From here, the time-independent Schrödinger equation may be written as:

    $$\hat{H}\phi_E(x) = E\phi_E(x)$$

    * Where $\phi_E(x)$ represents the wave function/eigenfunction
  - We may continue to get:

    $$\hat{p} = -i\hbar\frac{d}{dx}, \quad \hat{x} = x$$

    * This can be used to obtain:

    $$\hat{p}\phi(x) = -i\hbar\frac{d}{dx}\phi(x), \quad \hat{x}\phi(x) = x\phi(x)$$

  - From here, we get:

    $$\hat{H}\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^s}\psi(x) + V(x)\psi(x) = E\psi(x)$$

- The above is the wave equation we need to solve. The wave function can generically be written as:

$$\psi(x) = \sum_{n=0}^{d} \psi_n \phi_{E_n}(x)$$

  * Note that ψ_n is a scalar coefficient (projections of ψ along the n-th direction) and $\phi_{E_n}(x)$ represents basis functions
  * Also, note that, from previous lessons, we may recall that the probability of finding the system in a particular eigenstate is:

$$P_{E_n} = |\psi_n|^2$$

- In Dirac notation:

$$|\psi\rangle = \begin{pmatrix} \langle E_1|\psi\rangle \\ \langle E_2|\psi\rangle \\ \vdots \\ \langle E_n|\psi\rangle \end{pmatrix}$$

  * And also:

$$\langle\psi| = \begin{pmatrix} \langle E_1|\psi\rangle^* & \langle E_2|\psi\rangle^* & \cdots & \langle E_n|\psi\rangle^* \end{pmatrix}$$

- Change of Basis
  * Changing basis to a position representation allows us to obtain the probability of finding the particle at x as:

$$P_x = |\psi(x)|^2$$

  * This means that $|\psi(x)|^2$ is now a probability density such that:

$$\int_{-\infty}^{\infty} P(x)\,dx = \int_{-\infty}^{\infty} |\psi(x)|^2\,dx = 1$$

  * Furthermore, we may find the probability that the particle is in a certain range as:

$$P[a \leq x \leq b] = \int_a^b P(x)\,dx = \int_a^b |\psi(x)|^2\,dx$$

  * In summary, we determine:

$$\langle x|\psi\rangle = \psi(x)$$
$$\langle\psi|x\rangle = \psi^*(x)$$
$$\hat{A} = \hat{A}(x)$$

- Quantized Energies and Spectroscopy
  - Spectroscopy is an experimental technique for measuring the energy fingerprint of a system
  - Historically, hydrogen played an important role in the development of this technique
  - Downward transitions give rise to emission spectra
  - Upward transitions give rise to absorption spectra
  - $E_i + E_j$, there is a possible spectral line with photon energy $E_i - E_j$, with photon frequency f_{ij} and wavelength λ_{ij}:

$$f_{ij} = \frac{\omega_{ij}}{2\pi} = \frac{E_i - E_j}{h}$$
$$\lambda_{ij} = \frac{c}{f_{ij}} = \frac{hc}{E_i - E_j}$$

    * Assuming $E_i - E_j > 0$

- Infinite Square Well
  - We want to solve:

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\phi_E(x) = E\phi_E(x)$$

  - The solutions of the this depend critically on the functional dependence of $V(x)$
  - We create a variable k^2 such that:

$$k^2 = \frac{-2mE}{\hbar^2}$$

  - This gives us:

$$\frac{d^2}{dx^2}\phi_E(x) = k^2\phi_E(x)$$

  - There are two possible forms of the solution:

$$\phi_E(x) = Ae^{ikx} + Be^{-ikx}$$
$$\phi_E(x) = A\sin(kx) + B\cos(kx)$$

  - Applying boundary conditions, we obtain:

$$k_n = \frac{n\pi}{L}$$

– From this, we may determine:

$$E_n = \frac{n^2\hbar^2}{2mL^2}, \quad n = 1, 2, 3\cdots$$

– The general form of the wave function may be written:

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

– We can compute expectation values as:

$$< \hat{x} >= \langle E_n|\hat{x}|E_n\rangle = \int_{-\infty}^{\infty} \phi^*(x)x\phi_n(x)\,dx$$

This gives us:

$$\int_{-\infty}^{\infty} x|\phi_n(x)|^2\,dx = \frac{L}{2}$$

- Finite Square Well

  – In a finite well, we have potential energy defined by:

$$V(x) = \begin{cases} V_o, & x < -a \\ 0, & -a < x < a \\ V_o, & x > a \end{cases}$$

  – This gives us:

$$\left(-\frac{\hbar^2}{2m}d^2dx^2\right)\phi_E(x) = E\phi_E(x) \quad \text{(inside box)}$$
$$\left(-\frac{\hbar^2}{2m}d^2dx^2 + V_o\right)\phi_E(x) = E\phi_E(x) \quad \text{(outside box)}$$

  – We know that:

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{(inside)}$$
$$q = \sqrt{\frac{2m(V_o - E)}{\hbar^2}} \quad \text{(outside)}, 0 < E < V_o$$

  – We may find the solutions inside and outside of the box (respectively) as:

$$\phi_E(x) = e^{-ikx} \text{ or } \phi_E(x) = e^{-kx} \quad \text{(inside)}$$
$$\phi_E(x) = Ae^{qx} + Be^{-qx} \quad \text{(outside)}$$

– Thus, we may write:

$$\phi_E(x) = \begin{cases} Ae^{qx} + Be^{-qx}, & x < -a \\ C\sin(kx) + D\cos(kx), & -a < x < a \\ Fe^{qx} + Ge^{-qx}, & x > a \end{cases}$$

– Two boundary conditions:

1. $\phi_E(x)$ is continuous
2. $d\phi_E(x)/dx$ is continuous (unless the potential is infinite)

– Since our problem is symmetric about the origin, we have even and odd solutions:

$$\phi_{even}(x) = \begin{cases} Ae^{qx}, & x < -a \\ D\cos(kx), & -a < x < a \\ Ae^{-qx}, & x > a \end{cases}$$

$$\phi_{odd}(x) = \begin{cases} Ae^{qx}, & x < -a \\ C\sin(kx), & -a < x < a \\ -Ae^{-qx}, & x > a \end{cases}$$