

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:

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

- * 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:

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

- 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:

$$\langle\psi| = (\langle E_1|\psi\rangle^* \quad \langle E_2|\psi\rangle^* \quad \cdots \quad \langle E_n|\psi\rangle^*)$$

- 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:

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

- 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:

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

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:

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

- We know that:

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

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

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

- 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:

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

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

- General Remarks

- When $E > V$, the curvature of the wave function has the opposite sign
- When $E < V$, the curvature has the same sign as the wave function
- $k = \sqrt{2m(E - V)}$ and $\lambda = 2\pi/k$, so:

$$\lambda = \frac{h}{\sqrt{2m(E - V)}} \propto \frac{1}{\sqrt{T}}$$

- * We may say that the wavelength is inversely proportional to the square root of the kinetic energy

- In the forbidden region, the decay constant is:

$$e^{-qx} \rightarrow q = \frac{\sqrt{2m(V - E)}}{\hbar}$$

- Inversion Symmetry and Parity

$$\hat{H}(x) = \hat{H}(-x)$$

- The Hamiltonian is invariant under parity

$$[\text{Parity}, \hat{H}] = 0$$

- Energy eigenstates are also eigenstates of the parity operator

$$\hat{\text{Parity}}\phi_n(x) = +\phi_n(-x) \quad \text{even parity}$$

$$\hat{\text{Parity}}\phi_n(x) = -\phi_n(-x) \quad \text{odd parity}$$

- Superposition States and Time-Dependence

- We start from:

$$H|\psi\rangle = i\hbar \frac{d}{dt} |\psi\rangle$$

- * With:

$$|\psi\rangle = \sum_n c_n e^{-iE_n t/\hbar} |E_n\rangle$$

- * In general, an initial state will be of the form:

$$|\psi(0)\rangle = \sum_n c_n |E_n\rangle$$

$$\cdot \text{ Where } c_n = \langle E_n | \psi(0) \rangle = \int \phi_n^*(x) \psi(x, t=0) dx$$

- * We may observe that, with this, we get:

$$\langle \hat{x} \rangle = \frac{L}{2} \left[1 - \frac{32}{9\pi^2} \cos\left(\frac{3\pi^2\hbar}{2mL^2}t\right) \right] \quad (\text{note the oscillation with Bohr frequency})$$

$$\langle \hat{p} \rangle = \frac{8}{3} \frac{\hbar}{2} \sin\left(\frac{3\pi^2\hbar}{2mL^2}t\right)$$

- * This is another example of Ehrenfest's theorem: quantum expectation values obey classical laws