

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:

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

- 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:

$$\phi_E(x) = A e^{ikx} + B e^{-ikx}$$

$$\phi_E(x) = A \sin(kx) + B \cos(kx)$$

- 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

- Unbound States

- Occur when $E > V_o$
- The simplest unbound state is a free particle where $V(x) = 0$ everywhere:

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

- The solutions are:

$$\phi_E(x) = Ae^{ikx} + Be^{-ikx}$$

- * Where there is no condition to “fit” a certain number of wavelengths in a region

- To understand the free particle function, consider:

$$\begin{aligned}\psi_E(x, t) &= \phi_E(x) e^{-iEt/\hbar} \\ \psi_E(x, t) &= [Ae^{ikx} + Be^{-ikx}] e^{-iEt/\hbar} \\ \psi_E(x, t) &= Ae^{i(kx-\omega t)/\hbar} + Be^{-i(kx-\omega t)/\hbar}\end{aligned}$$

- * Observe that this function has a form familiar to classical physics: $f(x \pm vt)$
- * This form retains its shape as it moves with speed $v = \omega/k$, or the phase velocity
- * The energy eigenstate has a right and left-moving part
- It is convenient to use wave vector eigenstates:

$$\begin{aligned}\phi_k(x) &= Ae^{ikx} \\ \phi_E(x) &= \phi_{+k}(x) + \phi_{-k}(x)\end{aligned}$$

- Momentum Eigenstates

- We may find that:

$$p = \hbar k$$

- As well as:

$$\phi_p(x) = Ae^{ipx/\hbar}$$

- * Where x is a variable, and p is a particular momentum:

$$p = \hbar k = \frac{h}{2\pi} \cdot \frac{2\pi}{\lambda} = \frac{h}{\lambda}$$

- * This represents the de-Broglie wavelength:

$$\lambda_{dB} = \frac{h}{p}$$

$$E = \frac{p^2}{2m} \Rightarrow [H, p] = 0$$

- This implies that energy and momentum share eigenstates
- In our case, we have a degeneracy, where $|p\rangle$ and $|-p\rangle$ have the same energy
- Returning to the issue of the phase velocity, we can write:

$$\psi_p(x, t) = Ae^{i\frac{p}{\hbar}(x - \frac{pt}{m})}$$

- This implies that the wave's speed is $v = \frac{p}{m}$, despite the classical speed being p/m

- We should properly describe the velocity of a particle by the “group velocity of a wave function”
- * A more serious problem with the momentum eigenstates appears when one examines the probability density of the state

$$P(x) = |\phi_p(x)|^2 = |A|^2 \quad (\text{constant})$$

- This leads to two issues:
 1. The particle is equally likely to be at any location
 2. The wave function can not be normalized over all space
- Solution: construct wave packets built from a superposition of momentum eigenstates
- All of the discrete basis states we have encountered satisfy these conditions:

$$\langle a_i | a_{j \neq i} \rangle = 0 \quad (\text{orthogonality})$$

$$\langle a_i | a_i \rangle = 1 \quad (\text{normality})$$

$$\sum |a_i\rangle \langle a_i| = \mathbb{1} \quad (\text{completeness})$$

$$\langle a_i | a_j \rangle = \delta_{ij} \quad (\text{orthonormality})$$

- To extend orthonormality to a continuous basis, one promotes a Kronecker delta function to a Dirac delta function:

$$\langle p'' | p' \rangle = \delta(p'' - p')$$

- Where:

$$\int_{-\infty}^{\infty} \phi^*(x)_{p''}(x) \phi_{p'}(x) dx = \delta(p'' - p')$$

- For this to be the case, we must take:

$$A = \frac{1}{\sqrt{2\pi\hbar}} \Rightarrow \phi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$$

- This makes:

$$|\phi_p(x)|^2 dx$$

- have units of length divided by \hbar , which means so does the Dirac delta function

- * For momentum eigenstates, the completeness relation is:

$$\int_{-\infty}^{\infty} |p\rangle \langle p| dp = \mathbb{1}$$

* We may obtain:

$$\psi(x) = \int_{-\infty}^{\infty} \phi(p) \psi(p) dp$$

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \phi(p) e^{ipx/\hbar} dp$$

· This clearly shows that $\psi(x)$ is the Fourier transform of $\phi(p)$. Thus, $\phi(p)$ is the Fourier transform of the position wave function:

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \phi(p) e^{-ipx/\hbar} dx$$

- Wave Packets

- We may create discrete wave packets:

$$p_o - \delta p, p_o, p_o + \delta p$$

- * This leads to something local in space

- We begin by writing:

$$\psi(x, 0) = \sum_j c_j \phi_{p_j}(x)$$

- * This expands to:

$$\psi(x, 0) = \frac{1}{\sqrt{2\pi\hbar}} \left[\frac{1}{2} e^{i(p_o - \delta p)x/\hbar} + e^{ip_o x/\hbar} + \frac{1}{2} e^{i(p_o + \delta p)x/\hbar} \right]$$

- * We may get the time-dependent form as:

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} e^{ip_o(x - \frac{p_o t}{2m\hbar})} \left[1 + \cos\left(\frac{\delta p x}{\hbar} - \frac{p_o \delta p t}{m\hbar}\right) \right]$$

- We observe that:

$$v_{phase} = \frac{p_o}{2m}$$

- The exponential term in the time-dependent form is referred to as the “carrier wave”
 - The sinusoidal term is referred to as the “envelope”
 - Note that, in the envelope, the group velocity becomes:

$$v_{group} = \frac{p_o}{m}$$

- The sinusoid modulates the carrier wave

- We can make a continuous superposition of momentum states as:

$$\psi(x, 0) = \int_{-\infty}^{\infty} \phi(p) \frac{1}{\sqrt{2\phi\hbar}} e^{ipx/\hbar} dp$$

- We then get:

$$\begin{aligned} \psi(x, t) &= \int_{-\infty}^{\infty} \phi(p) \frac{1}{\sqrt{2\phi\hbar}} e^{ipx/\hbar} e^{-ip^2 t/2m\hbar} dp \\ \phi(p) &= \int_{-\infty}^{\infty} \psi(x, t) \frac{1}{\sqrt{2\phi\hbar}} e^{-ipx/\hbar} dp \end{aligned}$$

- We choose $\phi(p)$ to be a Gaussian centered at p_o :

$$\phi(p) = \left(\frac{1}{2\pi\beta} \right)^{1/2} e^{-(p-p_o)^2/4\beta^2}$$

* With $\langle p \rangle = p_o$, and $\Delta p = \beta$

- Using this, along with the commutator, we obtain:

$$\Delta x \Delta p = \frac{\hbar}{2} \sqrt{1 + \left(\frac{2\beta^2 t}{m\hbar} \right)^2}$$

* Note that at $t = 0$, we simply have the uncertainty as $\hbar/2$

• Unbound States and Scattering

- Consider the following potential:

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

- Bound states occurs at $E < 0$ and scattering states occur at $E > 0$
- This gives us:

$$\phi_E(x) = \begin{cases} Ae^{ik_1 x} + Be^{-ik_1 x}, & x < -a \\ Ce^{ik_2 x} + De^{-ik_2 x}, & -a < x < a \\ Fe^{ik_1 x} + Ge^{-ik_1 x}, & x > a \end{cases}$$

• Transmission Coefficient (T)

- We may write the coefficient as:

$$T = \left| \frac{F}{A} \right|^2 = \frac{1}{1 + \frac{(k_1 - k_2)^2}{4k_1^2 k_2^2} \sin^2(2k_2 a)}$$

- Reflection Coefficient (R)

- Similarly, we may write the coefficient as:

$$R = \left| \frac{B}{A} \right|^2 = \frac{1}{1 + \frac{4k_1^2 k_2^2}{(k_1^2 - k_2^2) \sin^2(2k_2 a)}}$$

- The two coefficients are related to each other in that:

$$T + R = 1$$