# 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 $\psi_n$ is a scalar coefficient (projections of $\psi$ 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 $\lambda_{ij}$:

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

    * 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:

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

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

- 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:

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

- Inversion Symmetry and Parity

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

– The Hamiltonian is invariant under parity

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

– 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:

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

      · 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:

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

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

    * 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:

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

* 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:

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

- 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:

$$\psi_p(x,t) = Ae^{i\frac{p}{\hbar}\left(x-\frac{pt}{2m}\right)}$$

· This implies that the wave's speed is $v = \frac{p}{2m}$, 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:

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

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

  · 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:

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

- 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:

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

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

- 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:

$$T + R = 1$$

- Angular Momentum
  - One of the most important problems in the history of quantum mechanics: the hydrogen atom
  - Bound states of a proton and an electron
  - We have 2 particles and 3 dimensions, so there are new technical challenges
  - There are a few problems we must solve, beginning with the hamiltonian of the system:

$$H_{sys}\psi_{sys}(\vec{R}, \vec{F}) = E_{sys}\psi_{sys}(\vec{R}, \vec{r})$$

    * This means we need to solve for the wave function of the system:

$$\psi_{sys}(\vec{R}, \vec{r}) = \psi_{cm}(\vec{R})\psi_{rel}(\vec{r})$$

    * We need to break these into:

$$H_{cm}\psi_{cm}(\vec{R}) = E_{cm}\psi_{cm}(\vec{R}) \quad \text{and } H_{rel}\psi_{rel}(\vec{r}) = E_{rel}\psi_{rel}(\vec{r})$$

    * Although the former is fairly simple since $\psi_{cm}(x, y, z)$ is in terms of $x, y, z$, the latter becomes trickier, since:

$$\psi_{rel}(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

    * Thus, the solution of the problem will take the form:

$$\psi_{sys}(\vec{R}, \vec{r}) = \psi_{cm}(x, y, z)\psi_{rel}(r, \theta, \phi)$$

    * We write the Hamiltonian as:

$$H_{sys} = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(\vec{r}_1, \vec{r}_2)$$

    * The Coulomb potential between the electron and proton is central:

$$V(\vec{r}_1, \vec{r}_2) = V(|\vec{r}_1 - \vec{r}_2|)$$

* We decompose the motion into center of mass motion, and motion about the center of mass (relative motion):

$$\text{Center of Mass:} \quad \vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}$$
$$\vec{r} = \vec{r}_2 - \vec{r}_1$$
$$\vec{p} = \vec{p}_1 + \vec{p}_2$$
$$\text{Relative Momentum:} \quad \vec{p}_{rel} = \frac{m_1\vec{p}_2 - m_2\vec{p}_1}{m_1 + m_2}$$
$$\frac{\vec{p}_{rel}}{\mu} = \frac{\vec{p}_2}{m_2} - \frac{\vec{p}_1}{m_1}$$
$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad \text{or } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

* Using the above, as well as $M = m_1 + m_2$, we write:

$$H_{sys} = \frac{\vec{p}^2}{2M} + \left(\frac{\vec{p}_{rel}^2}{2\mu} + V(r)\right)$$

* Using the independence of the coordinates, we may obtain the eigenvalue equations as:

$$\frac{\vec{p}^2}{2M}\psi_{cm}(\vec{R}) = E_{cm}\psi_{cm}(\vec{R})$$
$$\left(\frac{\vec{p}_{rel}^2}{2m} + V(r)\right)\psi_{rel}(\vec{r}) = E_{rel}\psi_{rel}(\vec{r})$$

* We can thus find the energy of the center of mass as:

$$E_{cm} = \frac{1}{2M}\left(p_x^2 + p_y^2 + p_z^2\right)$$

  · With wave function:

$$\psi_{cm}(x, y, z) = \frac{1}{(2\pi\hbar)^{3/2}} e^{i(p_x x + p_y y + p_z z)/\hbar}$$

* We now move to the more complex relative motion case (eigenvalue equation in spherical coordinates):

$$H = \frac{p^2}{2\mu} + V(r)$$
$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right)\psi(\vec{r}) = E\psi(\vec{r})$$

– Returning to Angular Momentum, we recall that, classically:

$$\vec{\tau} = \vec{r} \times \vec{p}$$

– For a central source, we know:

$$\frac{d\vec{\tau}}{dt} = 0$$

  * This implies $\vec{L}$ is a constant
  * Quantum Mechanically, we may write the components of the angular momentum as:

$$L_x = yp_z - zp_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$
$$L_y = zp_x - xp_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$
$$L_z = xp_y - yp_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

    · We may recall:

$$[x, p_x] = i\hbar$$
$$[x, p_y] = [x, p_z] = 0$$

  * We can then return to find:

$$[L_x, L_y] = i\hbar L_z$$

  * And ultimatelly we enter this into the above equations to write:

$$[L_x, L_y] = i\hbar L_z$$
$$[L_y, L_z] = i\hbar L_x$$
$$[L_z, L_x] = i\hbar L_y$$

  * Furthermore, we may consider:

$$[\vec{L}^2, L_x] = [\vec{L}^2, L_y] = [\vec{L}^2, L_z] = 0$$

  * Therefore, we may complete the analogy:

$$\vec{s}^2\,|sm_s\rangle = s(s+1)\hbar^2\,|sm_s\rangle \rightarrow \vec{L}^2\,|lm_l\rangle = l(l+1)\hbar^2\,|lm_l\rangle$$
$$L_z\,|lm_l\rangle = m_l\hbar\,|lm_l\rangle$$

    · Where $l$ is the orbital angular momentum quantum number, and $m_l$ is the orbital magnetic quantum number
    · It is important to note a crucial difference:

$$s = 0, 1/2, 1, 3/2, \cdots$$
$$l = 0, 1, 2, 3, \cdots$$

· For $m_l$, we are constrained by $2l + 1$:

$$m_l = -l, -l + 1, \cdots l - 1, l$$