Introduction to Quantum Mechanics

Part I Theory

1 The Wave Function

1.1 The Schrodinger Equation

Looking for Particle's wave function

$$\Psi(x, t)$$

by solving the Schrodinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi$$

Planck's constant

$$\hbar = \frac{h}{2\pi} = 1.054573 \times 10^{-34}\,\mathrm{Js}$$

1.2 The Statistical Interpretation

Born's statistical interpretation

$$\int_a^b |\Psi(x,t)|^2 \,\mathrm{d}x = \{\text{probability of finding the particle between a and b}\}$$

- All quantum mechanics has to offer is statistical information about the possible results.

1.3 Probability

1.3.1 Discrete Variables

The average value of some *function* of *j* is given by

$$\langle f(j) \rangle = \sum_{j=0}^{\infty} f(j) P(j)$$

The **variance** of the distribution

$$\sigma^2 \equiv \langle (\Delta j)^2 \rangle$$

The **standard deviation**

$$\sigma = \sqrt{\langle j^2 \rangle - \langle j \rangle^2}$$

1.3.2 Continuous Variables

$\rho(x)$: **probability density**

$$P_{ab} = \int_a^b \rho(x) \,\mathrm{d}x$$

Rules:

$$\int_{-\infty}^{\infty} \rho(x) \,\mathrm{d}x = 1$$
$$\langle x \rangle = \int_{-\infty}^{\infty} x \rho(x) \,\mathrm{d}x$$
$$\langle f(x) \rangle = \int_{-\infty}^{\infty} f(x) \rho(x) \,\mathrm{d}x$$

$$\sigma^2 \equiv \langle(\Delta x)^2\rangle = \langle x^2\rangle - \langle x\rangle^2$$

1.4 Normalization

Normalizing the wave function (square-integrable)

$$\int_{-\infty}^{\infty} |\Psi(x)|^2 \,\mathrm{d}x = 1$$

Proof the Schrodinger equation automatically preserves the normalization of the wave function:

$$\frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m}\frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar}V\Psi, \quad \frac{\partial \Psi^*}{\partial t} = -\frac{i\hbar}{2m}\frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar}V\Psi^*$$
$$\downarrow$$
$$\frac{\partial}{\partial t}|\Psi|^2 = \frac{\partial}{\partial t}(\Psi^*\Psi) = \Psi^*\frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t}\Psi$$
$$\downarrow$$
$$\frac{d}{dt}\int_{-\infty}^{\infty} |\Psi(x)|^2 \,\mathrm{d}x = \int_{-\infty}^{\infty} \frac{\partial}{\partial t}|\Psi(x)|^2 \,\mathrm{d}x = 0 \qquad \text{QED}$$

1.5 Momentum

For a particle in state Ψ, the expectation value of x is

$$\langle x\rangle = \int_{-\infty}^{\infty} x|\Psi(x)|^2 \,\mathrm{d}x = \int \Psi^* \,[x]\, \Psi \,\mathrm{d}x$$

the expectation value of **momentum** is

$$\langle p\rangle = m\frac{d\langle x\rangle}{dt} = -i\hbar\int\left(\Psi^*\frac{\partial \Psi}{\partial x}\right)dx = \int \Psi^* \,[-i\hbar(\partial/\partial x)]\, \Psi \,\mathrm{d}x$$

- operator: $x \rightarrow \text{position}; -i\hbar(\partial/\partial x) \rightarrow \text{momentum}$

the expectation of any $Q(x,p)$ is

$$\langle Q(x,p)\rangle = \int \Psi^*[Q(x, -i\hbar\partial/\partial x)]\Psi \,\mathrm{d}x$$

- **Ehrenfest's theorem**

$$\frac{d\langle p\rangle}{dt} = \left\langle \frac{\partial V}{\partial x}\right\rangle$$

proof: $\frac{d\langle p\rangle}{dt} = -i\hbar\int\frac{\partial}{\partial t}\left(\Psi^*\frac{\partial \Psi}{\partial x}\right) = -i\hbar\left(\frac{i}{\hbar}\right)\int -|\Psi|^2\frac{\partial V}{\partial x}dx$

1.6 The Uncertainty Principle

- **de Broglie formula**

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

- Heisenberg's **uncertainty principle**

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$

2 Time-Independent Schrodinger Equation

2.1 Stationary States

Separation of variables $\Psi(x,t) = \psi(x)\varphi((t)$

$$\frac{d\varphi}{dt} = -\frac{iE}{\hbar}\varphi \qquad \rightarrow \qquad \varphi(t) = e^{iEt/\hbar}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi \qquad \text{time-independent Schrodinger equation}$$

Three Answers:

- stationary states

$$\Psi(x,t) = \psi(x)e^{iEt/\hbar}$$

- *states of definite total energy*
  - **Hamiltonian** : $H(x,p) = \frac{p^2}{2m} + V(x)$
  - Hamiltonian *operator* :

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

  - Rewrite time-independent S_e :

$$\hat{H}\psi = E\psi$$

  - expectation value of the total energy : $\langle H \rangle = E$ & $\langle H^2 \rangle = E^2$
  - variance: $\sigma_H = 0$
- **linear combination** of separable solutions

$$\Psi(x,t)=\sum_{n-1}^{\infty} c_n\psi(x)e^{-iE_nt/\hbar}=\sum_{n-1}^{\infty} c_n\Psi_n(x,t)$$

- stationary states $\Psi_n(x,t)=\psi_n(x)e^{iEt/\hbar}$
- $|c_n|^2$: *probability* that a measurement of the energy would return the value E_n

$$\sum_{n-1}^{\infty}|c_n|^2=1$$

$$\langle H\rangle=\sum_{n-1}^{\infty}|c_n|^2E_n$$

Four therom

- For normalizable solutions, the separation constant E must be $real$
- $\psi(x)$ can always be taken to $real$
- If $V(-x)=V(x)$ then $\psi(x)$ can always be taken to be either even or odd
- E must $> V_{min}$

2.2 The Infinite Square Well

> $$V(x)=\begin{cases}0 & 0\leq x\leq a\\ \infty & otherwise\end{cases}$$

Outside the well, $\psi(x)=0$
Inside the well (**simple harmonic oscillator** equation)

$$\frac{d^2\psi}{dx^2}=-k^2\psi, \qquad \text{where } k\equiv\frac{\sqrt{2mE}}{\hbar}$$

- $E\geq 0$
- general solution: $\psi(x)=A\sin(kx)+B\cos(kx)$
- **boundary conditions**: $\psi(0)=\psi(a)=0$
- *distinct* solutions & normalize

$$\psi_n(x)\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right), \qquad \text{with } E_n=\frac{n^2\pi^2\hbar^2}{2ma^2} \quad (n=1,2,3,...)$$

- **ground state**: ψ_1
- propeties for ψ_n
  - alternately **even** or **odd**
  - each successive state has one more **node**(zero-crossing)

- matually **orthogonal**

$$\int \psi_m(x)^* \psi_n(x)\,\mathrm{d}x = \delta_{mn}$$

- **complete**

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) \qquad c_n = \int \psi_n(x)^* f(x)\,\mathrm{d}x$$

- ★

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}$$
$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \Psi(x,0)\,\mathrm{d}x$$

- $$\hat{H}\psi_n = E_n\psi_n \quad \rightarrow \quad \langle H \rangle = \sum |c_n|^2 E_n$$

2.3 The Harmonic Oscillator

> $$V(x) = \frac{1}{2} m\omega^2 x^2$$
> $$\hat{H} = \frac{1}{2m}\left[\hat{p} + (m\omega x)^2\right]$$

2.3.1 Algebraic Method

$$\left[\hat{A}, \hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \rightarrow [x, \hat{p}] = i\hbar$$

$$\hat{a}_\pm \equiv \frac{1}{\sqrt{2\hbar m\omega}}(\mp i\hat{p} + m\omega x) \rightarrow \begin{cases} x = \sqrt{\dfrac{\hbar}{2m\omega}}(\hat{a}_+ + \hat{a}_-) \\ \hat{p} = i\sqrt{\dfrac{\hbar m\omega}{2}}(\hat{a}_+ - \hat{a}_-) \end{cases}$$

$$\downarrow$$

$$\begin{cases} \hat{a}_+\hat{a}_- = \dfrac{1}{\hbar\omega}\hat{H} - \dfrac{1}{2} \\ \hat{a}_-\hat{a}_+ = \dfrac{1}{\hbar\omega}\hat{H} + \dfrac{1}{2} \end{cases} \qquad \rightarrow \qquad \bigstar \quad \hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)\psi = E\psi$$

$$\downarrow$$

$$\hat{H}(\hat{a}_+\psi) = (E + \hbar\omega)(\hat{a}_+\psi)$$
$$\hat{H}(\hat{a}_-\psi) = (E - \hbar\omega)(\hat{a}_-\psi)$$

There occurs a "lowest rung" : $\hat{a}_-\psi_0 = 0 \rightarrow$

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}, \qquad \text{with} \qquad E_0 = \frac{1}{2}\hbar\omega$$

Exited states, increasing the energy by $\hbar\omega$ with each step:

$$\psi_n = A_n(\hat{a}_+)^n\psi_0(x), \qquad \text{with} \qquad E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

Normalization algebraically

- $\hat{a}_+\psi_n = c_n\psi_{n+1}, \qquad \hat{a}_-\psi_n = d_n\psi_{n-1}$

$$\int_{-\infty}^{\infty} f^*(\hat{a}_\pm g)\,\mathrm{d}x = \int_{-\infty}^{\infty} (\hat{a}_\mp f)^* g\,\mathrm{d}x$$

$$\downarrow$$

$$\begin{cases} c_n = \sqrt{n+1} \\ d_n = \sqrt{n} \end{cases} \qquad \leftarrow \begin{cases} \int_{-\infty}^{\infty} (\hat{a}_\pm\psi_n)^*(\hat{a}_\pm\psi_n)\,\mathrm{d}x = \int_{-\infty}^{\infty} (\hat{a}_\mp\hat{a}_\pm\psi_n)^*\psi_n\,\mathrm{d}x \\ \hat{a}_+\hat{a}_-\psi_n = n\psi_n, \qquad \hat{a}_-\hat{a}_+\psi_n = (n+1)\psi_n \end{cases}$$

$$\Downarrow$$

$$\bigstar \quad \psi_n = \frac{1}{\sqrt{n!}}(\hat{a}_+)^n\psi_0(x)$$

2.3.2 Analytic Method

$$\frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\psi \qquad \xi \equiv \sqrt{\frac{m\omega}{\hbar}}x \quad K \equiv \frac{2E}{\hbar\omega}$$

To begin with at very large ξ

$$\frac{d^2\psi}{d\xi^2} \approx \xi^2\psi \qquad \xrightarrow{|x| \to \infty} \qquad \psi(\xi) = h(\xi)e^{-\xi^2/2}$$

$$\xrightarrow{\frac{d\psi}{d\xi},\,\frac{d^2\psi}{d\xi^2}} \qquad \frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (K-1)h = 0$$

In the form of *power serires* in ξ

$$h(\xi) = \sum_{j=0}^{\infty} a_j\xi^j \qquad \xrightarrow{\frac{dh}{d\xi},\,\frac{d^2h}{d\xi^2}}$$

$$\sum_{j=0}^{\infty}[(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j]\xi^j = 0$$

$$\Downarrow$$

$$a_{j+2} = \frac{(2j+1-K)}{(jh+1)(j+2)} a_j \quad \rightarrow \quad h(\xi) = h_{\text{even}}(\xi) + h_{\text{odd}}(\xi)$$

For physically acceptable solutions:

$$\begin{aligned} K =& 2n+1 \Rightarrow E = (n+1/2)\hbar\omega \quad \text{, for } n = 0, 1, 2, \ldots \\ &\downarrow \\ a_{j+2} =& \frac{-2(n-j)}{(jh+1)(j+2)} a_j \end{aligned}$$

Nomalized stationary state

$$\bigstar \qquad \psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}$$

- The first few of $H_n(\xi)$
  - $H_0 = 1$
  - $H_1 = 2\xi$
  - $H_2 = 4\xi^2 - 2$
  - $H_3 = 8\xi^3 - 12\xi$

2.4 The Free Particle

> $$V(x) = 0$$

$$\begin{gathered} \frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where} \quad k \equiv \frac{\sqrt{2mE}}{\hbar} \\ \downarrow \\ \Psi(x,t) = Ae^{ik\left(x - \frac{\hbar k}{2m}t\right)} + Be^{-ik\left(x - \frac{\hbar k}{2m}t\right)} \end{gathered}$$

Represents a wave traveling to *right* and another going to *left*, as well write

$$\Psi_k(x,t) = Ae^{i\left(kx - \frac{\hbar k^2}{2m}t\right)}$$

$$k \equiv \pm\frac{\sqrt{2mE}}{\hbar}, \text{with} \begin{cases} k > 0 \Rightarrow \text{traveling to the right} \\ k < 0 \Rightarrow \text{traveling to the left} \end{cases}$$

This wave function is not normalizable

$$\int_{-\infty}^{+\infty} \Psi_k^* \Psi_k \mathrm{d}x = |A|^2 \int_{-\infty}^{+\infty} \mathrm{d}x = |A|^2(\infty)$$

- **Plancherel's therem**

$$f(x)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}F(k)e^{ikx}\mathrm{d}k \leftrightarrow F(k)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}f(x)e^{-ikx}\mathrm{d}x$$

Now *this* can be normalized

$$\Psi(x,t)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\phi(k)e^{i\left(kx-\frac{\hbar k^2}{2m}t\right)}\mathrm{d}k$$
$$\begin{cases}\Psi(x,0)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\phi(k)e^{ikx}\mathrm{d}k\\ \phi(k)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\Psi(x,0)e^{-ikx}\mathrm{d}x\end{cases}$$

- $v_{\text{classical}}=v_{\text{group}}=2v_{\text{phase}}$

2.5 The Delta-Function Potential

2.5.1 Bound States and Scattering States

$$\begin{cases}E<V(\infty)\Rightarrow\text{bound state}\\ E>V(\infty)\Rightarrow\text{scattering state}\end{cases}$$

2.5.2 The Delta-Fuction Well

> $$V(x)=-\alpha\delta(x)$$

(1) bound state $E<0$

$$\frac{d^2\psi}{dx^2}=\kappa^2\psi,\quad\text{where}\quad\kappa\equiv\frac{\sqrt{-2mE}}{\hbar}$$
$$\Downarrow$$
$$\psi(x)=\begin{cases}Be^{\kappa x}, & (x<0)\\ Fe^{-\kappa x}, & (x>0)\end{cases}$$

- boundary conditions at $x=0$:
  - ψ is always continuous; $\Rightarrow F=B$
  - $d\psi/dx$ is continuous except at points where the potential is infinite.

$$\psi(0)=B\Rightarrow\kappa=\frac{m\alpha}{\hbar^2}$$

Proof: $(\epsilon\rightarrow 0)$

$$-\frac{\hbar^2}{2m}\int_{-\epsilon}^{+\epsilon}\frac{d^2\psi}{d^2x}dx+\int_{-\epsilon}^{+\epsilon}V(x)\psi(z)dx=E\int_{-\epsilon}^{+\epsilon}\psi(x)dx=0$$

$$\Rightarrow \Delta\left(\frac{d\psi}{dx}\right) = \frac{2m}{\hbar^2}\lim_{\epsilon\to 0}\int_{-\epsilon}^{+\epsilon} -\alpha\delta(x)\psi(z)dx = -\frac{2m\alpha}{\hbar^2}\psi(0)$$

$$\begin{cases} d\psi/dx|_+ = -B\kappa \\ d\psi/dx|_- = +B\kappa \end{cases} \Rightarrow \qquad \Delta\left(\frac{d\psi}{dx}\right) = -2B\kappa$$

Norminized $\rightarrow B = \sqrt{\kappa}$

$$\psi(x) = \frac{\sqrt{m\alpha}}{\hbar}e^{-m\alpha|x|/\hbar^2}; \qquad E = -\frac{m\alpha^2}{2\hbar^2}$$

(2) scattering state $E > 0$

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where} \quad k \equiv \frac{\sqrt{2mE}}{\hbar}$$
$$\Downarrow$$
$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & (x < 0) \\ Fe^{ikx} + Ge^{-ikx}, & (x > 0) \end{cases}$$

- Boundary conditions

$$F + G = A + B$$

$$\begin{cases} \Delta(d\psi/dx) = ik(F - G - A + B) \\ \psi(0) = (A + B) \end{cases} \Rightarrow$$

$$ik(F - G - A + B) = -\frac{2m\alpha}{\hbar^2}(A + B)$$

$$F - G = A(1 + 2i\beta) - B(1 - 2i\beta), \qquad \text{where } \beta \equiv \frac{m\alpha}{\hbar^2 k}$$

When wave come from left:
A: amplitude of the incident wave
B: amplitude of the reflected wave
F: amplitude of the transmitted wave

$$B = \frac{i\beta}{1 - i\beta}A, \qquad F = \frac{1}{1 - i\beta}A, \qquad G = 0$$

The *relative* probability of reflection and transmission:

$$R \equiv \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta} = \frac{1}{1 + (2\hbar^2 E/m\alpha^2)}$$

$$T \equiv \frac{|F|^2}{|A|^2} = \frac{1}{1+\beta} = \frac{1}{1+(m\alpha^2/2\hbar^2 E)}$$

Discussion:

- If $E > V_{\max}$, then $T = 1$ and $R = 0$
- If $E < V_{\max}$, then $T = 0$ and $R = 1$
  - if $T \neq 0$, **tunneling**

Show

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ikx}\, dk$$

Proof

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \delta(x) e^{-ikx} dx = \frac{1}{\sqrt{2\pi}}$$

2.6 The Finite Square Well

> $$V(x) = \begin{cases} -V_0, & -a \leq x \leq a \\ 0, & |x| > a \end{cases}$$

(1) bound state $E < 0$

$x < -a, V(x) = 0$

$$\frac{d^2\psi}{dx^2} = \kappa^2 \psi, \quad \text{where} \quad \kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$$
$$\Downarrow$$
$$\psi(x) = Be^{\kappa x}$$

$-a < x < a, V(x) = -V_0$

$$\frac{d^2\psi}{dx^2} = -l^2 \psi, \quad \text{where} \quad l \equiv \frac{\sqrt{2m(E+V_0)}}{\hbar}$$
$$\Downarrow$$
$$\psi(x) = C\sin(lx) + D\cos(lx)$$

$x > a, V(x) = 0$

$$\psi(x) = Fe^{-\kappa x}$$

- even solutions

$$\psi(x) = \begin{cases} Fe^{-\kappa x}, & (x > a) \\ D\cos(lx), & (0 < x < a) \\ \psi(-x), & (x < 0) \end{cases}$$

- boundary condition at $x = a$

$$\begin{cases} Fe^{-\kappa a} = D\cos(la) \\ -\kappa Fe^{-\kappa a} = -lD\sin(la) \end{cases} \qquad \Rightarrow \qquad \kappa = l\tan(la)$$

$$\begin{cases} z \equiv la \qquad z_0 \equiv \frac{a}{\hbar}\sqrt{2mV_0} \\ (\kappa^2 + l^2) = 2mV_0/\hbar^2 \end{cases} \qquad \Rightarrow \qquad \tan z = \sqrt{(z_0/z)^2 - 1}$$

Discussion:

- Wide, deep well

$$z_0 \to \infty \qquad \Rightarrow z_n = n\pi/2 \qquad \Rightarrow$$

$$E_n + V_0 \approx \frac{n^2\pi^2\hbar^2}{2m(2a)^2} \qquad (n = 1, 3, 5, \cdots)$$

- Shallow, narrow well
  - for $z_0 < \pi/2$, only one remains

(2) scattering state $E > 0$

When wave come from left

$$\psi(x) = \begin{cases} Ae^{ikx} + B^{-ikx}, & x < -a \\ C\sin(lx) + D\cos(lx) & -a < x < a \\ Fe^{ikx} & x > a \end{cases}$$

Boundary conditions

$$\begin{aligned} Ae^{-ika} + B^{ika} &= -C\sin(la) + D\cos(la) \\ ik[Ae^{-ika} - B^{ika}] &= l[C\cos(la) + D\sin(la)] \\ C\sin(la) + D\cos(la) + Fe^{ika} \\ l[C\cos(la) - D\sin(la)] &= ikFe^{ika} \end{aligned} \qquad \Rightarrow$$

Eliminate

$$B = i\frac{\sin(2la)}{2kl}(l^2 - k^2)F$$
$$F = \frac{e^{-2ika}A}{\cos(2la) - i\frac{(k^2+l^2)}{2kl}\sin(2la)} \qquad \Rightarrow$$

Transmission coefficient

$$T^{-1} = 1 + \frac{V_0^2}{4E(E+V_0)}\sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E+V_0)}\right)$$

when $T = 1$

$$\frac{2a}{\hbar}\sqrt{2m(E+V_0)} = n\pi \qquad \Rightarrow E_n + V_0 = \frac{n^2\pi^2\hbar^2}{2m(2a)^2}$$