Chapter 6

Quantum Mechanics

Erwin Schrödinger (1887-1961) was a theoretical and experimental physicist in Vienna, Zrich and Berlin and a significant contributor to the wave theory of matter. He mathematically devised an equation of wave mechanics that bears his name. Schrödinger's research was interrupted by two world wars, but he nonetheless advanced quantum theory and color theory. In 1933 he was a co-recipient of the Nobel Prize for physics. Today he is popularly known for the paradox of *Schrödinger's Cat*.

6.1 Schrödinger's Wave Equation

From the preceding chapters it became clear that a new set of equations is needed to describe the wave motion of particles; i.e. a *wave equation* is needed so that the wave function Ψ will be found that will allow us to calculate the probable values of the particle's position, energy, momentum and so on.

A plane wave traveling in the x-direction with velocity v having a wavelength λ and frequency f can be represented as:

$$\begin{aligned}\Psi_1 &= A\cos\omega\left(t-\frac{x}{v}\right), \quad \omega = 2\pi f, \quad v = \lambda f \\ &= A\cos\left(\omega t - \frac{2\pi x}{\lambda}\right)\end{aligned}$$

To represent a complex wave, let

$$\begin{aligned}\Psi_2 &= -jA\sin\left(\omega t - \frac{2\pi x}{\lambda}\right) \\ \therefore \Psi &= \Phi_1 + \Psi_2 = A\cos\left(\omega t - \frac{2\pi x}{\lambda}\right) - jA\sin\left(\omega t - \frac{2\pi x}{\lambda}\right)\end{aligned}$$

$$\Rightarrow \Psi = Ae^{-j\left(\omega t - \frac{2\pi x}{\lambda}\right)} \tag{6.1}$$

But $E = hf$, $\lambda = h/p$ and

$$\omega t - \frac{2\pi x}{\lambda} = 2\pi\left(ft - \frac{x}{\lambda}\right) = \frac{2\pi}{h}(Et - px)$$

$$\Psi = Ae^{-j\frac{1}{\hbar}(Et-px)} \tag{6.2}$$

§6.2 is the mathematical description of the wave equivalent of an *unrestricted particle* of total energy E and momentum p moving in $+x$-direction.

To get the fundamental differential equation in Ψ for a generally restricted particle, differentiate §6.2 twice with respect to x,

$$\frac{\partial^2\Psi}{\partial x^2} = -\frac{p^2}{\hbar^2}\Psi \tag{6.3}$$

and differentiate §6.2 with respect to t

$$\frac{\partial\Psi}{\partial t} = -j\frac{E\Psi}{\hbar} \tag{6.4}$$

The total energy E (assuming non-relativistic)

$$\begin{aligned} E &= E_k + E_p \\ E &= \frac{p^2}{2m} + E_p \end{aligned} \tag{6.5}$$

Multiplying all terms in §6.5 by Ψ, we have

$$E\Psi = \frac{p^2\Psi}{2m} + E_p\Psi \tag{6.6}$$

From §6.3 and §6.4,

$$p^2\Psi = -\hbar^2\frac{\partial^2\Psi}{\partial x^2} \tag{6.7}$$

$$E\Psi = j\hbar\frac{\partial\Psi}{\partial t} \tag{6.8}$$

Substituting these expressions in §6.6, we get the *time-dependent form of Schröinger's equation* for a particle of energy E moving in a potential E_p in one dimension,

$$\boxed{j\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + E_p\Psi(x,t)} \tag{6.9}$$

In three dimension, §6.9 becomes

$$j\hbar\frac{\partial\Psi(x,y,z,t)}{\partial t} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]\Psi(x,y,z,t) + E_p\Psi(x,y,z,t), \text{ or}$$

$$\boxed{j\hbar\frac{\partial\Psi(x,y,z,t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi(x,y,z,t) + E_p\Psi(x,y,z,t)} \tag{6.10}$$

6.2 Time-Independent Schrödinger Wave Equation

In many cases, the potential energy is a function of space positions only, so the wave amplitude §6.2 can be split into two independent parts- the space and time dependent functions

$$\begin{aligned}\Psi(x,t) &= Ae^{-j\frac{1}{\hbar}(Et-px)} \\ &= Ae^{-j\frac{Et}{\hbar}}e^{j\frac{px}{\hbar}} \\ &= \psi(x)e^{-j\frac{Et}{\hbar}} \end{aligned} \tag{6.11}$$

where $\psi(x) = Ae^{j\frac{px}{\hbar}}$.
By substititing §6.11 in §6.9, we have the *steady-state* form of Schrödinger's equation

$$\boxed{\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar}(E - E_p)\psi(x) = 0} \tag{6.12}$$

In three dimension, it becomes

$$\boxed{\nabla^2\psi(x,y,z) + \frac{2m}{\hbar}(E - E_p)\psi(x,y,z) = 0} \tag{6.13}$$

Exercise 6.1: The wave equation must be linear so that the superposition principle can be applied to form wave packets using many waves. Prove that §6.9 is linear by showing that it is satisfied for the wave function

$$\Psi(x,t) = a\Psi_1(x,t) + b\Psi_2(x,t)$$

where a and b are constants and Ψ_1 and Ψ_2 describe two waves each satisfying §6.9.

6.3 Normalization and Probability

The probability $p(x)dx$ of a particle being between x and $x + dx$ is

$$p(x)dx = \Psi(x,t)\Psi^*(x,t)dx \tag{6.14}$$

The probability of the particle being between x_1 and x_2 is given by

$$P = \int_{x_1}^{x_2} \Psi\Psi^* \tag{6.15}$$

The wave function must also be normalized so that the probability of the particle being somewhere on the x-axis is unity.

$$\int_{-\infty}^{\infty} \Psi\Psi^* dx = 1 \tag{6.16}$$

Example 6.1: Normalize the wave function $Ae^{-\alpha|x|}$ and find the probabilities of the particle being between 0 and $1/\alpha$, and between $1/\alpha$ and $2/\alpha$.

6.4 Operators

An operator is any mathematical entity which operates on any function and turns it into another function.

Example 6.2: Find $\hat{A}\psi(x)$ if the operator $\hat{A}$ is given by

1. $\hat{A}(x) = x$
2. $\hat{A}(\frac{\partial}{\partial x}) = \frac{\partial^2}{\partial x^2}$
3. $\hat{A}(x, \frac{\partial}{\partial x}) = \frac{\partial}{\partial x}x$

Example 6.3: If $\hat{A}(x, \frac{\partial}{\partial x})u_n(x) = a_n u_n(x)$, a_n is called the *eigenvalue* and $u_n(x)$ the *eigenfunction.* Find $u_n(x)$ and a_n for the operator $\hat{A}(x, \frac{\partial}{\partial x}) = -j\frac{\partial}{\partial x}$ with boundary condition that $u_n(x)$ is periodic in the range L.

Exercise 6.2: Establish the operator

$$\frac{\partial}{\partial x^n} = nx^{n-1} + x^n \frac{\partial}{\partial x}$$

Exercise 6.3: The *commutator* of two operators is defined as $\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$. Show that $\left[\frac{\partial}{\partial x}, x^n\right] = nx^{n-1}$

Exercise 6.4: Evaluate $\left[\frac{\partial}{\partial x}, \frac{\partial^n}{\partial x^n}\right]$

Exercise 6.5: Show that $u_n(x) = e^{-\frac{1}{2}x^2}$ is an eigenfunction of the operator $\hat{A}(x, \frac{\partial}{\partial x}) = \left(\frac{\partial^2}{\partial x^2} - x^2\right)$

Exercise 6.6: Verify the operator equations

$$\begin{aligned}\left(\frac{\partial}{\partial x} + x\right)\left(\frac{\partial}{\partial x} - x\right) &= \frac{\partial^2}{\partial x^2} - x^2 - 1 \\ \left(\frac{\partial}{\partial x} - x\right)\left(\frac{\partial}{\partial x} + x\right) &= \frac{\partial^2}{\partial x^2} - x^2 + 1\end{aligned}$$

The Momentum Operator $\hat{p}$

Consider $\Psi(x,t) = e^{-j(\omega t - \frac{2\pi x}{\lambda})} = e^{-j(\omega t - kx)}$

$$\begin{aligned} \frac{\partial \Psi}{\partial x} &= jke^{-j(\omega t-kx)} = jk\Psi \\ \text{since } k &= \frac{2\pi}{\lambda} = \frac{2\pi}{h/p} = \frac{p}{\hbar} \\ \therefore \frac{\partial \Psi}{\partial x} &= j\frac{p}{\hbar}\Psi \\ \Rightarrow p\Psi &= -j\hbar\frac{\partial \Psi}{\partial x} \end{aligned}$$

The momentum operator $\hat{p}$ is therefore

$$\boxed{\hat{p} = -j\hbar\frac{\partial}{\partial x}} \tag{6.17}$$

The Energy Operator $\hat{E}$

Again consider $\Psi(x,t) = e^{-j(\omega t - kx)}$

$$\begin{aligned} \frac{\partial \Psi}{\partial t} &= -j\omega\Psi, \text{ but } \omega = 2\pi f = 2\pi(\frac{E}{h}) = \frac{E}{\hbar} \\ \Rightarrow \frac{\partial \Psi}{\partial t} &= -j\frac{E}{\hbar}\Psi \\ E\Psi &= j\hbar\frac{\partial \Psi}{\partial t} \end{aligned}$$

Therefore

$$\boxed{\hat{E} = j\hbar\frac{\partial}{\partial t}} \tag{6.18}$$

Note:

- The position x is its own operator, i.e. $\hat{x} = x$
- To every *observable* there corresponds an operator

Example 6.4: Use the momentum and energy operators with the conservation of energy to determine the Schrödinger wave equation.

Example 6.5: Obtain the relativistic form of Schrödinger equation.

6.5 Expectation Values

The wave function is used to determine values of the measurable quantities like position, momentum and energy.
If we make many measurements of a particle along the x-axis, say N_1 times at x_1, N_2 times at x_2, N_i times at x_i, and so on, then the *average value* or *expectation value* of x denoted by $\langle x \rangle$ is

$$\begin{aligned} \langle x \rangle &= \frac{N_1 x_1 + N_2 x_2 + \cdots + N_i x_i + \cdots}{N_1 + N_2 + \ldots + N_i + \cdots} \\ &= \frac{\sum_i N_i x_i}{\sum_i N_i} \end{aligned}$$

changing to continuous variable

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x p(x)\, dx}{\int_{-\infty}^{\infty} p(x)\, dx}, \text{ or}$$

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x \Psi^*(x,t)\Psi(x,t)\, dx}{\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)\, dx} \tag{6.19}$$

If the wave function is normalized

$$\langle x \rangle = \int_{-\infty}^{\infty} x \Psi^*(x,t)\Psi(x,t)\, dx \tag{6.20}$$

Generally, the expectation value of any function $g(x)$ for normalized wave function $\Psi(x,t)$ is

$$\langle g(x) \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) g(x) \Psi(x,t)\, dx \tag{6.21}$$

Any measurable quantity for which we can calculate the expectation value is called a *physical observable* (e.g. position, linear momentum, angular momentum, energy, etc.) Each of the physical observable has an associated operator that is used to find the observable's expectation value. In order to compute the expectation value of some physical observable A, the operator $\hat{A}$ must be placed between Ψ^* and Ψ so that it operates on Ψ;

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) \hat{A} \Psi(x,t)\, dx \tag{6.22}$$

For example, the expectation value $\langle E \rangle$ of the energy is

$$\langle E \rangle = j\hbar \int_{-\infty}^{\infty} \Psi^*(x,t) \frac{\partial \Psi(x,t)}{\partial t}\, dx$$

6.6 Particle in Infinite Rectangular Potential Well

Consider a particle trapped in a rectangular one dimensional box (fig) 6.1 so that it is constrained to move along the x-axis subject to:

$$E_p = V(x) = \begin{cases} \infty, & x \leq 0,\ x \geq L; \\ 0, & 0 < x < L. \end{cases} \tag{6.23}$$

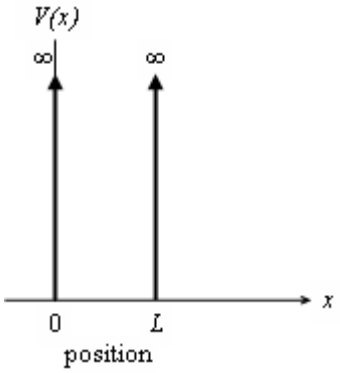

Figure 6.1: Particle in a rigid one-dimensional box

§6.12 becomes

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

Case 1: $x < 0$ or $x > L$.
$V = \infty \Rightarrow \psi = 0$ i.e. there is zero probability for the particle to be observed in $x < 0$ or $x > L$.

Case 2: $0 < x < L$

$$\begin{aligned} \frac{d^2\psi(x)}{dx^2} + \frac{2mE}{\hbar}\psi &= 0, \text{ let } k = \sqrt{\frac{2mE}{\hbar}} \\ \Rightarrow \frac{d^2\psi(x)}{dx^2} + k^2\psi &= 0 \\ \therefore \psi(x) &= A\sin kx + B\cos kx \end{aligned}$$

The wave function must be continuous;

$$\begin{aligned} \psi(x)|_{x=0,L} &= 0 \\ \Rightarrow \psi(x=0) &= B = 0 \\ \psi(x=L) &= A\sin kL = 0 \end{aligned}$$

$A = 0$ leads to trival solution; we must have

$$\begin{aligned} kL &= n\pi,\ n = 1, 2, \ldots \\ \therefore \psi_n(x) &= A \sin\left(\frac{n\pi x}{L}\right),\ n = 1, 2, \ldots \\ \text{but } \int_{-\infty}^{\infty} \psi_n^* \psi_n \, dx &= 1 \\ \Rightarrow A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx &= 1 \\ \Rightarrow A^2 \frac{L}{2} &= 1 \\ \Rightarrow A &= \sqrt{\frac{2}{L}} \end{aligned}$$

Therefore, the normalized wave function is

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right),\ n = 1, 2, 3, \ldots} \tag{6.24}$$

Since $kL = n\pi$,

$$\begin{aligned} k_n &= \frac{n\pi}{L} = \sqrt{\frac{2mE_n}{\hbar^2}} \\ \Rightarrow E_n &= \frac{\pi^2 \hbar^2}{2mL^2} n^2,\ n = 1, 2, 3, \ldots \end{aligned} \tag{6.25}$$

From §6.25, the possible energies E_n of the particle, called the *energy levels*, are *quantized*. n is called the *quantum number*. The lowest energy level ($n = 1$) is called the *ground state.*

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2}$$

Example 6.6: Find E_n for (a) an electron in a box 1 Å wide and (b) a rock 0.5 kg in a box 1 m wide. Discuss the results.

Example 6.7: For the infinite rectangular potential well, find the probability that a particle while in its ground state is in each third of the one-dimensional box, i.e. $0 \le x \le L/3,\ L/3 \le x \le 2L/3,$ and $2L/3 \le x \le L$.

Example 6.8: Determine the expectation values for $x, x^2, p,$ and p^2 of a particle in an infinite rectangular well for the first excited state.

Example 6.9: Calculate the transition energy from the first excited to the ground state for a proton confined to the nucleus (typical radius of nucleus $\approx 10^{-14}$m). Use the infinite rectangular well model.

Exercise 6.7: An electron moves with a speed $v = 10^{-3}c$ inside a one-dimensional box ($E_p = 0$) of length 9.7 nm. The potential is infinite elsewhere. What approximate quantum number does the electron posses? (*Answer*: $n = 8$)

Exercise 6.8: What is the minimum energy of (a) a proton and (b) an α-particle trapped in a one-dimensional region the size of a uranium nucleus (radius = 7×10^{-15}m)?

6.7 Finite Rectangular Potential Well

$$V(x) = \begin{cases} V_o, & x \leq 0; \text{ region I} \\ 0, & 0 < x < L; \text{ region II} \\ V_o, & x \geq L. \text{ region III} \end{cases} \tag{6.26}$$

with $V_o > E$.

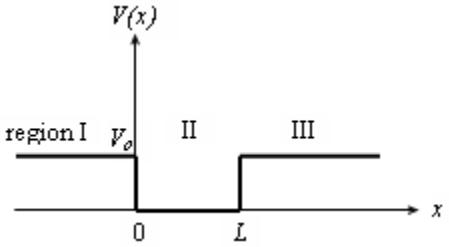

Figure 6.2: Particle in a non-rigid one-dimensional box

Case 1: In regions I and III

$$\begin{aligned} \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_o)\psi &= 0 \\ \text{Let } \gamma^2 &= \frac{2m}{\hbar^2}(E - V_o) \\ \therefore \frac{d^2\psi(x)}{dx^2} &= \gamma^2\psi(x) \\ \Rightarrow \psi(x) &= Ce^{\gamma x} + De^{-\gamma x} \end{aligned}$$

for $x < 0$ (region I):

$$\psi_{\text{I}}(x) = Ce^{\gamma x} \text{ (set } D = 0 \text{ because } De^{-\gamma x} \to \infty.) \tag{6.27}$$

for $x > L$ (region III):

$$\psi_{\text{III}}(x) = De^{-\gamma x} \tag{6.28}$$

Case 2: Inside the well, $V_o = 0$

$$\begin{aligned} \frac{d^2\psi_{\text{II}}}{dx^2} &= -k^2\psi_{\text{II}},\ k = \sqrt{\frac{2mE}{\hbar^2}} \\ \Rightarrow \psi_{\text{II}} &= Ae^{jkx} + Be^{-jkx},\ 0 < x < L \end{aligned} \tag{6.29}$$

Apply the boundary conditions and normalization to get $A, B, C,$ and D

$$\begin{aligned} \psi_{\text{I}}(x=0) &= \psi_{\text{II}}(x=0) \\ \psi_{\text{II}}(x=L) &= \psi_{\text{III}}(x=L) \end{aligned}$$

6.8 The Harmonic Oscillator

Harmonic motion occurs when a system vibrates about an equilibrium configuration.
Consider the system in fig 6.3;

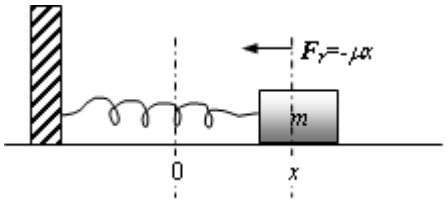

Figure 6.3: The Harmonic Oscillator

$$\begin{aligned} m\frac{d^2x}{dt^2} &= -\mu x \\ \Rightarrow \frac{d^2x}{dt^2} + \frac{\mu}{m}x &= 0,\ \text{let } \omega^2 = \frac{\mu}{m} \\ \Rightarrow \frac{d^2x}{dt^2} + \omega^2 x &= 0 \\ \Rightarrow x &= A\cos\omega t,\ A - \text{maximum amplitude} \end{aligned}$$

Potential energy of the particle is the work done to bring the particle from $x = 0$ to $x = x$ against the restoring force F_r.

$$E_p = V(x) = -\int_0^x F_r(x)\,dx = +\int_0^x \mu x\,dx = \frac{1}{2}\mu x^2$$

The total energy of the oscillator is $E = \frac{1}{2}\mu A^2$ and (classically) *can have any value.*
Schrödinger's equation for the harmonic oscillator ($E_p = \frac{1}{2}\mu x^2$) becomes

$$\begin{aligned} \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}\mu x^2\right)\psi &= 0 \\ \Rightarrow \frac{d^2\psi}{dx^2} + \left(\frac{2mE}{\hbar^2} - \frac{m\mu}{\hbar^2}x^2\right)\psi &= 0 \end{aligned} \tag{6.30}$$

Let $y^2 = \sqrt{\frac{m\mu}{\hbar^2}}x^2$, then $\frac{d^2\psi}{dx^2} = \sqrt{\frac{m\mu}{\hbar^2}}\frac{d^2\psi}{dy^2}$. §6.30 becomes

$$\frac{d^2\psi}{dy^2} + \left(\frac{2E}{\hbar\omega} - y^2\right)\psi = 0, \quad \text{where } \omega^2 = \mu/m \tag{6.31}$$

Let us try a solution of the form

$$\psi(y) = f(y)e^{-\frac{1}{2}y^2} \tag{6.32}$$

then §6.31 becomes

$$\begin{aligned} \frac{d^2f}{dy^2} - 2y\frac{df}{dy} + \left(\frac{2E}{\hbar\omega} - 1\right)f &= 0 \\ \text{set } \frac{2E}{\hbar\omega} - 1 &= 2n \qquad (6.33) \\ \therefore \frac{d^2f(y)}{dy^2} - 2y\frac{df(y)}{dy} + 2nf(y) &= 0 \qquad (6.34) \end{aligned}$$

This is a standard mathematical equation known as *Hermite's Equation*. The solution to it are called *Hermite's Polynomials*, given by:

$$f(y) = H_n(y) = (-1)^n e^{y^2}\frac{d^n}{dy^n}e^{-y^2}, \; n = 0, 1, 2, \ldots \tag{6.35}$$

The eigenfunctions of the harmonic oscillator, therefore, are

Table 6.1: Some Hermite Polynomials

n	$H_n(y)$	E_n
0	1	$\frac{1}{2}\hbar\omega$
1	$2y$	$\frac{3}{2}\hbar\omega$
2	$4y^2 - 2$	$\frac{5}{2}\hbar\omega$
3	$8y^3 - 12y$	$\frac{7}{2}\hbar\omega$
4	$16y^4 - 48y^2 + 12$	$\frac{9}{2}\hbar\omega$
5	$32y^5 - 160y^3 + 120y$	$\frac{11}{2}\hbar\omega$

$$\psi_n(y) = AH_n(y)e^{-\frac{1}{2}y^2}$$

where A is the normalization constant and is given by

$$A = \left(\frac{2mf}{\hbar}\right)^{\frac{1}{4}}(2^n n!), \quad \text{where } f = \frac{\omega}{2\pi} \text{ is the frequency of oscillation.}$$

$$\therefore \boxed{\psi_n(y) = \left(\frac{2mf}{\hbar}\right)^{\frac{1}{4}}(2^n n!)H_n(y)e^{-\frac{1}{2}y^2}} \tag{6.36}$$

From §6.33, the energy levels are given by

$$\frac{2E}{\hbar\omega} - 1 = 2n$$

$$\Rightarrow \boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega} \tag{6.37a}$$

$$\text{or } \boxed{E_n = \left(n + \frac{1}{2}\right)hf} \tag{6.37b}$$

The probability of finding the object at x is depicted in fig. 6.9. It is obvious that the disagreement between the classical and quantum mechanical results reduce as n increases. This is a consequence of the correspondence principle.