CHAPTER 6
The Schrödinger Equation

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A careful analysis of the process of observation in atomic physics has shown that the subatomic particles have no meaning as isolated entities, but can only be understood as interconnections between the preparation of an experiment and the subsequent measurement.

- Erwin Schrödinger

http://nobelprize.org/physics/laureates/1933/schrodingers-bio.html
Opinions on quantum mechanics

I think it is safe to say that no one understands quantum mechanics. Do not keep saying to yourself, if you can possibly avoid it, “But how can it be like that?” because you will get “down the drain” into a blind alley from which nobody has yet escaped. Nobody knows how it can be like that.

- Richard Feynman

Those who are not shocked when they first come across quantum mechanics cannot possibly have understood it.

- Niels Bohr

6.1: The Schrödinger Wave Equation

The Schrödinger wave equation in its time-dependent form for a particle of energy $E$ moving in a potential $V$ in one dimension is:

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

where $V = V(x,t)$

where $i$ is the square root of -1.

The Schrödinger Equation is THE fundamental equation of Quantum Mechanics.
General Solution of the Schrödinger Wave Equation when $V = 0$

Try this solution:

$$\Psi(x, t) = A e^{i(kx - \omega t)} = A \left[ \cos(kx - \omega t) + i \sin(kx - \omega t) \right]$$

$$\frac{\partial \Psi}{\partial t} = -i \omega A e^{i(kx - \omega t)} = -i \omega \Psi$$

$$ih \frac{\partial \Psi}{\partial t} = (ih)(-i \omega) \Psi = h \omega \Psi$$

$$\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = \frac{\hbar^2 k^2}{2m} \Psi$$

This works as long as:  
$$h \omega = \frac{\hbar^2 k^2}{2m}$$  
which says that the total energy is the kinetic energy.

The $i$ in the Schrodinger equation differentiates it from the classical wave equation.
General Solution of the Schrödinger Wave Equation when \( V = 0 \)

In free space (with \( V = 0 \)), the general form of the wave function is

\[
\Psi(x,t) = Ae^{ikx} = A[\cos(kx - \omega t) + i\sin(kx - \omega t)]
\]

which also describes a wave moving in the \( x \) direction. In general the amplitude may also be complex.

The wave function is also not restricted to being real. Notice that this function is complex.

Only the physically measurable quantities must be real. These include the probability, momentum and energy.
What is the Physical Significance of $\Psi$

The wave function $\Psi$ itself has no physical interpretation, however the square of its absolute magnitude $|\Psi|^2$ (or $\Psi^*\Psi$ if $\Psi$ is complex) gives experimentally the probability of finding the particle at a particular point and time.

The problem is to determine $\Psi$ for a particle when the motion is restricted by external forces.

$\Psi$ must fulfill certain requirements.
1. In order to avoid infinite probabilities, the wave function must be finite everywhere.
2. $\Psi$ must be single valued.
3. The wave function must be twice differentiable. This means that it and its derivative must be continuous. (An exception to this rule occurs when $V$ is infinite.)
4. If $\int_{-\infty}^{\infty} |\Psi|^2 \, dV$ is 0, the particle does not exist. If it is $\infty$ the particle is everywhere simultaneously.
Normalization

$|\Psi^2|$ cannot be negative or complex only positive, if integral is to be finite to describe a real body

$|\Psi^2|$ is equal to the probability $P$ of finding the particle described by $\Psi$.

The mathematical statement:

\[ \int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t) \, dx = 1 \]

Shows that the particle is somewhere at all time. A wave function that obeys this condition is said to be normalized.

Every acceptable wave function can be normalized by multiplying it with an appropriate constant.
Deriving the Schrödinger Equation

Exercise 1: Show that the \( \Psi = A e^{-i(\omega t - x/v)} \) can be written as \( \Psi = A e^{-i(h/2m)(E - px)} \).

Exercise 2: Derive the Schrodinger’s equation

\[
\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = \frac{\hbar^2}{2m} \nabla^2 \Psi - V \Psi
\]

form \( \Psi = A e^{-(i/h)(Et - px)} \).

Where \( \nabla^2 \Psi = \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \)

And \( \nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \) is the Laplacian operator.
The potential in many cases will not depend explicitly on time. The dependence on time and position can then be separated in the Schrödinger wave equation. Let:

$$\Psi(x, t) = \psi(x) f(t)$$

which yields:

$$i\hbar \psi(x) \frac{\partial f(t)}{\partial t} = \frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) \psi(x) f(t)$$

Now divide by the wave function $\psi(x) f(t)$:

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2 \psi(x)}{dx^2} + V(x)$$

The left side depends only on $t$, and the right side depends only on $x$. So each side must be equal to a constant. The time dependent side is:

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = B$$
Time-Independent Schrödinger Wave Equation

We integrate both sides and find: \[ \frac{\hbar}{i} \ln f = Bt + C \]
where \( C \) is an integration constant that we may choose to be 0.
Therefore:
\[
\ln f = \frac{Bt}{i\hbar} \quad f(t) = e^{\frac{Bt}{i\hbar}} = e^{-i\omega t} 
\]
But recall our solution for the free particle: \( \Psi(x, t) = A e^{i(k x - \omega t)} \)
In which \( f(t) = e^{-i\omega t} \), so: \( \omega = B / \hbar \) or \( B = \hbar \omega \), which means that: \( B = E \)

So multiplying by \( \psi(x) \), the spatial Schrödinger equation becomes:

\[
-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)
\]
**Time-Independent Schrödinger Wave Equation**

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

This equation is known as the **time-independent Schrödinger wave equation**, and it is as fundamental an equation in quantum mechanics as the time-dependent Schrodinger equation.

So often physicists write simply: \[\hat{H}\psi = E\psi\]

where:

\[\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V\]

is an operator.
Stationary States

The wave function can be written as:

\[ \Psi(x,t) = \psi(x)e^{-i\lambda t} \]

The probability density becomes:

\[
\Psi \cdot \Psi = \psi^2(x)(e^{i\lambda t}e^{-i\lambda t})
\]

\[
\Psi \cdot \Psi = \psi^2(x)
\]

The probability distribution is constant in time.

This is a standing wave phenomenon and is called a stationary state.
6-3: Infinite Square-Well Potential

The simplest such system is that of a particle trapped in a box with infinitely hard walls that the particle cannot penetrate. This potential is called an infinite square well and is given by:

\[ V(x) = \begin{cases} \infty & x \leq 0, \ x \geq L \\ 0 & 0 < x < L \end{cases} \]

Clearly the wave function must be zero where the potential is infinite.

Where the potential is zero (inside the box), the time-independent Schrödinger wave equation becomes:

\[ \frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2} \psi = -k^2 \psi \quad \text{where} \quad k = \sqrt{2mE/\hbar^2} \]

The general solution is:

\[ \psi(x) = A \sin kx + B \cos kx \]
6-3: How to make an Infinite Square-Well Potential

(a) [Diagram of a square well with an electron]

(b) [Graph showing potential energy vs. x]

(c) [Graph showing potential energy vs. x]

Potential energy

Potential energy
Boundary conditions of the potential dictate that the wave function must be zero at $x = 0$ and $x = L$. This yields valid solutions for integer values of $n$ such that $kL = n\pi$.

The wave function is:

$$\psi_n(x) = A\sin\left(\frac{n\pi x}{L}\right)$$

We normalize the wave function:

$$\int_{-\infty}^{\infty} \psi_n^*(x)\psi_n(x) \, dx = 1 \quad \Rightarrow \quad A^2 \int_{0}^{L} \sin^2\left(\frac{n\pi x}{L}\right) \, dx = 1 \quad \Rightarrow \quad A = \sqrt{\frac{2}{L}}$$

The normalized wave function becomes:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

These functions are identical to those obtained for a vibrating string with fixed ends.
Quantized Energy

The quantized wave number now becomes:

\[ k_n = \frac{n \pi}{L} = \sqrt{\frac{2mE_n}{\hbar^2}} \]

Solving for the energy yields:

\[ E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad (n = 1, 2, 3, \ldots) \]

Note that the energy depends on integer values of \( n \). Hence the energy is quantized and nonzero.

The special case of \( n = 1 \) is called the ground state.

\[ E_1 = \frac{\pi^2 \hbar^2}{2mL^2} \]
Wave Function and Probabilities
Exercise 2: An electron moving in a thin wire is a reasonable approximation of a particle in one-dimensional infinite well. If the wire is 1.0 cm long, compute the zero-point energy, and the probability of finding it in the region 0<x<L/4
6.4: Finite Square-Well Potential

The finite square-well potential is

\[
V(x) = \begin{cases} 
V_0 & x \leq 0 \\
0 & 0 < x < L \\
V_0 & x \geq L 
\end{cases}
\]

The Schrödinger equation outside the finite well in regions I and III is:

\[
-\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} = E - V_0 \quad \text{regions I, III}
\]

Letting:

\[
\alpha^2 = 2m(V_0 - E)/\hbar^2
\]

yields

\[
\frac{d^2\psi}{dx^2} = \alpha^2 \psi
\]

Considering that the wave function must be zero at infinity, the solutions for this equation are

\[
\begin{align*}
\Psi_I(x) &= A e^{\alpha x} & \text{region I, } x < 0 \\
\Psi_II(x) &= B e^{-\alpha x} & \text{region III, } x > L
\end{align*}
\]
Finite Square-Well Solution

Inside the square well, where the potential $V$ is zero, the wave equation becomes \( \frac{d^2\psi}{dx^2} = -k^2\psi \) where \( k = \sqrt{(2mE)/\hbar^2} \)

The solution here is:

The boundary conditions require that:

\[ \psi_I = \psi_{II} \text{ at } x = 0 \text{ and } \psi_{II} = \psi_{III} \text{ at } x = L \]

so the wave function is smooth where the regions meet.

Note that the wave function is nonzero outside of the box.
Penetration Depth

The penetration depth is the distance outside the potential well where the probability significantly decreases. It is given by

$$\delta x \approx \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(V_0 - E)}}$$

The penetration distance that violates classical physics is proportional to Planck’s constant.
6-4: Expectation Values

In quantum mechanics, we'll compute expectation values. The **expectation value**, \( \langle x \rangle \), is the weighted average of a given quantity. In general, the expected value of \( x \) is:

\[
\langle x \rangle = P_1 x_1 + P_2 x_2 + \cdots + P_N x_N = \sum_i P_i x_i
\]

If there are an infinite number of possibilities, and \( x \) is continuous:

\[
\langle x \rangle = \int P(x) \, x \, dx
\]

Quantum-mechanically:

\[
\langle x \rangle = \int \Psi(x) \Psi^*(x) \, x \, dx = \int \Psi^*(x) \, x \, \Psi(x) \, dx
\]

And the expectation of some function of \( x \), \( g(x) \):

\[
\langle g(x) \rangle = \int \Psi^*(x) \, g(x) \, \Psi(x) \, dx
\]
Expectation Values

Exercise 4: Calculate the expectation value of $x$ in a one-dimensional infinite square well potential. In quantum mechanics, we'll compute expectation values.

$$\langle x \rangle = \int \Psi^*(x) x \Psi(x) \, dx = \int \Psi^*(x) x \Psi(x) \, dx$$
Operators

An operator tells us what operation to carry out on the quantity that follows it.

For example the expectation value for any quantity that is a function of $x$ is

$$\langle x \rangle = \int \Psi(x) \Psi^*(x) x \, dx = \int \Psi^*(x) x \Psi(x) \, dx$$

Can we do the same for momentum and energy?
Yes we can as long as we recognize that $p$ and $E$ are functions of both $x$ and $t$ to carry out the integrations.
Momentum Operator

To find the expectation value of $p$, we first need to represent $p$ in terms of $x$ and $t$. Consider the derivative of the wave function of a free particle with respect to $x$:

$$\frac{\partial \Psi}{\partial x} = \frac{\partial}{\partial x} [e^{ik(x-xt)}] = ike^{ik(x-xt)} = ik\Psi$$

With $k = p / \hbar$ we have

$$\frac{\partial \Psi}{\partial x} = i\frac{p}{\hbar}\Psi$$

This yields

$$p[\Psi(x,t)] = -i\hbar \frac{\partial \Psi(x,t)}{\partial x}$$

This suggests we define the momentum operator as

$$\hat{p} = -i\hbar \frac{\partial}{\partial x}$$

The expectation value of the momentum is

$$\langle p \rangle = -i\hbar \int_{-\infty}^{\infty} \Psi^*(x,t) \frac{\partial \Psi(x,t)}{\partial x} \, dx$$
Position and Energy Operators

The position $x$ is its own operator. Done.

Energy operator: The time derivative of the free-particle wave function is:

$$\frac{\partial \Psi}{\partial t} = \frac{\partial}{\partial t} \left[ e^{i(x-\alpha t)} \right] = -i\omega e^{i(x-\alpha t)} = -i\omega \Psi$$

Substituting $\omega = E/\hbar$ yields $E|\Psi(x,t)\rangle = i\hbar \frac{\partial \Psi(x,t)}{\partial t}$

The energy operator is: $\hat{E} = i\hbar \frac{\partial}{\partial t}$

The expectation value of the energy is:

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

Exercise 5: Derive the Schrodinger Equation using the momentum and Energy operators.

Do it yourself
Simple harmonic oscillators describe many physical situations: springs, diatomic molecules and atomic lattices.

F is the restoring force and is equal to Hooke’s law for small amplitude of oscillations.
SHM – Schrödinger equation

Classical Oscillator
\[
\frac{d^2 x}{dt^2} + \frac{k}{m} x = 0
\]
\[x = A \cos(\omega t + \phi), \text{ where } \omega = \sqrt{\frac{k}{m}}\]

Oscillator Potential
\[V(x) = \frac{1}{2} k x^2 = \frac{1}{2} m \omega^2 x^2\]

Total Energy
\[E = \frac{1}{2} m \omega^2 A^2 \] Classically the particle is confined between \(-A\) and \(+A\)

Quantum mechanical Oscillator
\[-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + \frac{1}{2} m \omega^2 x^2 \psi(x) = E \psi(x)\]

How do we solve this Differential equation?
**SHM – Schrödinger equation**

The solution requires advanced techniques in differential equations. However, the solutions are of the form

\[ \psi_n(x) = C_n e^{\frac{-m\omega}{2\hbar}} H_n(x) \]

Where \( C_n \) are normalizing constants and \( H_n \) are Hermite polynomials of order \( n \).

\[ \psi_0(x) = A_0 e^{\frac{-m\omega}{2\hbar}} \]

\[ \psi_1(x) = A_1 \sqrt{\frac{m\omega}{\hbar}} xe^{\frac{-m\omega}{2\hbar}} \]

\[ \psi_2(x) = A_2 \left( 1 - \frac{2m\omega}{\hbar} \right) e^{\frac{-m\omega}{2\hbar}} \]

Schrödinger’s Trick – See class webpage
The Parabolic Potential Well

The energy levels are given by:

\[ E_n = (n + \frac{1}{2}) \hbar \sqrt{\kappa / m} = (n + \frac{1}{2}) \hbar \omega \]

The zero point energy is called the Heisenberg limit:

\[ E_0 = \frac{1}{2} \hbar \omega \]
Analysis of the Parabolic Potential Well

Classically, the probability of finding the mass is greatest at the ends of motion and smallest at the center. Contrary to the classical one, the largest probability for this lowest energy state is for the particle to be at the center.

As the quantum number increases, however, the solution approaches the classical result.
6-6 Reflection and Transmission of waves

Step Potential: We will do the math on the board.
Step Potential
Barriers and Tunneling

Consider a particle of energy \( E \) approaching a potential barrier of height \( V_0 \), and the potential everywhere else is zero.

First consider the case of the energy greater than the potential barrier.

In regions I and III the wave numbers are:

\[
k_1 = k_{III} = \frac{\sqrt{2mE}}{\hbar}
\]

In the barrier region we have

\[
k_{II} = \frac{\sqrt{2m(E-V')}}{\hbar}
\]

where \( V = V_0 \).
Reflection and Transmission

The wave function will consist of an incident wave, a reflected wave, and a transmitted wave.

The potentials and the Schrödinger wave equation for the three regions are as follows:

Region I ($x < 0$) \[ V = 0 \quad \frac{d^2 \psi_1}{dx^2} + \frac{2m}{\hbar^2} E \psi_1 = 0 \]
Region II ($0 < x < L$) \[ V = V_0 \quad \frac{d^2 \psi_2}{dx^2} + \frac{2m}{\hbar^2} (E - V_0) \psi_2 = 0 \]
Region III ($x > L$) \[ V = 0 \quad \frac{d^2 \psi_3}{dx^2} + \frac{2m}{\hbar^2} E \psi_3 = 0 \]

The corresponding solutions are:

Region I ($x < 0$) \[ \psi_1 = Ae^{\lambda x} + Be^{-\lambda x} \]
Region II ($0 < x < L$) \[ \psi_2 = C e^{\lambda x} + De^{-\lambda x} \]
Region III ($x > L$) \[ \psi_3 = Fe^{\alpha x} + Ge^{-\alpha x} \]

As the wave moves from left to right, we can simplify the wave functions to:

Incident wave \[ \psi_1 (\text{incident}) = Ae^{\lambda x} \]
Reflected wave \[ \psi_1 (\text{reflected}) = Be^{-\lambda x} \]
Transmitted wave \[ \psi_3 (\text{transmitted}) = Fe^{\alpha x} \]
Probability of Reflection and Transmission

The probability of the particles being reflected $R$ or transmitted $T$ is:

$$R = \frac{|\psi_{\text{reflected}}|^2}{|\psi_{\text{incident}}|^2} = \frac{B^* B}{A^* A}$$

$$T = \frac{|\psi_{\text{transmitted}}|^2}{|\psi_{\text{incident}}|^2} = \frac{F^* F}{A^* A}$$

Because the particles must be either reflected or transmitted we have: $R + T = 1$.

By applying the boundary conditions $x \to \pm \infty$, $x = 0$, and $x = L$, we arrive at the transmission probability:

$$T = \left[ 1 + \frac{V_0^2 \sin^2 (k_x L)}{4E(E - V_0)} \right]^{-1}$$

Note that the transmission probability can be 1.
Tunneling

Now we consider the situation where classically the particle doesn’t have enough energy to surmount the potential barrier, $E < V_0$.

The quantum mechanical result is one of the most remarkable features of modern physics. There is a finite probability that the particle can penetrate the barrier and even emerge on the other side!

The wave function in region II becomes:

$$\Psi_\Pi = C e^{i\kappa x} + D e^{-i\kappa x}$$

where

$$\kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar}}$$

The transmission probability that describes the phenomenon of tunneling is:

$$T = \left[1 + \frac{V_0^2 \sinh^2(\kappa L)}{4E(V_0 - E)}\right]^{-1}$$
Tunneling wave function

This violation of classical physics is allowed by the uncertainty principle. The particle can violate classical physics by $\Delta E$ for a short time, $\Delta t \sim \hbar / \Delta E$. 
Analogy with Wave Optics

If light passing through a glass prism reflects from an internal surface with an angle greater than the critical angle, total internal reflection occurs. However, the electromagnetic field is not exactly zero just outside the prism. If we bring another prism very close to the first one, experiments show that the electromagnetic wave (light) appears in the second prism. The situation is analogous to the tunneling described here. This effect was observed by Newton and can be demonstrated with two prisms and a laser. The intensity of the second light beam decreases exponentially as the distance between the two prisms increases.
Alpha-Particle Decay

The phenomenon of tunneling explains alpha-particle decay of heavy, radioactive nuclei.

Inside the nucleus, an alpha particle feels the strong, short-range attractive nuclear force as well as the repulsive Coulomb force.

The nuclear force dominates inside the nuclear radius where the potential is $\sim$ a square well.

The Coulomb force dominates outside the nuclear radius.

The potential barrier at the nuclear radius is several times greater than the energy of an alpha particle.

In quantum mechanics, however, the alpha particle can tunnel through the barrier. This is observed as radioactive decay.