CHAPTER 6 **Quantum Mechanics II**

- 6.1 The Schrödinger Wave Equation
- 6.2 Expectation Values
- 6.3 Infinite Square-Well Potential
- 6.4 Finite Square-Well Potential
- 6.5 Three-Dimensional Infinite-Potential Well
- 6.6 Simple Harmonic Oscillator
- 6.7 Barriers and Tunneling

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

1

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

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

 \blacksquare The extension into three dimensions is

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

where $i = \sqrt{-1}$ is an imaginary number.

General Solution of the Schrödinger Wave Equation

The general form of the wave function is

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

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 the sine term has an imaginary number. Only the physically measurable quantities must be real. These include the probability, momentum and energy.

Normalization and Probability

 The probability *P*(*x*) *dx* of a particle being between *x* and *X* + *dx* was given in the equation

$$
P(x) dx = \Psi^*(x,t)\Psi(x,t) dx
$$

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

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

 The wave function must also be normalized so that the probability of the particle being somewhere on the *x* axis is 1.

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

Properties of Valid Wave Functions

Boundary conditions

- 1) In order to avoid infinite probabilities, the wave function must be finite everywhere.
- 2) In order to avoid multiple values of the probability, the wave function must be single valued.
- 3) For finite potentials, the wave function and its derivative must be continuous. This is required because the second-order derivative term in the wave equation must be single valued. (There are exceptions to this rule when *V* is infinite.)
- 4) In order to normalize the wave functions, they must approach zero as *x* approaches infinity.
- **Solutions that do not satisfy these properties do not generally** correspond to physically realizable circumstances.

Time-Independent Schrödinger Wave **Equation**

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

Now divide by the wave function:
$$
i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2 \psi(x)}{dx^2} + V(x)
$$

 The left side of Equation (6.10) depends only on time, and the right side depends only on spatial coordinates. Hence each side must be equal to a constant. The time dependent side is

$$
i\hbar \frac{1}{f}\frac{df}{dt}=B
$$

Time-Independent Schrödinger Wave Equation Continued

We integrate both sides and find: $i\hbar \int \frac{df}{f} = \int B dt$ $i\hbar \ln f = Bt + C$

where *C* is an integration constant that we may choose to be 0. Therefore

$$
\ln f = \frac{Bt}{i\hbar}
$$

This determines *f* to be $f(t) = e^{Bt/\hbar} = e^{-iBt/\hbar}$

$$
i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = E
$$

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

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

Stationary State

The wave function can be written as: $\Psi(x,t) = \psi(x)e^{-i\omega t}$

- The probability density becomes: $\Psi^* \Psi = \psi^2(x) (e^{i\omega t} e^{-i\omega t})$ $\Psi^* \Psi = \psi^2(x)$
- The probability distributions are constant in time. This is a standing wave phenomena that is called the stationary state.

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*:

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

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 as seen above.
- **The time derivative of the free-particle wave function is**

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

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

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

The expectation value of the energy is

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

Comparison of Classical and Quantum **Mechanics**

- Newton's second law and Schrödinger's wave equation are both differential equations.
- Newton's second law can be derived from the Schrödinger wave equation, so the latter is the more fundamental.
- Classical mechanics only appears to be more precise because it deals with macroscopic phenomena. The underlying uncertainties in macroscopic measurements are just too small to be significant.

6.2: Expectation Values

- The **expectation value** is the expected result of the average of many measurements of a given quantity. The expectation value of *x* is denoted by <*x*>
- Any measurable quantity for which we can calculate the expectation value is called a **physical observable**. The expectation values of physical observables (for example, position, linear momentum, angular momentum, and energy) must be real, because the experimental results of measurements are real.
- The average value of *x* is

$$
\overline{x} = \frac{N_1x_1 + N_2x_2 + N_2x_2 + N_2x_2 + \dots}{N_1 + N_2 + N_3 + N_4 + \dots} = \frac{\sum_{i=1}^{n} N_ix_i}{\sum_{i=1}^{n} N_i}
$$

Continuous Expectation Values

- We can change from discrete to continuous variables by using the probability *P*(*x*,*t*) of observing the particle at a particular *x*.
- Using the wave function, the expectation value is:

$$
\overline{x} = \frac{\int_{-\infty}^{\infty} x P(x) dx}{\int_{-\infty}^{\infty} P(x) dx}
$$

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

 The expectation value of any function *g*(*x*) for a normalized wave function:

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

Some expectation values are sharp some others fuzzy

Hypothetical Data Set for Position of a Particle Table 6.1 as Recorded in Repeated Trials

$$
\overline{x} = \frac{(2.5 + 3.7 + 1.4 + \dots + 5.4 + 5.3)}{18} = 5.46
$$

$$
\langle x \rangle = \int_{-\infty}^{\infty} x |\Psi(x, t)|^2 dx
$$

Since there is scatter in the actual positions (x), the calculated expectation value will have an uncertainty, fuzziness (Note that x is its own operator.)

Some expectation values are sharp some others fuzzy, continued I

In classical physics all observables are sharp.¹³

¹³We discount in this discussion any random errors of measurement. In principle at least, the imprecision resulting from such errors can be reduced to arbitrarily low levels.

standard deviation, σ , of the data, defined as

$$
\sigma = \sqrt{\frac{\sum (x_i - \overline{x})^2}{N}}
$$

Writing out the square under the radical gives

x may as well stand for any kind of operator Q

 $\sigma = \sqrt{(x^2)} - (\overline{x})^2$

 Δx , is often called the *uncertainty* in position $\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$

 $\frac{\sum (x_i)^2}{N} - 2(\overline{x}) \frac{\sum (x_i)}{N} + (\overline{x})^2 \sum \left(\frac{1}{N}\right) = \overline{(x^2)} - 2(\overline{x})(\overline{x}) + (\overline{x})^2$

The degree to which particle position is fuzzy is given by the magnitude of Δx ; note that the position is sharp only if $\Delta x = 0$.

 $=\sqrt{x^2} - (\bar{x})^2$

For any observable, fuzzy or not

$$
\Delta Q = \sqrt{\langle Q^2 \rangle - \langle Q \rangle^2}
$$

If not fuzzy, $\Delta Q = 0$ Because $\langle Q^2 \rangle = \langle Q \rangle^2$

Some expectation values are sharp some others fuzzy, continued II

- Eigenvalues of operators are always sharp (an actual physical measurement may give some variation in the result, but the calculation gives zero fuzziness
- Say Q is the Hamiltonian operator A wavefunction that solves this

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

equation is an eigenfunction of this operator, E is the corresponding eigenvalue, apply this operator twice and you get E^2 – which sure is the same as squaring to result of applying it once (E)

¹⁴The eigenvalue problem for any operator [Q] is [Q] $\psi = q\psi$; that is, the result of the operation [Q] on some function ψ is simply to return a multiple q of the same function. This is possible only for certain special functions ψ , the *eigenfunctions*, and then only for certain special values of q , the *eigenvalues*. Generally, $[Q]$ is known; the eigenfunctions and eigenvalues are found by imposing the eigenvalue condition.

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 Schrödinger wave equation becomes $\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi$ where $k = \sqrt{2mE/\hbar^2}$.

■ The general solution is
$$
\psi(x) = A \sin kx + B \cos kx
$$
.

Quantization

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

■ We normalize the wave function

$$
\int_{-\infty}^{\infty} \psi_n^*(x) \psi_n(x) \, dx = 1 \qquad A^2 \int_0^L \sin^2 \left(\frac{n \pi x}{L} \right) dx = 1
$$

 \blacksquare 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 violet
- Solving for the energy yields

$$
E_n = n^2 \frac{\pi^2 \hbar^2}{2mL^2} \qquad (n = 1, 2, 3, ...)
$$

- Note that the energy depends on the integer values of *n*. Hence the energy is quantized and nonzero.
- The special case of *n* = 0 is called the ground state energy. $E_1 = \frac{\pi^2 h^2}{2 \pi^2}$

6.4: Finite Square-Well Potential

- The finite square-well potential is $V(x) = \begin{cases} V_0 & x \le 0 \\ 0 & 0 < x < L \\ V_0 & x \ge L \end{cases}$ region II
- The Schrödinger equation outside the finite well in regions I and III is $-\frac{\hbar^2}{2m w}\frac{1}{\omega} \frac{d^2 \psi}{dx^2} = E - V_0$ regions I, III or using $\alpha^2 = 2m(V_0 - E)/\hbar^2$

yields $\frac{V}{dx^2} = \alpha^2 \psi$. Considering that the wave function must be zero at infinity, the solutions for this equation are

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 $k = \sqrt{\frac{2mE}{\hbar^2}}$
- **If** Instead of a sinusoidal solution we have $\psi_{II} = Ce^{ikx} + De^{-ikx}$ region II, $0 < x < L$
- The boundary conditions require that $\psi_{\text{I}} = \psi_{\text{II}}$ at $x = 0$ and $\psi_{\text{II}} = \psi_{\text{III}}$ at $x = L$

and the wave function must be smooth where the regions meet.

 \blacksquare 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

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

 It should not be surprising to find that the penetration distance that violates classical physics is proportional to Planck's constant.

6.5: Three-Dimensional Infinite-Potential Well

- The wave function must be a function of all three spatial coordinates. We begin with the conservation of energy $E = K + V = \frac{p^2}{2m} + V$
- **Multiply this by the wave function to get**

$$
\frac{p^2}{2m}\psi + V\psi = E\psi
$$

 Now consider momentum as an operator acting on the wave function. In this case, the operator must act twice on each dimension. Given:

$$
p^2 = p_x^2 + p_y^2 + p_z^2
$$
, and $\hat{p}_x \psi = -i\hbar \frac{\partial \psi}{\partial x} + \hat{p}_y \psi = -i\hbar \frac{\partial \psi}{\partial y} + \hat{p}_z \psi = -i\hbar \frac{\partial \psi}{\partial z}$

 The three dimensional Schrödinger wave equation is $-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right) + V\psi = E\psi$ or $-\frac{\hbar^2}{2m}\nabla^2 \psi + V\psi = E\psi$

Degeneracy

- Analysis of the Schrödinger wave equation in three dimensions introduces three quantum numbers that quantize the energy.
- A quantum state is degenerate when there is more than one wave function for a given energy.
- Degeneracy results from particular properties of the potential energy function that describes the system. A perturbation of the potential energy can remove the degeneracy.

6.6: Simple Harmonic Oscillator

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

 Consider the Taylor expansion of a potential function: $V(x) = V_0 + V_1(x - x_0) + \frac{1}{2}V_2(x - x_0)^2 + ...$

Redefining the minimum potential and the zero potential, we have $V(x) = \frac{1}{2}V_2(x - x_0)^2$

Substituting this into the wave equation:

$$
\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2} \left(E - \frac{\kappa x^2}{2} \right) \psi = \left(-\frac{2mE}{\hbar^2} + \frac{m\kappa x^2}{\hbar^2} \right) \psi
$$

Let $\alpha^2 = \frac{m\kappa}{\hbar^2}$ and $\beta = \frac{2mE}{\hbar^2}$ which yields $\frac{d^2\psi}{dx^2} = (\alpha^2 x^2 - \beta)\psi$

Parabolic Potential Well

- **If the lowest energy level is zero, this violates the uncertainty principle.**
- The wave function solutions are $\psi_n = H_n(x) e^{-\alpha x^2/2}$ where $H_n(x)$ are Hermite polynomials of order *n*.
- In contrast to the particle in a box, where the oscillatory wave function is a sinusoidal curve, in this case the oscillatory behavior is due to the polynomial, which dominates at small *x*. The exponential tail is provided by the Gaussian function, which dominates at large *x*.

Analysis of the Parabolic Potential Well

Wave functions

 $\left(\sqrt{\alpha}x\right)(2\alpha x^2-3)e^{-\alpha x^2/2}$

 $\psi_3(x) = \left(\frac{\alpha}{\pi}\right)^{1/4}$.

@ 2006 Brooks/Cole - Thomson

- 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: $E_0=\frac{1}{2}\hbar\omega$
- Classically, the probability of finding the mass is greatest at the ends of motion and smallest at the center (that is, proportional to the amount of time the mass spends at each position).
- Contrary to the classical one, the largest probability for this lowest energy state is for the particle to be at the center.

6.7: Barriers and Tunneling

- Consider a particle of energy E approaching a potential barrier of height V_0 and the potential everywhere else is zero.
- We will first consider the case when the energy is greater than the potential barrier.

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) $V = 0$ $\frac{d^2 \psi_1}{dx^2} + \frac{2m}{h^2} E \psi_1 = 0$

Region II (0 < x < L) $V = V_0$ $\frac{d^2 \psi_{\text{II}}}{dx^2} + \frac{2m}{\hbar^2} (E - V_0) \psi_{\text{II}} = 0$ Region III (x > L) $V = 0$ $\frac{d^2 \psi_{III}}{dx^2} + \frac{2m}{h^2} E \psi_{III} = 0$

- \blacksquare The corresponding solutions are:
	- Region I (x < 0) $\psi_1 = Ae^{ik_1x} + Be^{-ik_1x}$ Region II (0 < x < L) $\psi_{II} = Ce^{ik_{II}x} + De^{-ik_{II}x}$ Region III $(x > L)$ $\psi_{III} = Fe^{ik_I x} + Ge^{-ik_I x}$
- **As the wave moves from left to right, we can simplify the wave functions to:**

Probability of Reflection and Transmission

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

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

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

- The maximum kinetic energy of the photoelectrons depends on the value of the light frequency *f* and not on the intensity.
- 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:

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

Notice that there is a situation in which the transmission probability is 1.

Tunneling

 Now we consider the situation where classically the particle does not have enough energy to surmount the potential barrier, $E < V_{0}$.

- The quantum mechanical result, however, is one of the most remarkable features of modern physics, and there is ample experimental proof of its existence. There is a small, but finite, probability that the particle can penetrate the barrier and even emerge on the other side.
- The wave function in region II becomes $\Psi_{II} = Ce^{\kappa x} + De^{-\kappa x}$ where $\kappa = \frac{\sqrt{2m(V_0 E)}}{2}$
- The transmission probability that The transmission probability that
describes the phenomenon of **tunneling** is $T = \left[1 + \frac{V_0^2 \sinh^2(\kappa L)}{4E(V_0 - E)}\right]^{-1}$

Uncertainty Explanation

Consider when *κL* >> 1 then the transmission probability becomes:

This violation allowed by the uncertainty principle is equal to the negative kinetic energy required! The particle is allowed by quantum mechanics and the uncertainty principle to penetrate into a classically forbidden region. The minimum such kinetic energy is:

$$
K_{\min} = \frac{(\Delta p)^2}{2m} = \frac{\pi^2 \kappa^2}{2m} = V_0 - E
$$

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.

 (a)

 (b)

@ 2006 Brooks/Cole - Thomson

- **Consider a particle passing through a potential well region rather than through a** potential barrier.
- Classically, the particle would speed up passing the well region, because $K = mv^2/2 =$ $E + V_{0}$.

According to quantum mechanics, reflection and transmission may occur, but the wavelength inside the potential well is smaller than outside. When the width of the potential well is precisely equal to half-integral or integral units of the wavelength, the reflected waves may be out of phase or in phase with the original wave, and cancellations or resonances may occur. The reflection/cancellation effects can lead to almost pure transmission or pure reflection for certain wavelengths. For example, at the second boundary $(x = L)$ for a wave passing to the right, the wave may reflect and be out of phase with the incident wave. The effect would be a cancellation inside the well.

Alpha-Particle Decay

- The phenomenon of tunneling explains the alpha-particle decay of heavy, radioactive nuclei.
- **If also 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** approximately a square well. $V(r)$
- **The Coulomb force dominates** outside the nuclear radius.
- \blacksquare The potential barrier at the nuclear radius is several times greater than the energy of an alpha particle.
- **According to quantum mechanics,** however, the alpha particle can "tunnel" through the barrier. Hence this is observed as radioactive decay.

