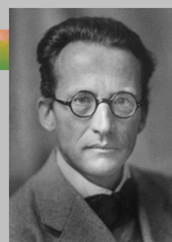
CHAPTER 6
Quantum Mechanics II

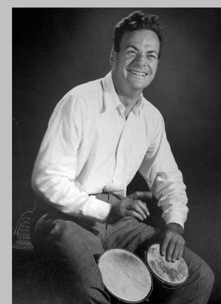


Erwin Schrödinger (1887-1961)

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

Opinions on quantum mechanics



Richard Feynman (1918-1988)

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 Schrodinger Equation is THE fundamental equation of Quantum Mechanics.

General Solution of the Schrödinger Wave Equation when V = 0

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

Try this solution:

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

$$\frac{\partial\Psi}{\partial t} = -i\omega Ae^{i(kx-\omega t)} = -i\omega\Psi \qquad \frac{\partial^2\Psi}{\partial x^2} = -k^2\Psi$$

$$i\hbar\frac{\partial\Psi}{\partial t} = (i\hbar)(-i\omega)\Psi = \hbar\omega\Psi \qquad \frac{-\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = \frac{\hbar^2k^2}{2m}\Psi$$

This works as long as:

$$\hbar\omega = \frac{\hbar^2k^2}{2m}$$

which says that the total energy is the kinetic energy.

General Solution of the Schrödinger Wave Equation when V = 0

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

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

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 this function is complex.

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 $x + dx$ is 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

Conditions on the wave function:

1. In order to avoid infinite probabilities, the wave function must be finite everywhere.
2. The wave function 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. In order to normalize a wave function, it 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 $\psi(x)\,f(t)$:

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

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:

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

Time-Independent Schrödinger Wave Equation

We integrate both sides and find: $i\hbar \ln f = Bt + C$

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

$$\ln f = \frac{Bt}{i\hbar} \qquad f(t) = e^{Bt/i\hbar} = e^{-iBt/\hbar}$$

But recall our solution for the free particle: $\Psi(x,t) = Ae^{i(kx-\omega t)}$

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:

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

Time-Independent Schrödinger Wave Equation

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

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

where:

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

$\hat{H}$ is an **operator**.

Stationary States

The wave function can be written as:

$$\boxed{\Psi(x,t) = \psi(x)e^{-i\omega t}}$$

The probability density becomes:

$$\Psi^*\Psi = \psi^2(x)(e^{i\omega t}e^{-i\omega t})$$

$$\Psi^*\Psi = \psi^2(x)$$

The probability distribution is constant in time.

This is a standing wave phenomenon and is called a stationary state.

6.2: 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:

$$\langle x\rangle = P_1x_1 + P_2x_2 + \cdots + P_Nx_N = \sum_i P_i\,x_i$$

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, $g(x)$:

$$\boxed{\langle g(x)\rangle = \int \Psi^*(x)\,g(x)\,\Psi(x)\,dx}$$

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:

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

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

The expectation value of the momentum is

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

Position and Energy Operators

The position x is its own operator. Done.

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

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

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

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

The expectation value of the energy is:

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

Deriving the Schrodinger Equation using operators

The energy is: $E = K + V = \frac{p^2}{2m} + V \quad\Rightarrow\quad E\Psi = \frac{p^2}{2m}\Psi + V\Psi$

Substituting operators:

E: $\quad E\Psi = i\hbar\frac{\partial\Psi}{\partial t}$

$K+V$: $\quad \frac{p^2}{2m}\Psi + V\Psi = \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2\Psi + V\Psi$

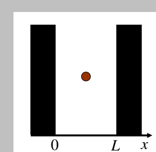
$$= -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi$$

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

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:

$$V(x) = \begin{cases}\infty & x \le 0,\ x \ge L\\ 0 & 0 < x < L\end{cases}$$



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

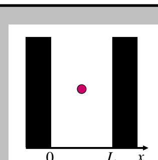
Where the potential is zero (inside the box), the time-independent Schrödinger wave equation becomes:

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

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

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

We normalize the wave function:

$\frac{1}{2} - \frac{1}{2}\cancel{\cos(2n\pi x/L)}$

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

The normalized wave function becomes: $\boxed{\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)}$

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

Quantized Energy

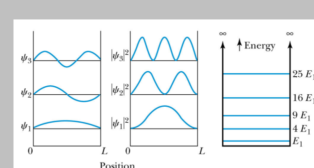
The quantized wave number now becomes: $k_n = \frac{n\pi}{L} = \sqrt{\frac{2mE_n}{\hbar^2}}$

Solving for the energy yields: $E_n = n^2\frac{\pi^2\hbar^2}{2mL^2} \quad (n = 1, 2, 3, \ldots)$

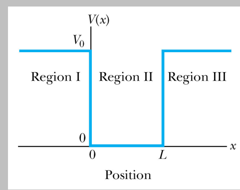
Note that the energy depends on integer values of n. Hence the energy is quantized and nonzero.

The special case of $n = 1$ is called the ground state.

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



6.4: Finite Square-Well Potential



The finite square-well potential is

$$V(x) = \begin{cases} V_0 & x \le 0 & \text{region I} \\ 0 & 0 < x < L & \text{region II} \\ V_0 & x \ge L & \text{region III} \end{cases}$$

The Schrödinger equation outside the finite well in regions I and III is: $-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} = E - V_0$ 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

$\psi_{\mathrm{I}}(x) = Ae^{\alpha x}$ region I, $x < 0$

$\psi_{\mathrm{III}}(x) = Be^{-\alpha x}$ region III, $x > L$

Finite Square-Well Solution

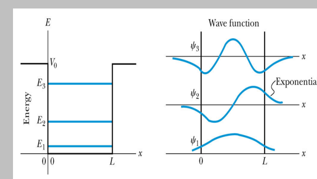
Inside the square well, where the potential V is zero, the wave equation becomes $\frac{d^2\psi}{dx^2} = -k^2\psi$ where $k = \sqrt{(2mE)/\hbar^2}$

The solution here is: $\psi_{\mathrm{II}} = Ce^{ikx} + De^{-ikx}$ region II, $0 < x < L$

The boundary conditions require that: $\psi_{\mathrm{I}} = \psi_{\mathrm{II}}$ at $x = 0$ and $\psi_{\mathrm{II}} = \psi_{\mathrm{III}}$ at $x = L$

so the wave function is smooth where the regions meet.

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

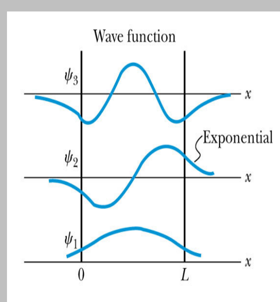


Penetration Depth

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

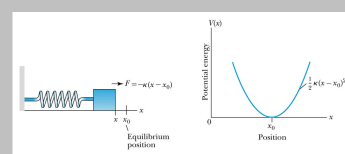
$$\delta x \approx \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(V_0 - E)}}$$

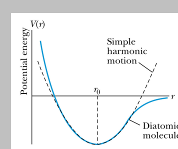
The penetration distance that violates classical physics is proportional to Planck's constant.



6.6: Simple Harmonic Oscillator

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





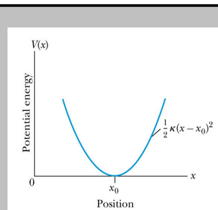
Consider the Taylor expansion of a potential function:

$$V(x) = V_0 + V_1(x - x_0) + \tfrac{1}{2}V_2(x - x_0)^2 + \ldots$$

Simple Harmonic Oscillator

Consider the second-order term of the Taylor expansion of a potential function:

$$V(x) = \tfrac{1}{2}V_2(x - x_0)^2$$



Substituting this into Schrödinger's 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: $\frac{d^2\psi}{dx^2} = (\alpha^2 x^2 - \beta)\psi$

The Parabolic Potential Well

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.

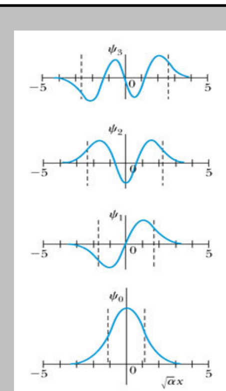
Wave functions

$$\psi_3(x) = \left(\frac{\alpha}{\pi}\right)^{1/4}\frac{1}{\sqrt{3}}\left(\sqrt{\alpha}x\right)(2\alpha x^2 - 3)e^{-\alpha x^2/2}$$

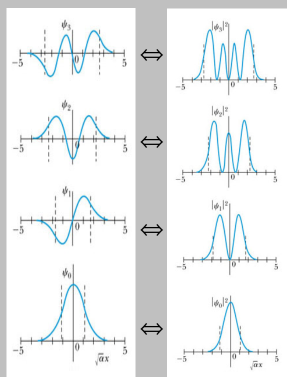
$$\psi_2(x) = \left(\frac{\alpha}{\pi}\right)^{1/4}\frac{1}{\sqrt{2}}(2\alpha x^2 - 1)e^{-\alpha x^2/2}$$

$$\psi_1(x) = \left(\frac{\alpha}{\pi}\right)^{1/4}\sqrt{2\alpha}\,xe^{-\alpha x^2/2}$$

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4}e^{-\alpha x^2/2}$$



The Parabolic Potential Well

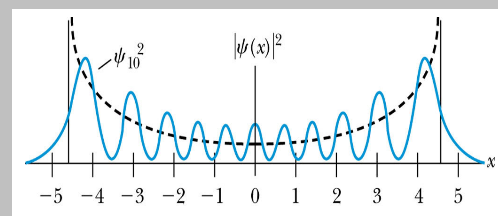


Classically, the probability of finding the mass is greatest at the ends of motion and smallest at the center.

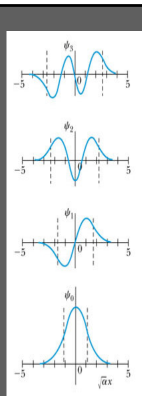
Contrary to the classical one, the largest probability for this lowest energy state is for the particle to be at the center.

Analysis of the Parabolic Potential Well

As the quantum number increases, however, the solution approaches the classical result.

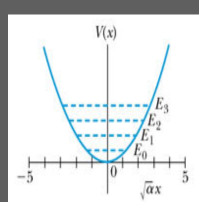


The Parabolic Potential Well



The energy levels are given by:

$$E_n = (n+\tfrac{1}{2})\hbar\sqrt{\kappa/m} = (n+\tfrac{1}{2})\hbar\omega$$



The zero point energy is called the Heisenberg limit:

$$E_0 = \frac{1}{2}\hbar\omega$$

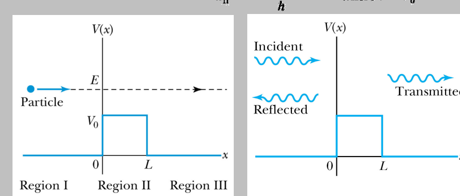
6.7: Barriers and Tunneling

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

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

In regions I and III the wave numbers are: $k_I = k_{III} = \dfrac{\sqrt{2mE}}{\hbar}$

In the barrier region we have $k_{II} = \dfrac{\sqrt{2m(E-V_0)}}{\hbar}$ 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 ($x < 0$) $\quad V = 0 \quad \dfrac{d^2\psi_I}{dx^2} + \dfrac{2m}{\hbar^2}E\psi_I = 0$

Region II ($0 < x < L$) $\quad V = V_0 \quad \dfrac{d^2\psi_{II}}{dx^2} + \dfrac{2m}{\hbar^2}(E - V_0)\psi_{II} = 0$

Region III ($x > L$) $\quad V = 0 \quad \dfrac{d^2\psi_{III}}{dx^2} + \dfrac{2m}{\hbar^2}E\psi_{III} = 0$

The corresponding solutions are:

Region I ($x < 0$) $\quad \psi_I = Ae^{ik_I x} + Be^{-ik_I x}$

Region II ($0 < x < L$) $\quad \psi_{II} = Ce^{ik_{II} x} + De^{-ik_{II} x}$

Region III ($x > L$) $\quad \psi_{III} = Fe^{ik_I x} + Ge^{-ik_I x}$

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

Incident wave $\quad \psi_I(\text{incident}) = Ae^{ik_I x}$

Reflected wave $\quad \psi_I(\text{reflected}) = Be^{-ik_I x}$

Transmitted wave $\quad \psi_{III}(\text{transmitted}) = Fe^{ik_I x}$

Probability of Reflection and Transmission

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

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

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

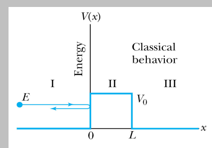
Because the particles must be either reflected or transmitted we have: $R + T = 1$.

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

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

Note that the transmission probability can be 1.

Tunneling



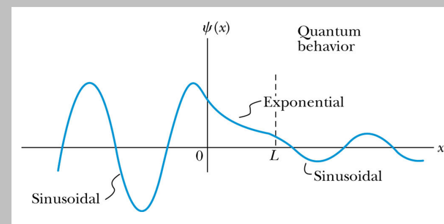
Now we consider the situation where classically the particle doesn't have enough energy to surmount the potential barrier, $E < V_0$.

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: $\psi_{II} = \cancel{Ce^{\kappa x}} + De^{-\kappa x}$ where $\kappa = \dfrac{\sqrt{2m(V_0 - E)}}{\hbar}$

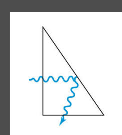
The transmission probability that describes the phenomenon of **tunneling** is: $T = \left[1 + \dfrac{V_0^2 \sinh^2(\kappa L)}{4E(V_0 - E)}\right]^{-1}$

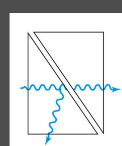
Tunneling wave function



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

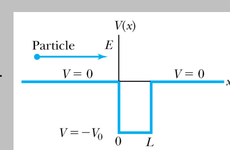
Analogy with Wave Optics





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.

Potential Well



Consider a particle passing through a potential well, rather than a barrier.

Classically, the particle would speed up in the well region because

$K = mv^2 / 2 = E + V_0$

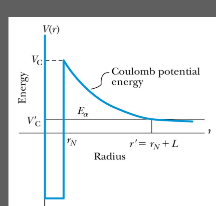
Quantum mechanically, reflection and transmission may occur, but the wavelength decreases inside the well. When the width of the potential well is precisely equal to half-integral or integral units of the wavelength, the reflected waves may be out of phase or in phase with the original wave, and cancellations 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 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 ~ 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.

6.5: Three-Dimensional Infinite-Potential Well

The wave function must be a function of all three spatial coordinates.

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

$$p^2 = p_x^2 + p_y^2 + p_z^2$$

$$\hat{p}_x \psi = -i\hbar \frac{\partial \psi}{\partial x} \qquad \hat{p}_y \psi = -i\hbar \frac{\partial \psi}{\partial y} \qquad \hat{p}_z \psi = -i\hbar \frac{\partial \psi}{\partial z}$$

So the three-dimensional Schrödinger wave equation is

$$\boxed{-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right) + V\psi = E\psi \quad \text{or} \quad -\frac{\hbar^2}{2m}\nabla^2 \psi + V\psi = E\psi}$$

The 3D infinite potential well

It's easy to show that:

$$\psi(x, y, z) = A \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

where: $k_x = \pi n_x / L_x$ $\quad k_y = \pi n_y / L_y$ $\quad k_z = \pi n_z / L_z$

and: $$E = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

When the box is a cube:

$$E = \frac{\pi^2 \hbar^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

Try 10, 4, 3
and 8, 6, 5

Note that more than one wave function can have the same energy.

Degeneracy

The Schrödinger wave equation in three dimensions introduces three quantum numbers that quantize the energy. And the same energy can be obtained by different sets of quantum numbers.

A quantum state is called 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.