# PHY2002 - Quantum Physics I

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## Introduction to wave-particle duality

Relation of Energy and Momentum (particle-like properties) to wavelength and frequency (wave-like properties):

$$E = \hbar\omega = hf$$

$$p = \hbar k = \frac{h}{\lambda}$$

Uncertainty Principle:

$$\Delta p \Delta x \geq \frac{\hbar}{2}$$

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

Can we describe a particle as a wave? The 1-dimensional electromagnetic wave equation:

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 \psi}{\partial t^2}$$

the solution is:

$$\Psi_{(x,t)} = A\exp[i(kx - \omega t)]$$

This is the **Free Particle wave function**:

$$\Psi_F = Ae^{i(kx-\omega t)} = Ae^{\frac{i}{\hbar}(px-Et)}$$

substituting $k = \frac{p}{\hbar}$ and $\omega = \frac{E}{\hbar}$ we get

$$\Psi_{(x,t)} = A\exp\left[\frac{i}{\hbar}(px - Et)\right].$$

When this itself is substituted into the 1-dimensional wave equation

$$-\frac{p^2}{\hbar^2}\Psi_{(x,t)} = -\frac{E^2}{c^2\hbar^2}\Psi_{(x,t)}$$

we are left with the equality

$$E = pc$$

and hence we **can** describe a (light) particle as a wave.

# Double slit experiment

Two electron beams produce an interference pattern which persists even when only one electron is fired at a time. Attempting to deduce which slit the electron passed through perturbs the electron and so destroys the interference pattern - the wavefunction collapses on to it passing through one particular slit.

Feynman provided a way of mathematically describing the interference pattern. We assume the electron explores all paths and the outcome is equal to the square of the magnitude of the sum of all possible wave functions. I.e.:

$$Outcome = |\text{Sum of all possible wavefunctions}|^2$$
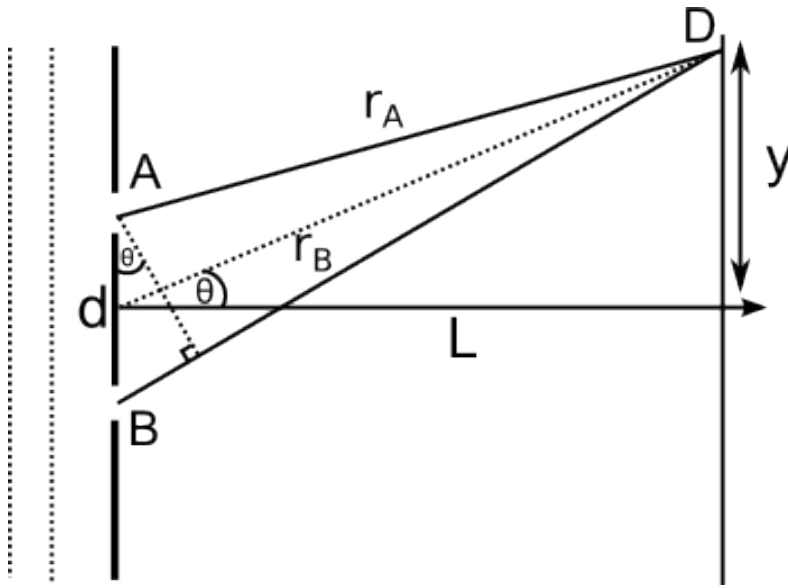


For interference to be constructive (and so produce bright fringe):

$$sin(\theta) = \frac{n\lambda}{d} = \frac{y}{L} \quad \therefore \quad y = \frac{n\lambda L}{d}$$

Wavefunction at D from A: $\Psi_A \sim e^{ikr_A}$ Wavefunction at D from b: $\Psi_B \sim e^{ikr_B}$

$$\text{Outcome} = \text{Intensity} = I = |\Psi_A + \Psi_B|^2$$

$$|\Psi_A + \Psi_B|^2 = \left[e^{ikr_A} = e^{ikr_B}\right]\left[e^{-ikr_a} + e^{-ikr_B}\right] = 2\left[1 + cos(k(r_a - r_b))\right]$$

Using trigonometry:
$(r_A - r_b) = dsin(\theta)$, for small $\theta$, $sin(\theta) \approx \theta \approx \frac{y}{L}$
So: $r_A - r_b = \frac{yd}{L}$ $\therefore$ $I = 2\left[1 + cos\left(\frac{kyd}{L}\right)\right]$, but $2cos^2(\theta) = 1 + cos(2\theta)$

$\therefore I = 4cos^2\left(\frac{kyd}{2L}\right)$ so the intensity is always positive and oscillates. Note that the intensity is effectively a measure of the probability of finding the particle at that point, and this is proportional to the square of the amplitude of the wavefunction. I.e.

$$P_{(x,t)} = |\Psi_{(x,t)}|^2$$

This is the Born statistical interpretation, note that for this equality to be true, the wavefunction must be normalized, otherwise it is simply proportional. In general, the probability of finding the particle in a region of space is equal to the probability density multiplied by the size of the space.

In 1-dimension,

$$P(x) \ dx = |\psi_{(x)}|^2 \ dx.$$

To ensure that over all space the probability of finding the particle is equal to one (ie., the particle exists), we must impose a normalisation condition

$$\int_{-\infty}^{+\infty} |\psi_N(x)|^2 \ dx = 1,$$

so that the pre-factor, $A$, of the un-normalised wavefunction $\psi(x)$ follows

$$|A|^2 = \frac{1}{\int_{-\infty}^{+\infty} |\psi(x)|^2 \ dx} \ ,$$

where the normalised wavefunction is equal to the pre-factor multiplied by the un-normalised wavefunction

$$\psi_N(x) = A\psi(x).$$

So the Born statistical interpretation can be summarised in one dimension as:

$$P(x,t)dx = \frac{|\Psi(x,t)|^2 \ dx}{\displaystyle\int_{-\infty}^{+\infty} |\Psi(x,t)|^2 \ dx}$$

## The One Dimensional Schrödinger Equation

Starting with the general plane wave equation in some wavefunction $\Psi$,

$$\frac{\partial^2 \Psi}{\partial x^2} = \alpha \frac{\partial \Psi}{\partial t}$$

where $\alpha$ is some constant determined by the substitution of a plane wave of the form $\Psi(x,t) = A\exp[i(kx - \omega t)]$ and obtaining:

$$-k^2 = -i\alpha\omega.$$

Using $E = \frac{p^2}{2m}$, $E = \hbar\omega$ and $p = \hbar k$, results in the specification

$$\alpha = -\frac{2mi}{\hbar},$$

and hence substituting for $\alpha$ leaves the *one dimensional, time-dependent Schrödinger wave equation* for free particles (ie., existing in zero potential)

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

This can be further generalised by invoking the conservation of energy relation; that the total energy, $E$, is equal to the sum of the kinetic, given by $\frac{p^2}{2m}$, and an arbitrary potential, $V$

$$E\Psi = \left(\frac{p^2}{2m} + V\right)\Psi,$$

giving the full *one dimensional, time-dependent Schrödinger wave equation*

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

If it is assumed that the form of the potential, $V$, is independent of time, $t$, the wavefunction can be written as the product of the time-dependent and time-independent equations

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

hence

$$\frac{\partial\Psi}{\partial t} = \psi\frac{df}{dt}, \quad \frac{\partial^2\Psi}{\partial x^2} = \frac{d^2\psi}{dx^2}f$$

and thus the Schrödinger equation transforms into

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

Where the left hand side is a function of $t$ alone, and the right hand side is a function of $x$ alone, implying that both sides are equal to a constant, $E$, chosen as the RHS is the quantum Hamiltonian, the sum of the potential and kinetic energies.[1]

We can then say

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

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[1]See Griffiths, p23.

which is the *time-independent one dimensional Schrödinger wave equation.*[2] This can also be written in terms of the Hamiltonian operator, $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V$.

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

The time-independent Schrödinger equation is a second order linear differential equation in $x$:

Second order $\implies$ two linearly independent solutions: $\psi_A(x)$, $\psi_B(x)$
Linear $\implies$ $\psi(x) = \alpha\psi_A(x) + \beta\psi_B(x)$
(i.e., any linear combination of the two linearly independent solutions is also a solution)

# The One Dimensional Schrödinger Equation - Barnes' way

Quantum states which don't change in time are call stationary states. In these states we can ignore $\frac{\partial}{\partial t}$ in the Schrödinger equation, as the time is not variant.
For the **Free Particle wavefunction** (assuming constant V):

$$\Psi_F(x, t) = e^{i(kx - \omega t)}$$

this can be written as two separate functions in x and t:

$$\Psi_F(x, t) = \phi(x)e^{-i\omega t}$$

But $E = \hbar\omega$ and so

$$\Psi_F(x, t) = \phi(x)e^{\frac{-iEt}{\hbar}}$$

(Note that the time part of all stationary states can be written this way, and $\phi$ is used to denote them (the function in only $x$)).
Note that this function is constant in time (despite the apparent time dependence), as the probability does not depend on time:

$$P \propto |\Psi|^2 \quad \therefore \quad \Psi\Psi^* = \phi(x)^2 e^{\frac{-iEt}{\hbar}} e^{\frac{iEt}{\hbar}} = \phi(x)^2$$

which is time independent.
So for stationary states: $\Psi(x, t) = \phi(x)e^{\frac{-iEt}{\hbar}}$. Substituting this in to the Time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\left[\phi(x)e^{\frac{-iEt}{\hbar}}\right] = \left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\phi(x)e^{\frac{-iEt}{\hbar}}$$

Calculating the derivative and dividing by $e^{\frac{-iEt}{\hbar}}$:

$$E\phi(x) = \left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\phi(x)$$

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[2]Note that $\Psi \neq \psi$. $\Psi(x, t)$, whereas $\psi(x)$.

this is the Time-Independent Schödinger equation.

Since this equation is a linear, second-order DE there are two linearly independent solutions and an infinite number of linearly dependent solutions.

## Example in a region of constant potential, $V(x) = V_0$

The time-independent Schrödinger equation becomes

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0$$

when $k'^2 = \frac{2m}{\hbar^2}(E - V_0)$

If

$$E > V_0 \implies \frac{d^2\psi}{dx^2} + k'^2\psi = 0$$

$$\psi(x) = \alpha \sin(k'x) + \beta \cos(k'x)$$

When a wavefunction exists in a potential less than the total energy, the function oscillates in space.

If

$$E < V_0 \implies \frac{d^2\psi}{dx^2} - |k'|^2\psi = 0$$

$$\psi(x) = \alpha \exp(|k'|x) + \beta \exp(-|k'|x)$$

When a wavefunction exists in a region where the potential is *greater* than the total energy of the wavefunction, the wavefunction *decays* to zero. This gives rise to *quantum tunneling*.

Solving the Schrödinger equation involves three things:
**1.** Finding the general form of $\psi_A(x)$ and $\psi_B(x)$ for a given $V(x)$
**2.** Enforcing boundary conditions to find the constants $\alpha$ and $\beta$
**3.** Normalising the wavefunction

## Boundary Conditions

**1.** The wavefunction must be a continuous, single-valued function of position and time.
**2.** The integral of the modulus squared of the wavefunction over all $x$ must be finite - no singularities. This ensures that the wavefunction can be normalised and represents a physical state.
**3.** The first derivative of the wavefunction with respect to $x$ must be continuous everywhere except where there is an infinite discontinuity in the potential.
**4.** Where $V(x) = \infty$, $\psi(x) = 0$. No tunnelling through a well of infinite potential!

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# Localisation and wave packets

Localisation concerns how we can specify the position of the particle.

## Infinite Delocalisation in the Free Particle wave function

For the Free Particle wavefunction: $\Psi_F(x, t) = Ae^{\frac{i}{\hbar}(px - Et)}$

There is infinite delocalisation, since the probability of finding the particle at any particular position is the same for every position:

$P \propto \Psi_F \Psi_F^*$, $\Psi_F \Psi_F^* = A^2 e^{\frac{i}{\hbar}(px - Et)} e^{-\frac{i}{\hbar}(px - Et)} = A^2 \therefore P \propto A^2$

The probability is constant at every position and so the particle exists everywhere. In terms of Heisenberg's Uncertainty Principle this means that: $\Delta x = \infty$ and $\Delta p_x = 0$, and so the momentum is clearly defined (and so by extension the wavelength is clearly defined).

## Infinite localisation with the Dirac delta function

Dirac delta function: $\delta(x_0 - x)$ is zero if $x \neq x_0$ and is $\infty$ if $x = x_0$.

This provides complete localisation, as the position is clearly defined meanwhile the momentum is totally indeterminate, i.e. $\Delta x = 0$ and $\Delta p_x = \infty$.

## The Gaussian as a compromise

If we were to add many different frequency cosine waves (all with a value of 1 at $x = 0$) we would obtain a net result about the centre (whilst the values cancelled elsewhere). If we were to add an infinity of such waves we would produce a Dirac delta function.

The Gaussian function provides a compromise between complete localisation and delocalisation. It is defined by the function:

$\psi(x) = e^{\frac{-x^2}{2L^2}}$
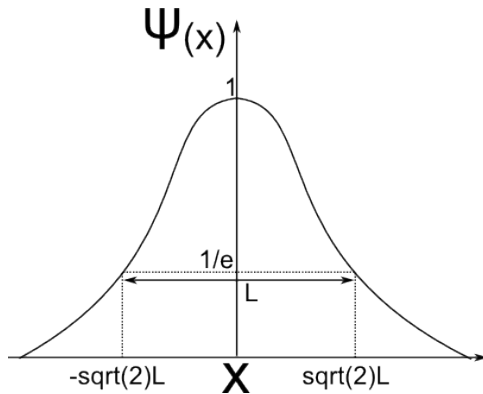


It is useful to express the Gaussian in terms of plane waves such that it can be used with the Schrödinger equation.

## Representing wavepackets as a sum of plane waves

If we sum an infinity of plane waves about the centre, we obtain a Dirac delta function:

$$\delta(x_0 - x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ik(x_0 - x)} dk \quad \text{where} \quad k = \frac{2\pi}{\lambda}$$

To obtain the Gaussian we must add a weighting factor $g(k)$ such that there is a greater contribution from waves of lower frequency (and a lower contribution from waves of higher frequency) so the total about $x = 0$ is not entirely cancelled out.

$$\text{Gaussian:} \quad \psi(x) = \int_{-\infty}^{+\infty} g(k) e^{ik(x_0 - x)} dk$$

This is a Fourier Transform.

For a Gaussian Distribution we want $\psi(x) = e^{\frac{-x^2}{2L^2}}$
and so we choose the weighting factor: $g(k) = e^{\frac{-\alpha^2 k^2}{2}}$
For this choice of $g(k)$:

$$\psi(x) = \sqrt{\frac{2\pi}{L^2}} e^{\frac{-x^2}{2L^2}}$$

Probability Distribution $\propto |\psi(x)|^2 \propto e^{\frac{-x^2}{L^2}}$ and so it is a Gaussian distribution of width $L$.

Note that moving particles require the time evolution of the Gaussian wave packet. This means there is spreading associated with propagation (and so it is like diffraction).

## Application to Double-Slit experiment

If we know which slit the particle went through then at the slit: $\Delta y < \frac{d}{2}$
This means there is a related uncertainty in $p_y$.
At best: $\Delta p_y \Delta y = \frac{\hbar}{2}$, and so for $\Delta y < \frac{d}{2}$: $\Delta p_y > \frac{\hbar}{d}$

But we know that: $p_y = p \sin(\theta) = \frac{p\lambda}{d}$ and $p = \frac{h}{\lambda}$, therfore $p_y = \frac{h}{d}$.

The position on the screen $\propto p_y$. The fractional uncertainty: $\frac{\Delta p_y}{p_y} = \frac{1}{2\pi} = \Delta k k$ (using $p = \hbar k$).

This is 1 radian of phase and so the interference pattern is significantly disrupted.
$\Delta k$ is the wavepacket spread.

## Example: Ultrafast laser pulse

Titanium Sapphire Laser ($Ti^{3+}Al_2O_3$) has gain of 750 to 950 nm (angular frequenices of $2.5 \times 10^{15} \ rad \ s^{-1}$ and $2.0 \times 10^{15} \ rad \ s^{-1}$ respectively).
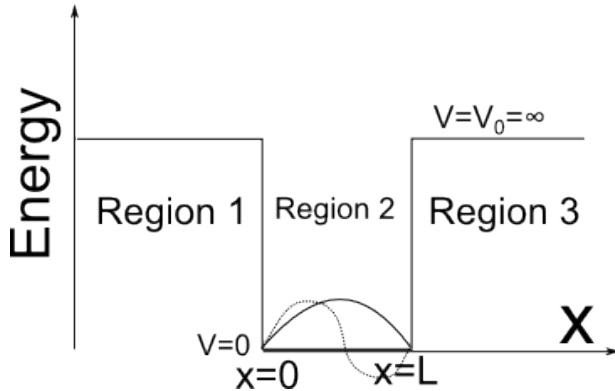
$\Delta E \Delta t \sim \frac{\hbar}{2} \ \therefore \ \Delta E = \hbar \Delta \omega \ \therefore \Delta \omega \Delta t \sim \frac{1}{2}$
$\therefore \ \Delta t = \frac{1}{2 \times 0.5 \times 10^{15}} = 10^{-15} s$

To build lasers with pulses faster than this, we must have greater gain.

# Finding the eigenfunctions and eigenvalues for a particle in an infinite square well

The particle "*in a box*" means a particle bound in a square potential well.



The eigenfunctions are the wavefunctions that fit in the well, in this case they are sinusoidal as shown in the diagram.
We let $V_0 = \infty$ so that quantum tunneling is prohibited.
Note $V(x) = 0$ for $0 < x < L$ (region 2), $V(x) = V_0 = \infty$ for $x < 0$, $x > L$ (regions 1 and 3).
From Boundary Condition 4 (" *Where $V(x) = \infty$, $\psi(x) = 0$. No tunnelling through a well of infinite potential.*"):
$\phi(x < 0) = 0, \ \phi(x > L) = 0$
From the solution to the Time Independent Schrödinger equation, we know that inside the well (a region of constant potential):

$$\phi(x) = \alpha sin(kx) + \beta cos(kx) \text{ where } k^2 = \frac{2mE}{\hbar^2}$$

.

From Boundary Condition 1 ("*The wavefunction must be a continuous, single-valued function of position and time.*"):
$\phi(L) = 0, \ \phi(0) = 0$ as $\phi(x > L) = 0, \ \phi(x < 0) = 0$

Using this condition: if $\phi(0) = 0$ then $\beta = 0$, from $\phi(x) = \alpha sin(kx) = \beta cos(kx)$ (remember that k is a constant from solving the DE and **NOT** the wavenumber).

$$\therefore \alpha sin(kL) = 0 \ \therefore \ kL = 0, \pi, 2\pi, \cdots \ \therefore \ kL = n\pi$$

Note that $n = 0$ corresponds to $k = 0$ and so $E = 0$, that is to say, there is no particle present. This is a useless solution and so we take $n = 1, 2, 3, \cdots$

And so the eigenfunctions (permitted solutions) are given by:

$$\phi(x)_n = \alpha sin\left(\frac{n\pi}{L}x\right)$$
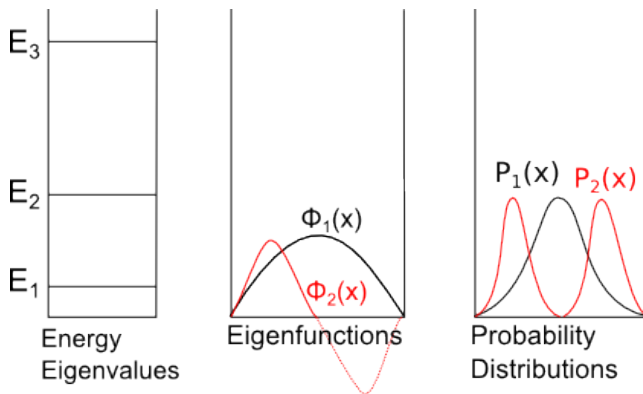
when $0 \leq x \leq L$, else $\phi(x) = 0$.

We can also calculate the energy eigenvalues:

$$k_n = \frac{n\pi}{L}$$

$$\therefore \ \frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{L^2}$$

$$\therefore \ E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2}$$

These permitted quantized energy levels are called the energy eigenvalues.



Note that the energy levels increase with differences of squares and even though the energy is increasing, the wavefunctions still start at 0 in the well and have the same magnitude peaks.

### Finding the value of $\alpha$

To find the value of the constant $\alpha$ we must normalize the wavefunction: $\int_{-\infty}^{+\infty} \phi^2(x)dx = 1$

The trick to doing this is to realize that our particle only exists within the bounds $0 < x < L$ and so we can integrate the probability density between $0$ and $L$ to avoid the troublesome infinities.

$$\int_0^L \alpha^2 sin^2\left(\frac{n\pi}{L}x\right), \quad \text{let } sin^2(x) = \frac{1}{2}\left(1 - cos(2x)\right), \quad \therefore \ = \frac{1}{2}\alpha^2 \int_0^L 1 - cos\left(\frac{2n\pi}{L}x\right)$$

$$= \frac{1}{2}\alpha^2 \left[x - \frac{L}{2n\pi}sin\left(\frac{2n\pi}{L}x\right)\right]_0^L = \frac{1}{2}\alpha^2\left(\left(L - \frac{L}{2n\pi}sin(2n\pi)\right) - (0 - 0)\right)$$

$$\therefore \frac{1}{2}\alpha^2 L = 1 \ \therefore \ \alpha^2 = \frac{2}{L} \ \therefore \ \alpha = \sqrt{\frac{2}{L}}$$

And so:
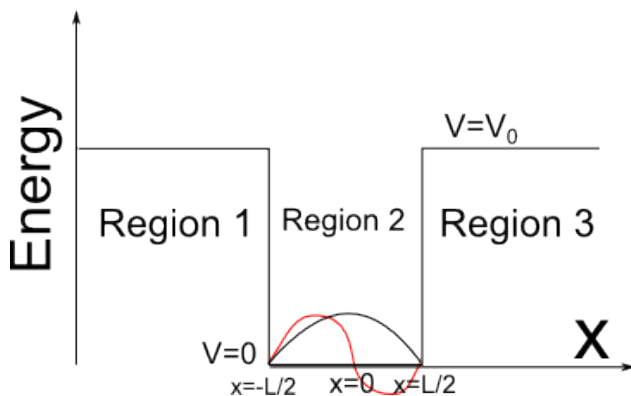
$$\phi_n(x) = \sqrt{\frac{2}{L}}sin\left(\frac{n\pi x}{L}\right) \ \therefore \ P_n(x) = \frac{2}{L}sin^2\left(\frac{n\pi x}{L}\right)$$

Finally note that the eigenfunctions are mutually orthogonal so:

$$\int_0^L \phi_1\phi_2 = 0$$

i.e. the functions cancel each other out when the areas are summed.

## Finding the eigenfunctions and eigenvalues for a particle in a finite square well



In the case of the finite square well:

$$V(x) = \begin{cases} V_0 & \text{if } x < -\frac{L}{2}, x > \frac{L}{2} \\ 0 & \text{if } -\frac{L}{2} \leq x \leq \frac{L}{2} \end{cases}$$

**Inside the well (region 2):**

The potential is constant and so the general solution (from the Time-Independent Schrödinger Equation) is:

$$\phi(x) = \alpha sin(kx) + \beta cos(kx), \text{ where } k^2 = \frac{2mE}{\hbar^2}$$

This yields two possible forms of $\phi(x)$:

$$\phi(x) = \alpha sin(kx), \text{ which is an odd function.}$$

$$\phi(x) = \beta cos(kx), \text{ which is an even function.}$$

**Outside the well (region 3):**

Here $V(x) = V - 0$ and so the Time-Independent Schrödinger Equation becomes:

$$\frac{\partial^2 \phi}{\partial x^2} + k'^2 \phi = 0, \text{ where } k'^2 = \frac{2m}{\hbar^2}(E - V_0)$$

Note that since the particle is trapped in the potential well: $E < V_0$. This implies that $k'$ is imaginary and so the wavefunction takes the form:

$$e^{ik'x} \rightarrow e^{-|k'|x}$$

So the solutions are damped. To include both possibilities of the square root we must write:

$$\phi(x) = Ae^{+|k'|x} + Be^{-|k'|x}$$

However for $\phi(x)$ to remain finite as $x \to \infty$, then $A = 0$, and so:

$$\phi(x) = Be^{-|k'|x}$$

Note that this wavefunction is a decaying exponential, not oscillating. This decaying exponential gives rise to the phenomenon of quantum tunneling.

**Applying Boundary Conditions:**

At $x = \frac{L}{2}$: $\phi(x)$ must be continuous and $\frac{\partial \phi}{\partial x}$ must be continuous.

$$\text{Using the condition for } \phi(x): \beta cos\left(\frac{kL}{2}\right) = Be^{\frac{-|k'|L}{2}}$$

$$\text{Using the condition for } \frac{\partial \phi}{\partial x}: -k\beta sin\left(\frac{kL}{2}\right) = -|k'|Be^{\frac{-|k'|L}{2}}$$

$$\text{Recall that: } k^2 = \frac{2mE}{\hbar^2}, \ |k'|^2 = \frac{2m}{\hbar^2}(E - V_0)$$

And so by dividing the equation for $\frac{\partial phi}{\partial x}$ by the equation for $\phi(x)$:

$$tan\left(\frac{kL}{2}\right) = \frac{|k'|}{k}$$

This equation has no analytical solution, and so must be solved numerically (by repeatedly guessing solutions) or graphically.

Once we have the energy eigenvalues we can use the fact that $\phi(x)$ must be continuous to find that at $x = \frac{L}{2}$:

$$\phi(x) = \beta cos\left(\frac{kL}{2}\right) = \beta e^{\frac{-|k'|L}{2}}$$

This gives $B$ in terms of $\beta$.

And so the unnormalized wavefunction is:

$$\phi_n(x) = \beta cos(k_n x), \quad \text{for: } 0 \leq x \leq \frac{L}{2}$$

$$\phi_n(x) = \frac{\beta cos(k_n x)}{e^{\frac{-|k'_n|L}{2}}} e^{-|k'_n|x}, \quad \text{for: } x > \frac{L}{2}$$

This was obtained since:

$$B = \frac{\beta cos\left(\frac{kL}{2}\right)}{e^{\frac{-|k'|L}{2}}}$$

And the eigenfunction outside the well is:

$$\phi(x) = Be^{-|k'|x}$$

For even eigenfunctions the wavefunction in regions 1 and 3 will be the same, and so the above eigenfunction would hold for $x < \frac{-L}{2}$. However this is not true for odd eigenfunctions.

## Odd/Asymmetric Eigenfunctions

The wavefunction is:

$$\phi(x) = \alpha sin(kx) \quad \text{for: } 0 \leq x \leq \frac{L}{2}$$

$$\phi(x) = \beta e^{-|k'|x} \quad \text{for: } x > \frac{L}{2}$$

From the boundary conditions:

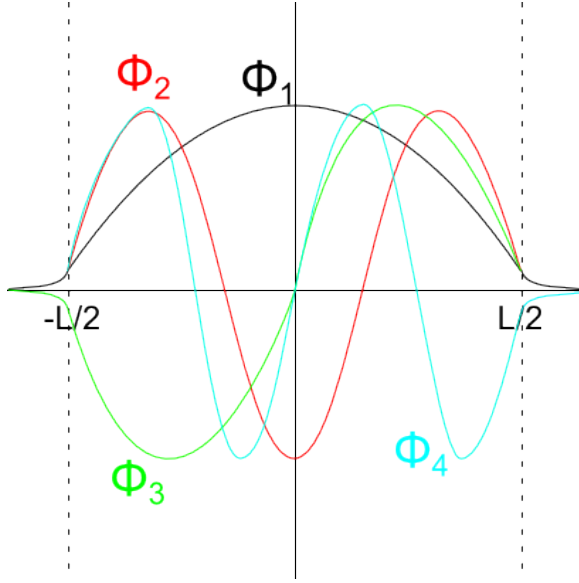$$\phi(x) \text{ is continuous } \therefore \ \alpha sin\left(\frac{kL}{2}\right) = \beta e^{-|k'|\frac{L}{2}}$$

$$\frac{\partial \phi}{\partial x} \text{ is continuous } \therefore \ k\alpha cos(\frac{kL}{2}) = -|k'|\beta e^{-|k'|\frac{L}{2}}$$

Dividing the latter equation by the former:

$$-cot\left(\frac{kL}{2}\right) = \frac{|k'|}{k}$$

where

$$k^2 = \frac{2mE}{\hbar^2} \ , \ |k'|^2 = \frac{2m}{\hbar^2}(E - V_0)$$

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As previously this can only be solved by choosing values of E and testing it with an iterative method.

Note this is simplified to a 1-Dimensional, Flat-bottomed well, we will investigate harmonic wells, etc. in the future.

# Flux of Particles

In one dimension, the flux is defined as the number of particles passing a certain point per unit of time. There are two ways to describe a stream of particles in terms of a wavefunction that can be normalised, confining them to a large box width $L$ or considering a beam of particles with inter-particle distance $L$. Both of these result in a wavefunction of the form

$$\psi = \frac{1}{\sqrt{L}} \exp(ikx).$$

Much like charge in electromagnetism, probability in quantum mechanics a conserved quantity.

Change in probability $\iff$ Flux into/out of region.

In 1D

$$j(x_1) - j(x_2) = \frac{dP}{dt}$$

$$\frac{dP}{dt} = \frac{\partial}{\partial t} \int_{x_1}^{x_2} |\psi\psi^*| \, dx = \int_{x_1}^{x_2} \left( \psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} \right) dx$$

$$j(x) = -\frac{i\hbar}{2m}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right)$$

In 3D

$$j(x, y, z) = -\frac{i\hbar}{2m}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right)$$

The conservation of probability can also be written as the *continuity equation*, where $j$ is the probability flux and $P(x, t)$ is the probability (ie, $|\psi\psi^*|$).

$$\frac{\partial}{\partial t}P(x, t) + \nabla \cdot j = 0$$

So this yields an equation for the flux of:

$$\vec{j} = \frac{\hbar\vec{k}}{mL} = \frac{\vec{p}}{mL}$$

where L is the inter-particle distance.

## Potential Step

Consider a potential of the form

$$V(x) = \begin{cases} V_0 & \text{if } x \geq 0 \\ 0 & \text{if } x < 0 \end{cases}$$

and a particle stream, inter-particle spacing $L$ incident on the 'step' at $x = 0$. The wavefunction of this can be given as

$$\psi_1(x) = \frac{1}{\sqrt{L}}\left[\exp(ikx) + R\exp(-ikx)\right]$$

where the second term is the reflected part of the incident wavefunction, amplitude $R$.

The probability flux of this is therefore

$$j = -\frac{i\hbar}{2mL}\left[\exp(-ikx) + R^*\exp(ikx)\right]\left[ik\exp(ikx) - ikR\exp(-ikx)\right]$$
$$- \left[\exp(ikx) + R\exp(-ikx)\right]\left[-ik\exp(-ikx) + ikR\exp(ikx)\right]$$

$$j = \frac{\hbar k}{mL}(1 - |R|^2)$$

the left and right representing incident and reflected waves, respectively.

For $x > 0$, the transmitted wavefunction is of the form

$$\psi_2(x) = \frac{1}{\sqrt{L}} T \exp(ik'x)$$

where $T$ is the amplitude of the transmitted wavefunction.

Therefore,
for $E > V_0$, $k + ve$, $k' real$, $\implies$ propagating solution
for $E < V_0$, $k - ve$, $k' imaginary$, $\implies$ exponentially decaying solution

Utilising the boundary conditions

$$\psi_1\big|_{x=0} = \psi_2\big|_{x=0} \implies 1 + R = T$$

$$\frac{\partial \psi_1}{\partial x}\bigg|_{x=0} = \frac{\partial \psi_2}{\partial x}\bigg|_{x=0} \implies ik(1 - R) = ik'T$$

Hence,

$$R = \frac{k - k'}{k + k'}$$

$$T = \frac{2k}{k + k'}$$

Incident flux:

$$\frac{\hbar k}{mL}$$

Reflected flux:

$$\frac{\hbar k}{mL} \left[\frac{k - k'}{k + k'}\right]^2$$

Transmitted flux:

$$\frac{\hbar k}{mL} \frac{4k|k'|}{(k + |k'|)^2}$$

## Summary

**i)** Finite probability of reflection when a QM particle impinges on a potential step when $E >> V_0$.

**ii)** For $E >> V_0$, reflected probability $\to 0$

**iii)** For $E << V_0$, reflected probability $= 1$.

**iv)** For $E < V_0$, reflected probability $= 1$, but there is some probability of finding the particle

beyond the step **if it is looked for.**

For a barrier of potential $V_0$, $[0, d]$:

$$\psi(x) = \begin{cases} A_1 \exp(ikx) + B_1 \exp(-ikx) & \text{if } x < 0 \\ A_2 \exp(-|k'|x) + B_2 \exp(|k'|x) & \text{if } d \geq x \geq 0 \\ A_3 \exp(ikx) & \text{if } x > d \end{cases}$$

To remove the arbitrary constants we can apply the boundary conditions that $\psi$ and $\frac{d\psi}{dx}$ must be continuous at $x = 0$ and $x = d$, and then normalize the wavefunctions. To the left of the
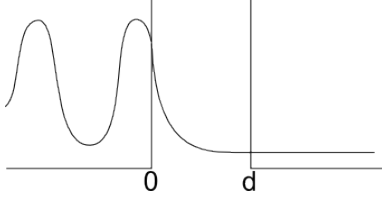


barrier, the probability is sinusoidal due to the interference between incident and reflected waves. Inside the barrier, probability exponentially decays. On the right side of the barrier, the probability is constant.[3]

If the probability of tunneling is small (i.e., barrier is thick/high), transmitted amplitude:

$$T = |t|^2 = \frac{16E(V_0 - E)}{V_0^2} \exp(-2d|k'|)$$

Where d is the thickness of the barrier, $|k'| = \sqrt{\frac{2m|E - V_0|}{\hbar^2}}$.

# 1   Two potential steps

We can create two potential steps by having a semiconductor which changes material, such that it goes from having a lower conduction band, to a higher one, creating an effective potential step for the conducting electrons.

To create this we need atomic resolution, and so we must use molecular beam epitaxy (crystalline growth).

The electron energy in between the potential steps is quantised, and so the electron energy must equal a quantised level in order to tunnel through - i.e. there must be an allowed state for the electron to enter.

When there is no bias voltage applied:

With zero bias and a low relative incoming electron energy, there is low transmission (and so T is low), as the incoming electrons cannot occupy any allowed states. When a bias voltage

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[3]Note, this is the probability, *not* the wave function. The wave function is never constant and is continuous everywhere.
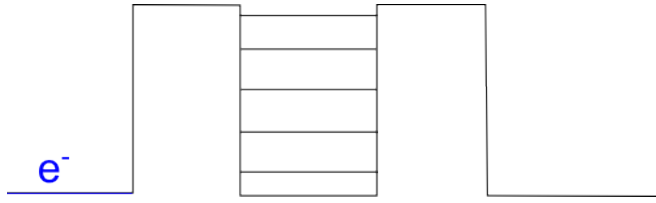
$V_B$ is applied such that the incoming electrons fit an allowed state:
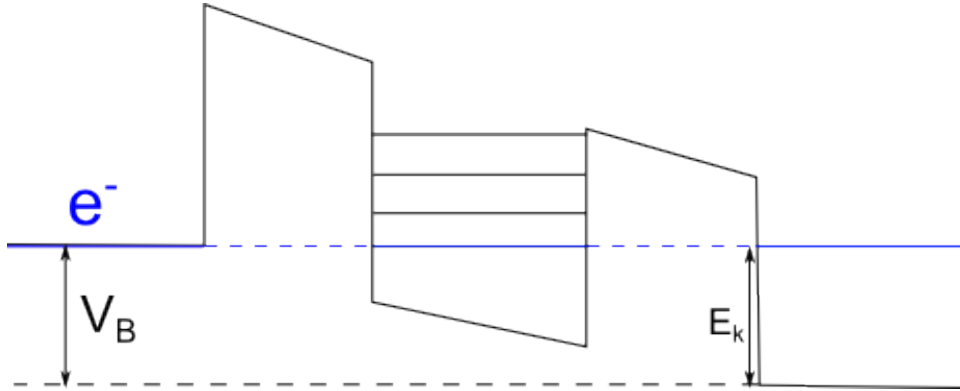


There is an allowed state at the required energy and so tunneling is observed. This means T is high as there is high transmission, note that the applied voltage adds an energy $E_k$ to the electrons.

Note that if $V_B$ was such that the electrons did not have an energy aligned with an allowed state then there would be low transmission.

If we plot the current against the bias voltage, we note that the quantization means that we observe **negative differential resistance**. That is the resistance does not follow Ohm's Law, and instead becomes inversely proportional to the applied voltage for some periods.

This is a **resonant tunneling device** since tunneling only occurs at specific allowed energies.
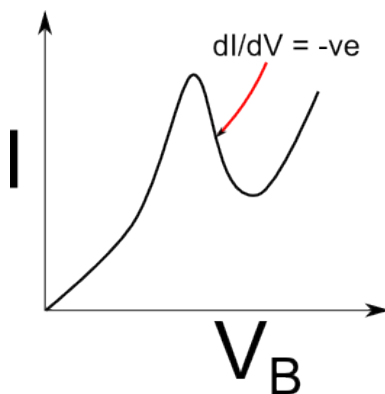


## 1.1 Scanning Tunneling Microscopy (STM)

For STM, the tunneling probability is given by:

$$|t|^2 = Ge^{-2|k'|L}, \quad \text{where } G = 16\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)$$

This means that there is a big change in tunneling probability for a relatively small change in distance, and so we can get excellent resolution (0.6 Å at worst).

# Operators

We use operators to calculate expected results for quantities from the wavefunction.
For example, for the free particle wavefunction:

$$\Psi_F(x,t) = A\,exp\left(\frac{i}{\hbar}(px - Et)\right)$$

We can see that:

$$i\hbar\frac{\partial\Psi}{\partial t} = E\Psi \ , \quad -i\hbar\frac{\partial\Psi}{\partial x} = p_x\Psi$$

And so $i\hbar\frac{\partial}{\partial t}$ is the energy operator and is denoted by $\hat{E}$. Note that this operator is actually $\hat{T}$, the kinetic energy operator, but in the case of the free particle wavefunction there is no potential energy and so this becomes the total energy operator.

Whilst $-i\hbar\frac{\partial}{\partial x}$ is the momentum operator in the x-direction, and is denoted by $\hat{p}_x$.

Note that E, p, etc. are called **dynamical variables**. These are the properties of a system that we can measure, and they are represented by operators in Quantum Mechanics.

In general we apply an operator on a function to obtain a result.

An eigenvalue equation is an equation of the form operator(function) $= N \times$ function. In general an eigenvalue equation is given by:

$$\hat{A}\Psi = a\Psi$$

where $\hat{A}$ is an arbitrary operator, representing the measurement of a dynamical variable $A$ , $a$ is the associated eigenvalue (i.e. the expected result of $A$) and $\Psi$ is the associated eigenstate of $a$.

Each operator, $\hat{A}$, has a set of eigenfunctions, $\Psi_A$, and associated eigenvalues satisfying the above equation. The eigenvalues, $a$, are the set of all possible outcomes of the dynamical variable, $A$, when it is measured. The eigenfunctions, $\Psi_A$ represent the set of special states, the eigenstates, which are unchanged when $A$ is measured.

An eigenfunction $\Psi_A$ describes a state called an eigenstate, for which a measurement of the dynamical variable $A$ always gives the same value, $a$.
Note that:

- $\Psi_A$ is a stationary state, and so does not vary in time.

- $A$ is a conserved quantity.

However, this determinancy only holds when the system is an eigenfunction of the dynamical variable we wish to measure. If we wish to measure a dynamical variable when the system is *not* in an eigenfunction of this variable then we can only predict the outcome statistically.

In this case we measure the *expectation value* of the variables, note that this is the *average* value (mean) of the results **not** the most common value (mode) which we might usually consider to be the expected value.

In this case we obtain[4]:

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi dx$$

Note that $\Psi$ **must** be normalized.
Re-visiting the Schrödinger equation we see it can be written as:

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

And so from our knowledge of operators we see that this is simply a non-relativistic relation between energy and momentum. And a statement that:

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

i.e. that total energy, $E_T = KE + PE$.
The right-hand side of the Schrödinger equation is the Hamiltonian operator, operating on $\Psi$. The Hamiltonian operator returns the total energy of the system. So in operator form, the Schrödinger equation can be written as:

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

Note that in operator form:

$$\hat{H} = \hat{T} + \hat{V}$$

Note that this definition of the Hamiltonian ignores energy due to spin, rotational energy, vibrational energy, etc. - if we wish to take account of these we must modify the Hamiltonian, and so the Schrödinger equation, but this is not covered in this module.
Note that if we wish to apply multiple operators to a function, e.g.:

$$\hat{p}_x \hat{p}_x \Psi = -i\hbar \frac{\partial}{\partial x} \left( -i\hbar \frac{\partial}{\partial x} \right) \Psi$$

We start from the right (the function) and apply the operators moving leftwards.

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[4]Note that this is often referred to as the 'operator sandwich'. The wavefunction, $\Psi$ and it's conjugate playing the part of the bread in this sordid analogy, while the operator $\hat{A}$ plays the part of the filling, eg, ham, cheese, or perhaps coronation chicken for a complex operator, such as those for angular momentum. Butter, being a classical quantity, can be ignored without loss of generality.

| Dynamical Variable | Operator Symbol | Operations applied |
|---|---|---|
| Co-ordinates | $\hat{x},\ \hat{y},\ \hat{z},\ \hat{r}$ | $x,\ y,\ z,\ r$ |
| Momentum | $\hat{p}_x,\ \hat{p}_y,\ \hat{p}_z,\ \hat{p}$ | $\frac{\hbar}{i}\frac{\partial}{\partial x},\ \frac{\hbar}{i}\frac{\partial}{\partial y},\ \frac{\hbar}{i}\frac{\partial}{\partial z},\ \frac{\hbar}{i}\nabla$ |
| Kinetic Energy | $\frac{\hat{p}^2}{2m}$ | $\frac{-\hbar^2}{2m}\nabla^2$ |
| Kinetic Energy | $T$ | $-\frac{\hbar}{i}\frac{\partial}{\partial t}$ |
| Potential Energy | $\hat{V}$ | $V(q_i)$ |
| Hamiltonian | $\hat{H}$ | $\frac{-\hbar^2}{2m}\nabla^2 + V(q_i)$ |
| Angular Momentum (cartesian) | $\hat{L}_z$ | $\frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$ |
| Angular Momentum (polar) | $\hat{L}_z$ | $\frac{\hbar}{i}\frac{\partial}{\partial \phi}$ |

# The Superposition Principle

- It is impossible to make a measurement without disturbing the system, (*cf.* uncertainty principle).

- Eigenstates describe *pure* states, (states of a single eigenfunction).

- Any arbitrary quantum system can be viewed as a sum of its eigenfunctions.

- If $Q$ is an observable of $\psi$, then upon measuring $Q$, one is certain to observe one of the *eigenvalues* of $Q$. The system is then in an *eigenstate* of this observable.

- If an observable has only one eigenvalue, it will collapse to that value with 100% probability. This explains why the potential wells have a definable set of energy levels.

When the operator of observable $A$, $\hat{A}$, acts on a wavefunction, it returns one of the eigenvalues of $A$, and the wavefunction is in the corresponding eigenstate.

$$\hat{A}\psi = a\psi_a$$

This is a pure state.

A state can also be written as a linear sum of (orthogonal) pure states.

$$\psi = \sum_n c_n^A \psi_n^A$$

or for the same system

$$\psi = \sum_m c_m^B \psi_m^B$$

Where $c_n^A$ is an eigenvalue of the eigenstate $\psi_n^A$.

These are mixed states. A pure state cannot be written as the sum of mixed states.

The orthonormality condition can be exploited in 'Fourier's trick', which allows the components $c_n^A$ to be determined. Recalling the orthonormality condition

$$\int_{-\infty}^{\infty} \psi_n^* \psi_m = \delta_{m,n}$$

Where

$$\delta_{ij} = \begin{cases} 0 & \text{for } i \neq j \\ 1 & \text{for } i = j \end{cases}$$

Hence,

$$\int (\psi_m^A)^* \psi \; dv = \sum_n c_n^A \int (\psi_m^A)^* \psi_n^A \; dv = \sum_n c_n^A \; \delta_{m,n}$$

and therefore

$$\int (\psi_m^A)^* \psi = c_m^A$$

where the integrals are over all space. $c_m^A$ can be considered as the Fourier coefficients.

A pure state is described by a single eigenfunction, however a mixed or 'superposition' state is a weighted sum of eigenfunctions. It is worth noting that given two arbitrary eigenfunctions $\psi^A$ and $\psi^B$, a system can be in a superposition state of $\psi^B$, and yet in a pure state of $\psi^B$.

$$\psi = \sum_n c_n^A \psi_n^A = \psi_m^B$$

Where m, n are dummy variables.

## Measurements on Superposition States

Consider the outcome of measuring A on $\psi$.

$\psi$ must be expressed as a superposition of the eigenfunctions of $\hat{A}$.

$$\psi = \sum_n c_n^A \psi_n^A$$

Where $c_n$ is the weighting coefficient or probability amplitude.

If the measurement gave the eigenvalue $a_n$, then the system goes from $\psi$ to $\psi_n^A$, the eigenstate of $a_n$.

The statistical outcome of a measurement $\hat{A}$ on an ensemble of *identically prepared systems* described by $\psi$ will yield $a_n$ with probability $P_n = \frac{|c_n^A|^2}{\sum |c_n^A|^2}$. Hence, $c_n$ can be considered as probability amplitudes.

The mean of $a$ is given as

$$\bar{a} = \sum_n a_n P_n = \sum_n a_n |c_n^A|^2.$$

So the Normalisation condition for superposition states is:

$$k^2 = \frac{1}{\displaystyle\sum_n |C_n|^2}$$

where $k\psi$ is the normalised wavefunction.

After a measurement is taken, the system *collapses* into an eigenstate, and all subsequent measurements yield this same eigenstate for an indeterminate amount of time. Hence, to generate statistical information, an ensemble of identical systems must be considered. It is possible to 'freeze' a quantum system in an eigenstate by repeatedly measuring it; this is known as the quantum zeno effect.

The expectation value (the value obtained from many identically prepared systems described by $\psi$), can be calculated as

$$\langle \hat{A} \rangle = \frac{\int \psi^* \hat{A} \ \psi \ dv}{\int \psi^* \psi \ dv}$$

In the numerator, the operator acts on the wavefunction $\psi$ to 'pick out' the information $A$. This is then turned into a real number (the eigenvalue) by multiplying it by the complex conjugate of the wavefunction[5].

The denominator acts to normalise the result.

If

$$\psi = \sum_n c_n^A \psi_n^A,$$

Then

$$\langle \hat{A} \rangle = \sum_n |c_n^A|^2 a_n = \sum_n a_n P_n.$$

A common type of question is:

> *A quantum system is prepared in a superposition state of the eigenfunctions associated with the dynamical varible $T$. The superposition state may be written as:*
> $$\Psi = 12\psi_1^T + 4\psi_2^T + 3\psi_3^T$$
>
> 1. *Find the normalized wavefunction.*
> 2. *If the associated eigenvalues are $t_1 = 1$, $t_2 = 0$ and $t_3 = -1$ then what are the possible results of a measurement of $T$ on this quantum system and what is the probability of obtaining each result?*

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[5] *Cf.* the pdf on Dirac notation so thoughtfully provided by our benefactors.

*3. What is the expectation value of T?*

Solution:

1. We use the condition $\sum |C_n|^2 = 1$ and so the normalization factor is: $A^2(144+16+9) = 1$ $\therefore A = \frac{1}{13}$. So the normalised wavefunction is:

$$\Psi = \frac{12}{13}\psi_1 + \frac{4}{13}\psi_2 + \frac{3}{13}\psi_3$$

2. The possible results are 1, 0 and -1. And the respective probabilities are $\left(\frac{12}{13}\right)^2$, $\left(\frac{4}{13}\right)^2$ and $\left(\frac{3}{13}\right)^2$.

3. The expectation value is:

$$\left(\frac{12}{13}\right)^2 \cdot 1 + \left(\frac{4}{13}\right)^2 \cdot 0 + \left(\frac{3}{13}\right)^2 \cdot -1 = 0.7988$$

# Simultaneous Observables

$$\psi = \psi_m^B = \sum_n c_{m,n}^A \psi_m^A$$

$\psi$ is an eigenstate of B, but a superposition (mixed) state of A. In this case, a measurement of A *then* B, will yield a different result to measuring B *then* A.

The exception to this is when A and B have *simultaneous* eigenstates.

$$\psi_{m,n}^{A,B} \implies \hat{A}\psi_{m,n}^{A,B} = a_n \psi_{m,n}^{A,B}$$

and

$$\hat{B}\psi_{m,n}^{A,B} = a_m \psi_{m,n}^{A,B}$$

and *vice versa.*

This implies that

$$\hat{A}\hat{B} = \hat{A}(b_m \psi_{m,n}^{A,B}) = b_m \hat{A}\psi_{m,n}^{A,B} = b_m a_n \psi_{m,n}^{A,B}$$

and *vice versa.* $a_n$ and $b_m$ are necessarily commutative, as eigenvalues of hermitian operators are real numbers.

In other words

$$(\hat{A}\hat{B} - \hat{B}\hat{A})\psi_{m,n}^{A,B} = 0$$

The quantity in brackets is known as the *commutator* or *commutation relation,* and is a measure of the commutativity of two structures.

When two operators do not commute, this gives rise to an associated uncertainty principle.

The quantum commutator for the operators $\hat{p}_x$ and $\hat{x}$ is

$$[\hat{p}_x, \hat{x}] = \hat{p}_x \hat{x} \psi - \hat{x} \hat{p}_x \psi = -i\hbar$$

and the associated uncertainty relation is Heisenberg uncertainty relation

$$\Delta p_x \Delta x \geq \frac{\hbar}{2}.$$

The generalised uncertainty principle is given as[6]

$$\sigma_A \sigma_B \geq \frac{1}{2} |\langle [A, B] \rangle|$$

---

[6]The derivation of which is long, boring and, more importantly, in Griffiths and Rae. Unless you're interested in what the Schwarz inequality can do for you, in which case it's a hoot.