PHYS201
Wave Mechanics

Semester 1 2009
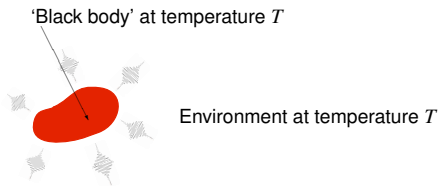
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## Quantum Mechanics and Wave Mechanics I

- Quantum mechanics arose out of the need to provide explanations for a range of physical phenomena that could not be accounted for by 'classical' physics:

  - Black body spectrum

  - Spectra of the elements

  - photoelectric effect

  - Specific heat of solids . . .

- Through the work of Planck, Einstein and others, the idea arose that electromagnetic and other forms of energy could be exchanged only in definite quantities (quanta)

- And through the work of De Broglie the idea arose that matter could exhibit wave like properties.

  - It was Einstein who proposed that waves (light) could behave like particles (photons).

- Heisenberg proposed the first successful *quantum theory*, but in the terms of the mathematics of matrices — matrix mexhanics.

Quantum Mechanics and Wave Mechanics II

- Schrödinger came up with an equation for the waves predicted by de Broglie, and that was the start of wave mechanics.

    - Schrödinger also showed that his work and that of Heisenberg's were mathematically equivalent.

- But it was Heisenberg, and Born, who first realized that quantum mechanics was a theory of probabilities.

    - Something that Einstein would never accept, even though he helped discover it!

- Through the work of Dirac, von Neumann, Jordan and others, it was eventually shown that matrix mechanics and wave mechanics were but two forms of a more fundamental theory — quantum mechanics.

- Quantum mechanics is a theory of information

    - It is a set of laws about the information that can be gained about the physical world.

- We will be concerned with wave mechanics here, the oldest form of quantum mechanics.

'Black body' at temperature T

Environment at temperature T

Rayleigh-Jeans spectrum

S

Observed spectrum

f

- The first inkling of a new physics lay in understanding the origins of the black body spectrum:

  - A black body is any object that absorbs all radiation, whatever frequency, that falls on it.

- The blackbody spectrum is the spectrum of the radiation emitted by the object when it is in thermal equilibrium with its surroundings.

- Classical physics predicted the Rayleigh-Jeans formula which diverged at high frequencies — the ultra-violet catastrophe.

The Black Body Spectrum II
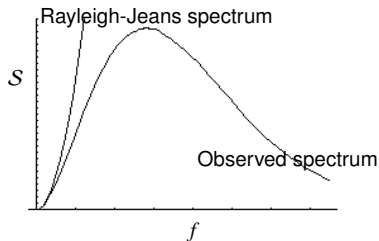
- Planck assumed that matter could absorb or emit black body radiation energy of frequency f in multiples of hf where h was a parameter to be taken to zero at the end of the calculation.

- But he got the correct answer for a small but non-zero value of h:

$$\mathcal{S}(f, T) = \frac{8\pi h f^3}{c^3} \frac{1}{\exp(hf/kT) - 1}.$$

where

$$h = 6.6218 \times 10^{-34} \text{Joules-sec}$$
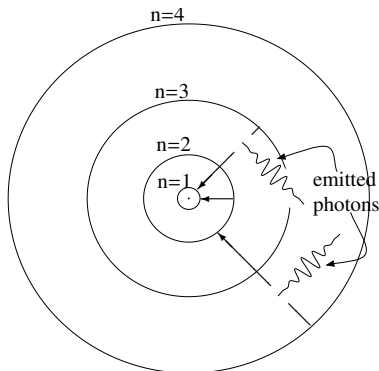
now known as Planck's constant.

Einstein's hypothesis

- Einstein preferred to believe that the formula hf was a property of the electromagnetic field

    - Planck thought it was a property of the atoms in the blackbody.

- Einstein proposed that light of frequency f is absorbed or emitted in packets (i.e. quanta) of energy E where

$$E = hf \qquad \text{Einstein/Planck formula}$$

    - Sometime later he extended this idea to say that light also had momentum, and that it was in fact made up of particles now called photons.

- Einstein used this idea to explain the photo-electric effect (in 1905).

- A first example of wave-particle duality: light, a form of wave motion, having particle-like properties.

- Rutherford proposed that an atom consisted of a small positively charged nucleus with electrons in orbit about this nucleus.

- According to classical EM theory, the orbiting electrons are accelerating and therefore ought to emit EM radiation.

  - The electron in a hydrogen atom should spiral into the nucleus in about 10^{-12} sec.

- Bohr proposed existence of stable orbits (*stationary states*) of radius r such that

$$\text{angular momentum} = pr = n\frac{h}{2\pi}, \ \ n = 1, 2, 3, \dots$$

- Leads to orbits of radii r_n and energies E_n:

$$r_n = n^2\frac{\epsilon_0 h^2}{\pi e^2 m_e} \ \ \ E_n = -\frac{1}{n^2}\frac{m_e e^4}{8\epsilon_0^2 h^2} \ \ n = 1, 2, \dots$$

The Bohr model of the hydrogen atom II

- Bohr radius — radius of lowest energy orbit — $a_0 = r_1 = \dfrac{\epsilon_0 h^2}{\pi e^2 m_e} = 0.05$ nm.

- The atom emits EM radiation by making a transition between stationary states, emitting a photon of energy hf where

$$hf = E_m - E_n = \frac{m_e e^4}{8\epsilon_0^2 h^2}\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

  - Einstein later showed that the the photon had to carry both energy *and* momentum — hence it behaves very much like a particle.

  - Einstein also showed that the time at which a transition will occur and the direction of emission of the photon was totally unpredictable.

  - The first hint of 'uncaused' randomness in atomic physics.

- Bohr's model worked only for hydrogen-like atoms

  - It failed miserably for helium

  - It could not predict the dynamics of physical systems

  - But it 'broke the ice', and a search for classical physics answers was abandoned.

De Broglie's Hypothesis

- In 1924 Prince Louis de Broglie asked a philosophical question:

  If waves can sometimes behave like particles, can particles sometimes exhibit wave-like behaviour?

- To specify such a wave, need to know its

    - frequency f — use Einstein's formula $E = hf$

    - wavelength λ — make use of another idea of Einstein's

- Special relativity tells us that the energy E of a zero rest mass particle (such as a photon) is given in terms of its momentum p by
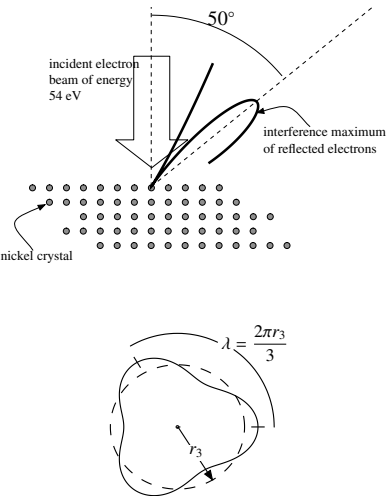
$$E = pc = hf.$$

- Using the fact that $f\lambda = c$ gives $\quad pc = hc/\lambda$

  which can be solved for $\lambda \qquad \lambda = h/p.$

- As there is *no mention in this equation of anything to do with light*, de Broglie assumed it would hold for particles of matter as well.

Evidence for wave properties of matter

- In 1926 Davisson and Germer accidently showed that electrons can be diffracted (Bragg diffraction)

  - Fired beam of electrons at nickel crystal and observed the scattered electrons.

  - They observed a diffraction pattern identical to that observed when waves (X-rays) were fired at the crystal.

  - The wavelengths of the waves producing the diffraction pattern was identical to that predicted by the de Broglie relation.

  - G P Thompson independently carried out the same experiment. His father (J J Thompson) had shown that electrons were particles, the son showed that they were waves.

- Fitting de Broglie waves around a circle gives Bohr's quantization condition

$$n\lambda = 2\pi r_n \implies pr_n = n\frac{h}{2\pi}$$

The Wave Function

- Accepting that these waves exist, we can try to learn what they might mean.

- We know the frequency and the wavelength of the wave associated with a particle of energy E and p.

- Can write down various formulae for waves of given f and λ.

  - Usually done in terms of angular frequency ω and wave number k:

  $$\omega = 2\pi f \qquad k = 2\pi/\lambda$$

  In terms of $\hbar = h/2\pi$

  $$E = hf = (h/2\pi)(2\pi f) \quad \text{and} \quad p = h/\lambda = (h/2\pi)(2\pi/\lambda)$$
  $$\text{i.e.} \quad E = \hbar\omega \quad \text{and} \quad p = \hbar k$$

- Some possibilities for these waves:

  $$\Psi(x, t) = A\cos(kx - \omega t)$$
  $$\text{or} \ = A\sin(kx - \omega t)$$
  $$\text{or} \ = Ae^{i(kx - \omega t)}$$
  $$\text{or} \ = \ldots$$

- But what is 'doing the waving'?? What are these waves 'made of'?

What can we learn from the wave function? I

- To help us understand what Ψ might be, let us reverse the argument

    - I.e. if we are given $\Psi(x, t) = A\cos(kx - \omega t)$, what can we learn about the particle?

- This wave will be moving with a *phase velocity* given by $v_{phase} = \dfrac{\omega}{k}$.

    - Phase velocity is the speed of the crests of the wave.

- Using $E = \hbar\omega = \frac{1}{2}mv^2$ and $p = \hbar k = mv$ where v is the velocity of the particle we get:

$$v_{phase} = \frac{\omega}{k} = \frac{E}{p} = \frac{\frac{1}{2}mv^2}{mv} = \frac{1}{2}v$$

That is, the wave is moving with half the speed of its associated particle.
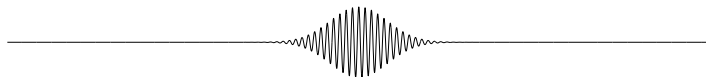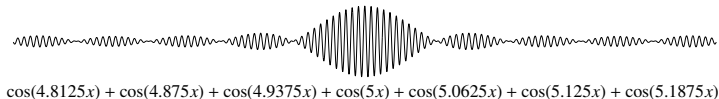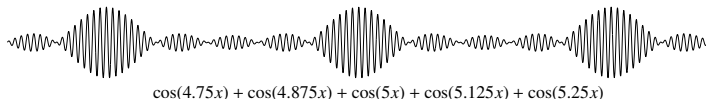
- Thus, from the phase velocity of the wave, we can learn the particles velocity via $v = 2v_{phase}$.

- What else can we learn — E and p, of course.

- But what about the position of the particle?
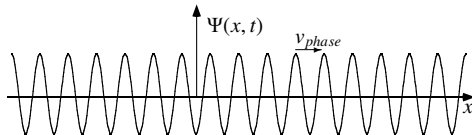
- This is a wave function of constant amplitude and wavelength. The wave is the same everywhere and so there is no distinguishing feature that could indicate one possible position of the particle from any other.

- Thus, we cannot learn *where* the particle is from this wave function.

Wave Packets I

- We can get away from a constant amplitude wave by adding together many waves with a range of frequencies and wave numbers.

$$\cos(5x) + \cos(5.25x)$$

$$\cos(4.75x) + \cos(4.875x) + \cos(5x) + \cos(5.125x) + \cos(5.25x)$$

$$\cos(4.8125x) + \cos(4.875x) + \cos(4.9375x) + \cos(5x) + \cos(5.0625x) + \cos(5.125x) + \cos(5.1875x)$$
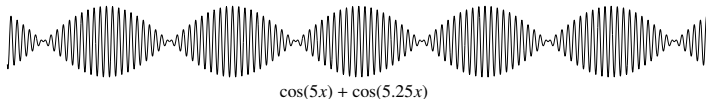
An integral over a continuous range of wave numbers produces a single wave packet.

Wave Packets II

- To form a single wave packet we need to carry out the sum (actually, an integral):

$$\Psi(x, t) = A(k_1) \cos(k_1 x - \omega_1 t) + A(k_2) \cos(k_2 x - \omega_2 t) + \ldots$$

$$= \sum_n A(k_n) \cos(k_n x - \omega_n t)$$

(a) (b)
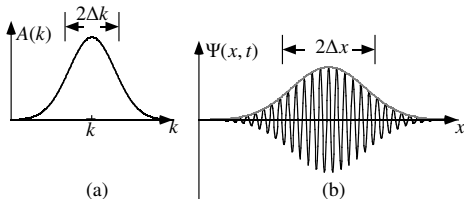
- (a) The distribution of wave numbers k of harmonic waves contributing to the wave function $\Psi(x, t)$. This distribution is peaked about $\bar{k}$ with a width of $2\Delta k$.

- (b) The wave packet $\Psi(x, t)$ of width $2\Delta x$ resulting from the addition of the waves with distribution $A(k)$. The oscillatory part of the wave packet (the 'carrier wave') has wave number $\bar{k}$.

Wave packets III
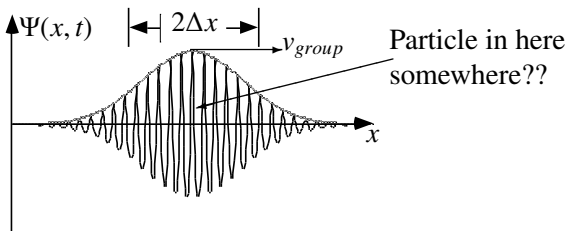
- The wave function of a wave packet is effectively zero everywhere except in a region of size $2\Delta x$.

- Reasonable to expect particle to be found in region where wave function is largest in magnitude.

- The wave packet ought to behave in some way like its associated particle e.g. does it move like a free particle.

- We can check the speed with which the packet moves by calculating its *group* velocity

$$v_{group} = \left(\frac{d\omega}{dk}\right)_{k=\bar{k}}.$$

From $\quad E = \dfrac{p^2}{2m} \quad$ we get $\quad \hbar\omega = \dfrac{\hbar^2 k^2}{2m}$

and hence $\quad \omega = \dfrac{\hbar k^2}{2m}$ — a dispersion relation — which gives $v_{group} = \dfrac{\hbar\bar{k}}{m} = \dfrac{\bar{p}}{m}$

- The wave packet moves as a particle of mass m and momentum $\bar{p} = \hbar\bar{k}$.

- Thus the wave packet is particle-like:

    - It is confined to a localized region is space . . .

    - It moves like a free particle.

- But at the cost of combining together waves with wave numbers over the range

$$\overline{k} - \Delta k \lesssim k \lesssim \overline{k} + \Delta k$$

    - This corresponds to particle momenta over the range

$$\overline{p} - \Delta p \lesssim p \lesssim \overline{p} + \Delta p$$

    - and which produces a wave packet that is confined to a region of size $2\Delta x$.

- I.e. the wave packet represents a particle to a certain extent, but it does not fix its momentum to better than $\pm \Delta p$ nor fix its position to better than $\pm \Delta x$.

- The bandwidth theorem (or, Fourier theory) tells us that $\Delta x \Delta k \gtrsim 1$.

- Multiplying by $\hbar$ gives the Heisenberg Uncertainty Relation.

$$\Delta x \Delta p \gtrsim \hbar$$

- Heisenberg's uncertainty relation is a direct result of the basic principles of quantum mechanics

  - It is saying something very general about the properties of particles

    - No mention is made of the kind of particle, what it is doing, how it is created . . .

  - It is tells us that we can have knowledge of the position of a particle to within an uncertainty of $\pm \Delta x$, and its momentum to within an uncertainty $\pm \Delta p$, with $\Delta x \Delta p \gtrsim \hbar$

    - If we know the position exactly $\Delta x = 0$, then the momentum uncertainty is infinite and vice versa

  - It does not say that the particle definitely has a precise position and momentum, but we cannot measure these precise values.

- It can be used to estimate size of an atom, the lowest energy of simple harmonic oscillator, temperature of a black hole, the pressure in the centre of a collapsing star . . .

The size of an atom
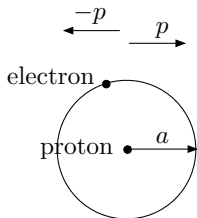
- Can estimate the size of an atom by use of the uncertainty relation.

- The position of the electron with respect to the nucleus will have an uncertainty $\Delta x = a$

- The momentum can swing between p and $-p$ so will have an uncertainty of $\Delta p = p$

- Using the uncertainty relation in the form $\Delta x \Delta p \approx \hbar$ we get $ap \approx \hbar$.

- The total energy of the atom is then

$$E = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 a} \approx \frac{\hbar^2}{2ma^2} - \frac{e^2}{4\pi\epsilon_0 a}$$

- The radius a that minimizes this is found from $\dfrac{dE}{da} = 0$, which gives

$$a \approx \frac{4\pi\epsilon_0 \hbar^2}{me^2} \approx 0.05 \text{ nm} \quad \text{(Bohr radius)} \quad \text{and} \quad E_{min} \approx -\tfrac{1}{2}\frac{me^4}{(4\pi\epsilon_0)^2\hbar^2} \approx -13.6 \text{ eV}.$$

- Shall be considered in three forms:

  - With macroscopic particles (golf balls);

  - With 'classical' waves (light waves);

  - With electrons.

- The first two merely show us what we would expect in our classical world.

- The third gives counterintuitive results with both wave and particle characteristics that have no classical explanation.

An Experiment with Golf balls: Both Slits Open.

- We notice three things about this experiment:

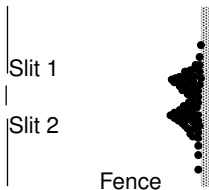- The golf balls arrive in lumps: for each golf ball hit that gets through the slits, there is a single impact on the fence.

- The golf balls arrive at random.

- If we wait long enough, we find that the golf ball arrivals tend to form a pattern:

- This is more or less as we might expect:
  - The golf balls passing through hole 1 pile up opposite hole 1 . . .
  - The golf balls passing through hole 2 pile up opposite hole 2.

.

- If we were to perform the experiment with one or the other of the slits closed, would expect something like:
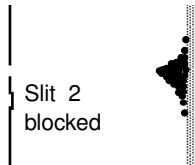
- i.e. golf ball arrivals accumulate opposite the open slits.

- expect that the result observed with both slits open is the 'sum' of the results obtained with one and then the other slit open.

- Express this sum in terms of the *probability* of a ball striking the fence at position x.

Probability for golf ball strikes

- Can sketch in curves to represent the probability of a golf ball striking the back fence at position x.

- Thus, for instance,

    $P_{12}(x)\delta x$ = probability of a golf ball striking screen between x and $x + \delta x$ when both slits are open.
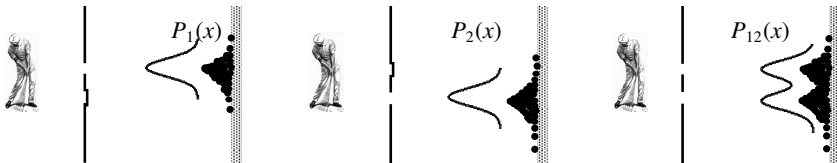
- Now make the claim that, for golf balls: $\qquad P_{12}(x) = P_1(x) + P_2(x)$

Probability distributions of golf ball strikes . . .
Golf balls behave like classical particles

- The fact that we add the probabilities $P_1(x)$ and $P_2(x)$ to get $P_{12}(x)$ is simply stating:

  - The probability of a golf ball that goes through slit 1 landing in $(x, x + \delta x)$ is *completely independent of whether or not slit 2 is open.*

  - The probability of a golf ball that goes through slit 2 landing in $(x, x + \delta x)$ is *completely independent of whether or not slit 1 is open.*

- The above conclusion is perfectly consistent with our classical intuition.

  - Golf balls are particles: they arrive in lumps;

  - They independently pass through *either* slit 1 *or* slit 2 before striking the screen;

  - Their random arrivals are due to erratic behaviour of the source (and maybe random bouncing around as they pass through the slit), all of which, in principle can be measured and allowed for and/or controlled.

An Experiment with Waves

- Now repeat the above series of experiments with *waves* — shall assume light waves of wavelength λ.

- Shall measure the time averaged intensity of the electric field $E(x, t) = E(x) \cos \omega t$ of the light waves arriving at the point x on the observation screen.

  - The time averaged intensity will then be

$$I(x) = \overline{E(x, t)^2} = \tfrac{1}{2} E(x)^2$$

- Can also work with a *complex* field

$$\mathcal{E}(x, t) = \frac{1}{\sqrt{2}} E(x) e^{-i\omega t}$$

so that

$$E(x, t) = \sqrt{2} \operatorname{Re} \mathcal{E}(x, t)$$

and

$$I(x) = \mathcal{E}^*(x, t) \mathcal{E}(x, t) = |\mathcal{E}(x, t)|^2$$

- $I_1(x)$ and $I_2(x)$ are the intensities of the waves passing through slits 1 and 2 respectively and reaching the screen at x. (They are just the central peak of a single slit diffraction pattern.)

- Waves arrive on screen 'all at once', i.e. they do not arrive in lumps, but . . .

- Results similar to single slits with golf balls in that the intensity is peaked directly opposite each open slit.

$I_{12}(x)$

Two slit interference pattern
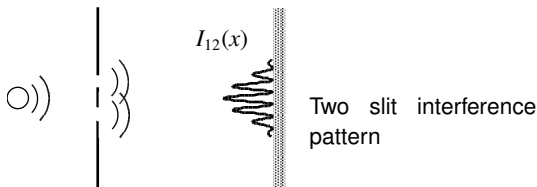
- Interference if both slits are open:

$$I_{12}(x) = \overline{(E_1(x,t) + E_2(x,t))^2} = I_1(x) + I_2(x) + 2E_1E_2\cos\left(\frac{2\pi d\sin\theta}{\lambda}\right)$$

$$= I_1(x) + I_2(x) + 2\sqrt{I_1(x)I_2(x)}\cos\delta$$

- Last term is the *interference* term which explicitly depends on slits separation d — the waves 'probe' the presence of both slits.

- We notice three things about these experiments:

    - The waves arrive 'everywhere at once', i.e. they do not arrive in lumps.

    - The single slit result for waves similar to the single slit result for golf balls.

    - We see interference effects if both slits open for waves, but not for golf balls.

- Now repeat experiment once again, this time with electrons.

- Shall assume a beam of electrons, all with same energy E and momentum p incident on a screen with two slits.

- Shall also assume weak source: electrons pass through the apparatus one at a time.

- Electrons strike a fluorescent screen (causing a flash of light) whose position can be monitored.

fluorescent flashes
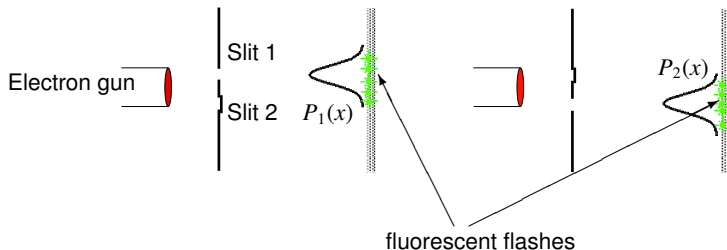
- With one slit open observe electrons striking fluorescent screen in a random fashion, but mostly directly opposite the open slit — exactly as observed with golf balls.

- Can construct probability distributions $P_1(x)$ and $P_2(x)$ for where electrons strike, as for golf balls.

- Apparent randomness in arrival of electrons at the screen could be put down to variations in the electron gun (cf. erratic golfer for golf balls).

An experiment with electrons: both slits open

Electron gun

$P_{12}(x)$

Two slit interference pattern!
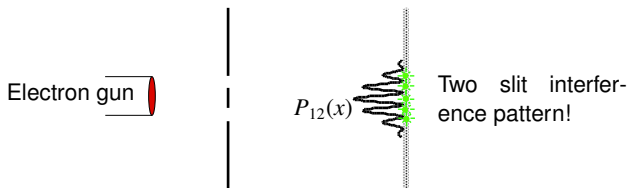
- The following things can be noted:

    - Electrons strike the screen causing individual flashes, i.e. they arrive as particles, just as golf balls do;

    - They strike the screen at random — same as for golf balls.

    - Can construct probability histograms $P_1(x)$, $P_2(x)$ and $P_{12}(x)$ exactly as for golf balls.

- Find that the electron arrivals, and hence the probabilities, form an *interference* pattern — as observed with waves:

$$P_{12}(x) = P_1(x) + P_2(x) + 2\sqrt{P_1(x)P_2(x)} \cos\left(\frac{2\pi d \sin\theta}{\lambda}\right)$$

$$\neq P_1(x) + P_2(x) \text{ — The expected result for particles.}$$

An experiment with electrons: both slits open
Interference of de Broglie waves

- Problem: we have particles arriving in lumps, just like golf balls, i.e. one at a time at localised points in space . . .

- but the pattern formed is that of waves . . .

- and waves must pass through both slits simultaneously, and arrive 'everywhere' on the observation screen at once to form an interference pattern.

- Moreover, from the pattern can determine that $\lambda = h/p$ — the de Broglie relation.

- Interference of de Broglie waves seems to have occurred here!

What is going on here?

- If electrons are particles (like golf balls) then each one must go through either slit 1 or slit 2.

  - A particle has no extension in space, so if it passes through slit 1 say, it cannot possibly be affected by whether or not slit 2, a distance d away, is open.

  - That's why we claim we ought to find that

    $$P_{12}(x) = P_1(x) + P_2(x)$$

    — but we don't.

- In fact, the detailed structure of the interference pattern depends on d, the separation of the slits.

  - So, if an electron passes through slit 1, it must somehow become aware of the presence of slit 2 a distance d away, in order to 'know' where to land on the observation screen so as to produce a pattern that depends on d.

  - i.e. the electrons would have to do some strange things in order to 'know' about the presence of both slits such as travel from slit 1 to slit 2 then to the observation screen.

- Maybe we have to conclude that it is *not true* that the electrons go through either slit 1 or slit 2.

Watching the electrons

- We can check which slit the electrons go through by watching next to each slit and taking note of when an electron goes through each slit.

- If we do that, we get the alarming result that the interference pattern disappears — we regain the result for bullets.

- It is possible to provide an 'explanation' of this result in terms of the observation process unavoidably disturbing the state of the electron.

- Such explanations typically rely on invoking the Heisenberg Uncertainty Principle.
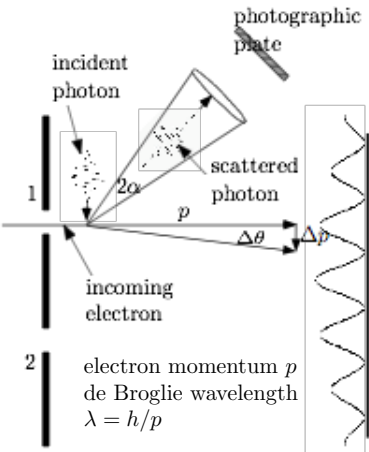
- Weak incident light field: minimum of one photon scatters off electron.

- In order to distinguish the images of the slits in the photographic plate of the microscope, require wavelength of photon at least $\lambda_l \approx d$. Momentum of photon is then $\geq h/d$

- Photon-electron collision gives electron a sideways 'momentum kick' of $\Delta p = h/d$.

- So electron deflected by angle of

$$\Delta\theta \approx \Delta p/p \approx (h/\lambda. \cdot d/h) = d/\lambda$$

- $\Delta\theta$ is approximately the angular separation between an interference maximum and a neighbouring minimum!

An uncertainty relation explanation

- Recall the Heisenberg uncertainty relation for a particle:

$$\Delta x \Delta p \geq \tfrac{1}{2}\hbar$$

  where Δx is the uncertainty in position and Δp is the uncertainty in momentum.

- We could also argue that we are trying to measure the position of the electron to better than an uncertainty $\Delta x \approx d$, the slit separation

  - This implies an uncertainty in 'sideways momentum' of $\Delta p \geq \hbar/2d$

  - This is similar to (but not quite the same as) the deflection $\Delta p = h/d$ obtained in the microscope experiment — a more refined value for Δx is needed.

  - I.e., the requirement that the uncertainty principle (a fundamental result of wave mechanics) has to be obeyed implies that the interference fringes are washed out.

- What if we observed the position of the electron by some other means?

The uncertainty relation protects quantum mechanics

- For *any* means of measuring which slit the electron passes through.

    - The uncertainty relation 'gets in the way' somewhere.

- We always find that

    Any attempt to measure which slit the electron passes through results in no interference pattern!

- The uncertainty relation appears to be a fundamental law that applies to *all* physical situations to guarantee that if we observe 'which path', then we find 'no interference'.

- But: it also appears that a physical intervention, an 'observation' is needed to physically scrambled the electron's momentum.

- In fact, this is not the case!!

    - There exist *interaction-free measurements* that tell 'which path' without touching the electrons!

- Recall: the probability distribution of the electron arrivals on the observation screen is

$$P_{12}(x) = P_1(x) + P_2(x) + 2\sqrt{P_1(x)P_2(x)}\cos\delta$$

- This has the same mathematical form as interference of waves:

$$I_{12}(x) = \overline{(E_1(x,t) + E_2(x,t))^2} = I_1(x) + I_2(x) + 2E_1E_2\cos\left(\frac{2\pi d\sin\theta}{\lambda}\right)$$

$$= I_1(x) + I_2(x) + 2\sqrt{I_1(x)I_2(x)}\cos\delta$$

- Note that the interference term occurs because waves from two slits are added, and then the square is taken of the sum.

- The time average is not an important part of the argument — it is there simply as we are dealing with rapidly oscillating light waves.

- So, it looks like the interference pattern for electrons comes about because waves from each slit are being added, and then the square taken of the sum!!

Interference of de Broglie waves II

- Moreover, the wavelength of these waves in case of electrons is the de Broglie wavelength $\lambda = h/p$

- So can be understood electron interference pattern as arising from the interference of de Broglie waves, each emanating from slit 1 or slit 2, i.e.

$$\Psi_{12}(x,t) = \Psi_1(x,t) + \Psi_2(x,t)$$

and hence

$$\begin{aligned}
P_{12}(x) = |\Psi_1(x,t) + \Psi_2(x,t)|^2 &= |\Psi_1(x,t) + \Psi_2(x,t)|^2 \\
&= |\Psi_1(x,t)|^2 + |\Psi_2(x,t)|^2 + 2\mathrm{Re}\left[\Psi_1^*(x,t)\Psi_2(x,t)\right] \\
&= P_1(x) + P_2(x) + 2\sqrt{P_1(x)P_2(x)}\cos\delta.
\end{aligned}$$

- Probabilities are time independent as we have averaged over a huge number of electron arrivals.

- Note that we have taken the 'modulus squared' since (with the benefit of hindsight) the wave function often turns out to be complex.

Born interpretation of the wave function

- But $\Psi_{12}(x, t)$ is the wave function at the point x at time t.

- And $P_{12}(x) = |\Psi_{12}(x, t)|^2$ is the probability of the particle arriving at x (at time t)

  - So squaring the wave function — a wave amplitude — gives the probability of the particle being observed at a particular point in space.

- This, and other experimental evidence, leads to the interpretation:

  $P(x, t) = |\Psi(x, t)|^2 dx =$ probability of finding the particle in region $(x, x + dx)$ at time t.

  - This is the famous Born probability interpretation of the wave function.

  - As $P(x, t)$ is a probability, then $\Psi(x, t)$ is usually called a probability amplitude (as well as the wave function).

  - From this interpretation follows the result that energy is quantized!

- The Born interpretation of the wave function $\Psi(x, t)$ is

  $P(x, t) = |\Psi(x, t)|^2 dx$ = probability of finding the particle in region $(x, x + dx)$ at time t.

- So what does probability mean?

- To illustrate the idea, consider the following setup:
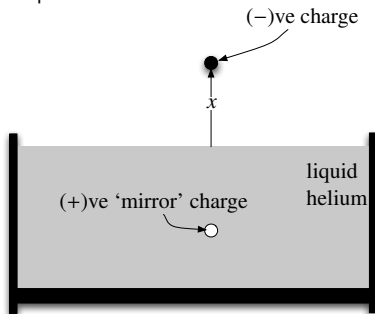
- A negatively charged electron 'floats' above a sea of liquid helium.

  - It is attracted by its 'mirror image charge'

  - But repelled by the potential barrier at the surface of the liquid

  - Classical physics says that it should come to rest on the surface.

  - Quantum mechanics says otherwise.

  - Suppose we have $N = 300$ identical copies of the same arrangement, and we measure the height of the electron above the surface.

Probability interpretation of the wave function II

- Suppose we divide the distance above the surface of the liquid into small segments of size δx

- Measure the height of the electron in each of the N identical copies of the experimental arrangement.

- Let $\delta N(x)$ be the number of electrons found to be in the range x to $x + \delta x$, and form the ratio

$$\frac{\delta N(x)}{N \delta x}$$

$\dfrac{x}{a_0}$	no. of detections $\delta N(x)$ in interval $(x, x + \delta x)$
0	28
0.5	69
1.0	76
1.5	58
2.0	32
2.5	17
3.0	11
3.5	6
4.0	2
4.5	1

$\dfrac{\delta N(x)}{N \delta x}$

$P(x, t) = |\Psi(x, t)|^2 = 4(x^2/a_0^3)e^{-2x/a_0}$

Distance x from surface in units of a_0

- Data on the left plotted as a histogram.

- The ratio $\dfrac{\delta N(x)}{N}$ is the fraction of all the electrons found in the range x to $x + \delta x$.

- In other words

$\dfrac{\delta N(x)}{N} \approx$ probability of finding an electron in the range x to $x + \delta x$

Probability interpretation of the wave function III

- So the **probability** of finding the electron at a certain distance from the liquid helium surface

  - is just the **fraction** of the times that it is found to be at that distance if we repeat the measurement many many times over under identical conditions.

  - The results of the measurements will vary randomly from one measurement to the next.

  - According to the Born interpretation:

    $$\frac{\delta N(x)}{N} \approx \text{probability of finding an electron in the range } x \text{ to } x + \delta x$$
    $$\approx P(x, t)\delta x$$
    $$\approx |\Psi(x, t)|^2 \delta x$$

    where $\Psi(x, t)$ is the wave function for the electron.

- Since the electron **must** be found somewhere between $-\infty$ and ∞, then

$$\sum_{\text{all } \delta x} \frac{\delta N(x)}{N} = \frac{N}{N} = 1$$

Probability interpretation of the wave function IV

- Or, in terms of the wave function, for any particle confined to the x axis, we must have:

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

  - This is known as the **normalization** condition.

  - All acceptable wave functions must be 'normalized to unity'.

  - This means that the integral must converge

- Which tells us that the wave function **must** vanish as $x \to \pm\infty$.

  - This is an important conclusion with enormous consequences.

  - There is one exception: the harmonic wave functions like $A\cos(kx - \omega t)$ which go on forever. See later for their interpretation.

- The requirement that $\Psi(x, t) \to 0$ as $x \to \pm\infty$ is known as a *boundary condition*.

- Used when finding the solution to the Schrödinger equation.

Expectation value

- The results of measuring the position of a particle varies in a random way from one measurement to the next.

- We can use the standard tools of statistics to work out such things as the average value of all the results, or their standard deviation and so on.

- Thus, suppose we have data for the position of a particle in the form

  $\dfrac{\delta N(x)}{N} = $ fraction of all measurements that lie in the range $(x, x + \delta x)$.

  The average of all the results will then be

  $$\langle x \rangle \approx \sum_{\text{all } \delta x} x \frac{\delta N(x)}{N} \approx \sum_{\text{all } \delta x} x P(x, t) \delta x$$
  $$\approx \sum_{\text{all } \delta x} x |\Psi(x, t)|^2 \delta x.$$

- So, in the usual way of taking a limit to form an integral:

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

  known as the expectation value of the position of the particle.

Uncertainty

- We can also calculate the expectation value of any function of x:

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

- A most important example is $\langle x^2 \rangle$:

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

because then we can define the *uncertainty* in the position of the particle:

$$(\Delta x)^2 = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2.$$

- This is a measure of how widely spread the results are around the average, or expectation, value $\langle x \rangle$.

  - The uncertainty Δx is just the *standard deviation* of a set of randomly scattered results.

Example of expectation value and uncertainty I

- Can use the data from before (where $a_0 \approx 7.6$ nm)

$\dfrac{x}{a_0}$	no. of detections $\delta N(x)$ in interval $(x, x + \delta x)$
0	28
0.5	69
1.0	76
1.5	58
2.0	32
2.5	17
3.0	11
3.5	6
4.0	2
4.5	1

- The average value of the distance of the electron from the surface of the liquid helium will be

$$\langle x \rangle \approx 0 \times \frac{28}{300} + 0.5a_0 \times \frac{69}{300} + a_0 \times \frac{76}{300} + 1.5a_0 \times \frac{58}{300}$$
$$+ 2a_0 \times \frac{32}{300} + 2.5a_0 \times \frac{17}{300} + 3a_0 \times \frac{11}{300} + 3.5a_0$$
$$+ 4a_0 \times \frac{2}{300} + 4.5a_0 \times \frac{1}{300}$$
$$= 1.235a_0.$$

This can be compared with the result that follows for the expectation value calculated from the wave function for the particle:

$$\langle x \rangle = \int_{-\infty}^{+\infty} x \, |\Psi(x,t)|^2 \ dx = \frac{4}{a_0^3} \int_0^\infty x^3 \, e^{-2x/a_0} \ dx = 1.5a_0$$

Example of expectation value and uncertainty II

- Similarly for the uncertainty:
$$(\Delta x)^2 \approx \sum_{\text{all } \delta x} (x - \langle x \rangle)^2 \frac{\delta N(x)}{N}$$

- Using the data from earlier:

$$
\begin{aligned}
(\Delta x)^2 \approx \ & (0 - 1.235)^2 a_0^2 \times \frac{28}{300} + (0.5 - 1.235)^2 a_0^2 \times \frac{69}{300} \\
& + (1 - 1.235)^2 a_0^2 \times \frac{76}{300} + (1.5 - 1.235)^2 a_0^2 \times \frac{58}{300} \\
& + (2 - 1.235)^2 a_0^2 \times \frac{32}{300} + (2.5 - 1.235)^2 a_0^2 \times \frac{17}{300} \\
& + (3 - 1.235)^2 a_0^2 \times \frac{11}{300} + (3.5 - 1.235)^2 a_0^2 \times \frac{6}{300} \\
& + (4 - 1.235)^2 a_0^2 \times \frac{2}{300} + (4.5 - 1.235)^2 a_0^2 \times \frac{1}{300} \\
= \ & 0.751 a_0^2
\end{aligned}
$$

which gives $\Delta x = 0.866 a_0$.

- The exact result using the wave function turns out to be the same.

Particle in infinite potential well I

- Consider a single particle of mass m confined to within a region $0 < x < L$ with potential energy $V = 0$ bounded by infinitely high potential barriers, i.e. $V = \infty$ for $x < 0$ and $x > L$.
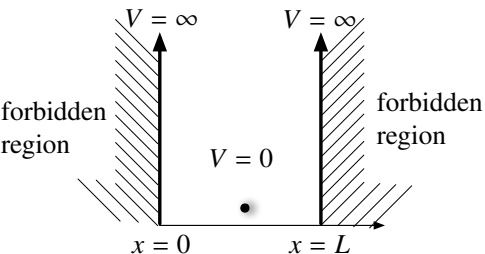
- This simple model is sufficient to describe (in one dimension):
  1. the properties of the conduction electrons in a metal (in the so-called free electron model).
  2. properties of gas particles in an ideal gas where the particles do not interact with each other.

- More realistic models are three dimensional, and the potential barriers are not infinitely high (i.e. the particle can escape).

Deriving the boundary conditions

- The first point to note is that, because of the infinitely high barriers, the particle cannot be found in the regions $x > L$ and $x < 0$.

  - The wave function has to be zero in these regions to guarantee that the probability of finding the particle there is zero.

- If we make the not unreasonable assumption that the wave function has to be continuous, then we must conclude that

$$\Psi(0, t) = \Psi(L, t) = 0.$$

  - These conditions on $\Psi(x, t)$ are known as *boundary conditions*.

- These boundary conditions guarantee that the particle wave function vanishes as $x \to \pm\infty$.

  - The wave function is zero even before we get to infinity!

Constructing the wave function I

- Between the barriers, the energy E of the particle is purely kinetic, i.e. $E = \dfrac{p^2}{2m}$.

- Using the de Broglie relation $p = \hbar k$ we then have $E = \dfrac{\hbar^2 k^2}{2m} \;\Rightarrow\; k = \pm\dfrac{\sqrt{2mE}}{\hbar}$

  - We will use k to be the positive value i.e. $k = \dfrac{\sqrt{2mE}}{\hbar}$.

  - The negative value will be written $-k$.

- From the Einstein-Planck relation $E = \hbar\omega$ we also have $\omega = E/\hbar$.

- So we have the wave number(s) and the frequency of the wave function, but we have to find a wave function that

  - Satisfies the boundary conditions $\Psi(0, t) = \Psi(L, t) = 0$

  - And is normalized to unity.

Constructing the wave function II

- In the region $0 < x < L$ the particle is free, so the wave function must be of the form
  $\Psi(x, t) = A \cos(kx - \omega t)$

  - Or perhaps a combination of such wave functions as we did to construct a wave packet.

  - In fact , we *have* to try a combination as a single term like $\Psi(x, t) = A \cos(kx - \omega t)$ is not zero at $x = 0$ or $x = L$ for all time.

  - Further, we have the picture of the particle bouncing back and forth between the walls, so waves travelling in both directions are probably needed.

- The easiest way to do this is to guess

$$\Psi(x, t) = \underbrace{Ae^{i(kx-\omega t)} + Be^{-i(kx-\omega t)}}_{\text{wave travelling to the right}} + \underbrace{Ce^{i(kx+\omega t)} + De^{-i(kx+\omega t)}}_{\text{wave travelling to the left}}$$

- A, B, C, and D are coefficients that we wish to determine from the boundary conditions and from the requirement that the wave function be normalized to unity for all time.

- First, consider the boundary condition at $x = 0$. Here, we must have

$$\Psi(0, t) = Ae^{-i\omega t} + Be^{i\omega t} + Ce^{i\omega t} + De^{-i\omega t}$$
$$= (A + D)e^{-i\omega t} + (B + C)e^{i\omega t}$$
$$= 0.$$

This must hold true for all time, which can only be the case if $A + D = 0$ and $B + C = 0$.

- Thus we conclude that we must have

$$\Psi(x, t) = Ae^{i(kx-\omega t)} + Be^{-i(kx-\omega t)} - Be^{i(kx+\omega t)} - Ae^{-i(kx+\omega t)}$$
$$= A(e^{ikx} - e^{-ikx})e^{-i\omega t} - B(e^{ikx} - e^{-ikx})e^{i\omega t}$$
$$= 2i\sin(kx)(Ae^{-i\omega t} - Be^{i\omega t}).$$

- Now check on the other boundary condition, i.e. that $\Psi(L, t) = 0$, which leads to:

$$\sin(kL) = 0$$

and hence

$$kL = n\pi \quad n \text{ an integer}$$

- This implies that k can have only a restricted set of values given by

$$k_n = \frac{n\pi}{L} \quad n = 1, 2, 3, \ldots$$

  - The negative n do not give a new solution, so we exclude them.

- An immediate consequence of this is that the energy of the particle is limited to the values

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\pi^2 n^2 \hbar^2}{2mL^2} = \hbar\omega_n \quad n = 1, 2, 3, \ldots$$

  i.e. the energy is 'quantized'.

Normalizing the wave function I

- Now check for normalization:

$$\int_{-\infty}^{+\infty} |\Psi(x,t)|^2\, dx = 4\left|Ae^{-i\omega t} - Be^{i\omega t}\right|^2 \int_0^L \sin^2(k_n x)\, dx = 1$$

  - We note that the limits on the integral are $(0, L)$ since the wave function is zero outside that range.

- This integral must be equal to unity for all time, i.e. the integral cannot be a function of time. But

$$\left|Ae^{-i\omega t} - Be^{i\omega t}\right|^2 = (Ae^{-i\omega t} - Be^{-i\omega t})(A^* e^{i\omega t} - B^* e^{-i\omega t})$$
$$= AA^* + BB^* - AB^* e^{-2i\omega t} - A^* B e^{2i\omega t}$$

which is time dependent!!

- Can make sure the result is time independent by supposing either $A = 0$ or $B = 0$.

  - It turns out that either choice can be made — we will make the conventional choice and put $B = 0$.

Normalizing the wave function II

- The wave function is then

$$\Psi(x, t) = 2iA \sin(k_n x)e^{-i\omega t}$$

but we still haven't finished normalizing the wave function!

- I.e. we still have to satisfy

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 \, dx = 4|A|^2 \int_0^L \sin^2(k_n x) = 2|A|^2 L = 1$$

- This tells us that

$$A = \sqrt{\frac{1}{2L}}e^{i\phi}$$

where ϕ is an unknown phase factor.

- Nothing we have seen above can give us a value for ϕ, but it turns out not to matter (it always found to cancel out).

Normalizing the wave function III

- We can choose ϕ to suit ourselves so we will choose $\phi = -\pi/2$ and hence

$$A = -i\sqrt{\frac{1}{2L}}.$$

- The wave function therefore becomes

$$\Psi_n(x,t) = \sqrt{\frac{2}{L}}\sin(n\pi x/L)e^{-i\omega_n t} \quad 0 < x < L$$
$$= 0 \qquad\qquad\qquad x < 0, \quad x > L.$$

  with associated energies $\quad E_n = \dfrac{\pi^2 n^2 \hbar^2}{2mL^2} \quad n = 1, 2, 3, \ldots.$

- The wave function and the energies have been labelled by the quantity n, known as a *quantum number*.

- The quantum number n can have the values $n = 1, 2, 3, \ldots$ (negative numbers do not give anything new)

  - $n = 0$ is excluded, for then the wave function vanishes everywhere — there is no particle!

- The particle can only have *discrete* energies E_n

  - The lowest energy, E_1 is greater than zero, as is required by the uncertainty principle.

  - Recall uncertainty in position is $\Delta x \approx \frac{1}{2}L$ and uncertainty in momentum is $\Delta p \approx p$, so, by the uncertainty relation

  $$\Delta x \Delta p \gtrsim \hbar \;\; \Rightarrow \;\; p \gtrsim \frac{2\hbar}{L} \;\; \Rightarrow \;\; E \gtrsim \frac{2\hbar^2}{mL^2} \approx E_1.$$

- Classically the particle can have any energy ≥ 0.

- This phenomenon of energy quantization is to be found in all systems in which a particle is confined by an attractive potential.

  - E.g. the Coulomb potential binding an electron to a proton in the hydrogen atom, or the attractive potential of a simple harmonic oscillator.

- In all cases, the boundary condition that the wave function vanish at infinity *guarantees that only a discrete set of wave functions are possible*.

- Each allowed wave function is associated with a certain energy – hence the energy levels of the hydrogen atom, for instance.

Some Properties of Infinite Well Wave Functions

The above wave functions can be written in the form

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} \sin(n\pi x/L) e^{-iE_n t/\hbar} = \psi_n(x) e^{-iE_n t/\hbar}$$

the time dependence is a complex exponential of the form $\exp[-iE_n t/\hbar]$. The time dependence of the wave function for any system in a state of given energy is always of this form.

The factor $\psi_n(x)$ contains all the spatial dependence of the wave function.

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

Note a 'pairing' of the wave function $\psi_n(x)$ with the allowed energy E_n. The wave function $\psi_n(x)$ is known as an energy eigenfunction and the associated energy is known as the energy eigenvalue.

Probability Distributions I

- The probability distributions corresponding to the wave functions obtained above are

$$
\begin{aligned}
P_n(x) &= |\Psi_n(x, t)|^2 \\
&= \left| \sqrt{\frac{2}{L}} \sin(n\pi x/L) e^{-iE_n t/\hbar} \right|^2 \\
&= \frac{2}{L} \sin^2(n\pi x/L) \qquad 0 < x < L \\
&= 0 \qquad\qquad\qquad x < 0, \quad x > L
\end{aligned}
$$

- These are all independent of time, i.e. these are analogous to the stationary states of the hydrogen atom introduced by Bohr – states whose properties do not change in time.

- The nomenclature 'stationary state' is retained in modern quantum mechanics for such states.

Probability Distributions II
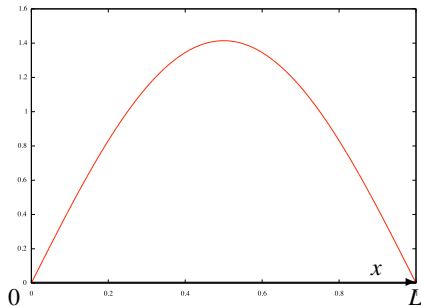
$$\psi_1(x) = \sqrt{\frac{2}{L}} \sin(\pi x/L) \qquad\qquad P_1(x) = \frac{2}{L} \sin^2(\pi x/L)$$
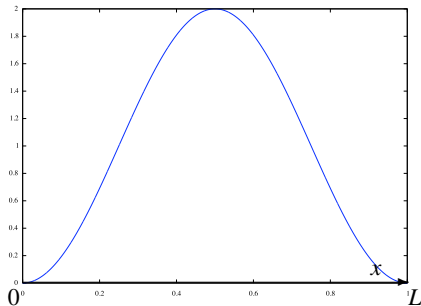
- Note that the probability is not uniform across the well. In this case there is a maximum probability of finding the particle in the middle of the well.

Probability Distributions III
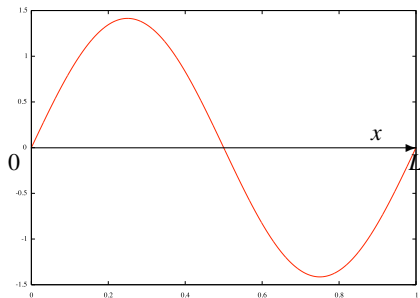
$$\psi_2(x) = \sqrt{\frac{2}{L}} \sin(2\pi x/L) \qquad P_2(x) = \frac{2}{L} \sin^2(2\pi x/L)$$
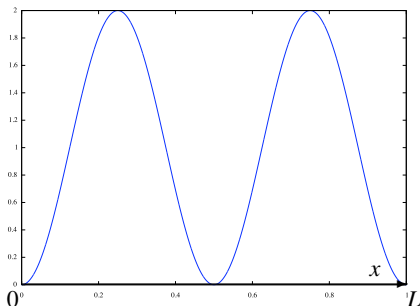
- Once again, the probability distribution is not uniform.

- However, here, there is are two maxima, at $x = L/3$ and $x = 2L/3$ with a zero in between.

- Seems to suggest that the particle, as it bounces from side to side does not pass through the middle!

$$\psi_3(x) = \sqrt{\frac{2}{L}} \sin(3\pi x/L)$$

$$P_3(x) = \frac{2}{L} \sin^2(3\pi x/L)$$
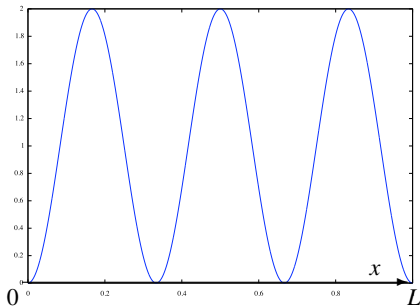
- Yet more maxima.
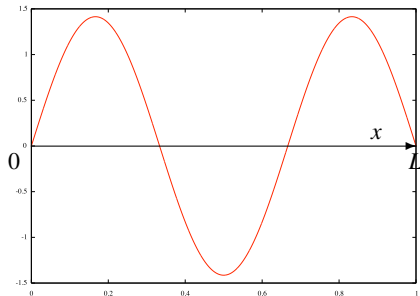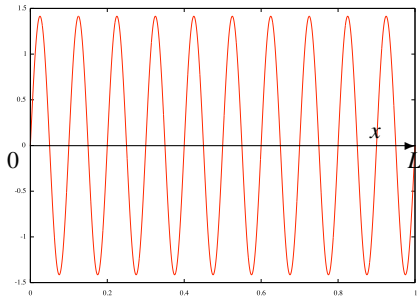
$$\psi_{20}(x) = \sqrt{\frac{2}{L}} \sin(20\pi x/L) \qquad\qquad P_{20}(x) = \frac{2}{L} \sin^2(20\pi x/L)$$
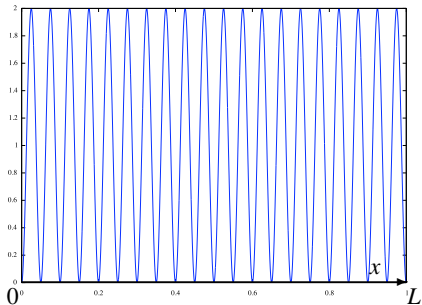
- If n becomes very large the probability oscillates very rapidly, averaging out to be $1/L$, so that the particle is equally likely to be found anywhere in the well.

- This is what would be found classically if the particle were simply bouncing back and forth between the walls of the well and observations were made at random times, i.e. the chances of finding the particle in a region of size δx will be $\delta x/L$.

Expectation values and uncertainties I

- Recall that if we were to measure the position of the particle in the well many many times

    - Making sure before each measurement that the particle has the *same* wave function $\Psi(x, t)$ each time — it is in the same state each time.

    - We get a random scatter of results whose average value will be

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

    - And whose standard deviation Δx is

    $$(\Delta x)^2 = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$$

- For a particle in an infinite potential well in the state given by the wave function $\Psi_n(x, t)$, we have

$$|\Psi_n(x,t)|^2 = \frac{2}{L} \sin^2(n\pi x/L) \quad 0 < x < L$$

so the expectation value is

$$\langle x \rangle = \frac{2}{L} \int_0^L x \sin^2(n\pi x/L) \, dx = \tfrac{1}{2}L$$

Expectation values and uncertainties II

- I.e. the expectation value is in the middle of the well.

  - Note that this does not necessarily correspond to where the probability is a maximum. In fact, for, say $n = 2$, the particle is most likely to be found in the vicinity of $x = L/4$ and $x = 3L/4$.

- To calculate the uncertainty in the position, we need

$$\langle x^2 \rangle = \frac{2}{L} \int_0^L x^2 \sin^2(n\pi x/L)\, dx = L^2 \frac{2n^2\pi^2 - 3}{6n^2\pi^2}.$$

- Consequently, the uncertainty in position is

$$(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2 = L^2 \frac{n^2\pi^2 - 3}{n^2\pi^2} - \frac{L^2}{4} = L^2 \frac{n^2\pi^2 - 6}{12n^2\pi^2}.$$

Further developments

- The basic ideas presented till now can be extended in a number of ways:

  - Look at the properties of combinations of infinite square well wave functions, e.g.

  $$\Psi(x, t) = \frac{1}{\sqrt{2}} \left(\Psi_1(x, t) + \Psi_2(x, t) \right)$$

  - This we can do already: find that this is not a stationary state, i.e. the probability $|\Psi(x, t)|^2$ oscillates in time.

- Work out expectation values of other quantities e.g. energy or momentum.

- Work out the wave function for particles in other potentials, or for more complex particles (e.g. atoms, molecules, solid state, gases, liquids, . . .)

  - The last set of aims can only be realised once we have the equation that the wave function satisfies: the Schrödinger wave equation.

- There is no true derivation of this equation.

    - But its form can be motivated by physical and mathematical arguments at a wide variety of levels of sophistication.

- Here we will 'derive' the Schrödinger equation based on what we have learned so far about the wave function.

- The starting point is to work out, once and for all, what the wave function is for a particle of energy E and momentum p.

    - In the absence of any further information, we have used $\cos(kx - \omega t)$ and other harmonic functions.

    - But the correct result we get from the solution for the wave function of a particle in an infinite potential well.

Derivation of the Schrödinger wave equation II

- For the particle of energy $E = \hbar\omega$ and momentum $p = \hbar k$ (we won't worry about the n subscript here), this wave function is:

$$\Psi(x,t) = \sqrt{\frac{2}{L}} \sin kx e^{-i\omega t} = -i\sqrt{\frac{1}{2L}} \left(e^{ikx} - e^{-ikx} \right) e^{-i\omega t} = -i\sqrt{\frac{1}{2L}} \left(e^{i(kx-\omega t)} - e^{-i(kx+\omega t)} \right)$$

  - Classically, we would expect the particle to bounce back and forth within the well.

  - Here we have (complex) waves travelling to the left: $e^{-i(kx+\omega t)}$, and right: $e^{-i(kx-\omega t)}$.

  - This suggests that the correct wave function for a particle of momentum p and energy E travelling in the positive x direction is

    $$\Psi(x,t) = Ae^{i(kx-\omega t)}$$

    .

- We want to find out what equation this particular function is the solution of.

  - All dynamical laws in nature involve 'rates of change' e.g. velocity and acceleration in Newton's laws.

  - The rates of change here will be with respect to both time t and position x, i.e. we will end up with *a partial differential equation*.

Derivation of the Schrödinger wave equation III

- Taking derivatives with respect to position first gives:

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

- This can be written, using $E = p^2/2m = \hbar^2 k^2/2m$ as:

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

- Similarly, taking the derivatives with respect to time:

$$\frac{\partial \Psi}{\partial t} = -i\omega \Psi$$

- This can be written, using $E = \hbar\omega$ as

$$i\hbar \frac{\partial \Psi}{\partial t} = \hbar\omega\psi = E\Psi.$$

Derivation of the Schrödinger wave equation IV

- We now generalize this to the situation in which there is both a kinetic energy and a potential energy present, then $E = p^2/2m + V(x)$ so that

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

where Ψ is now the wave function of a particle in the presence of a potential $V(x)$.

- Assuming that $-\dfrac{\hbar^2}{2m}\dfrac{\partial^2\Psi}{\partial x^2} = \dfrac{p^2}{2m}\Psi$ and $i\hbar\dfrac{\partial\Psi}{\partial t} = \hbar\omega\psi = E\Psi$ still hold true then we get

$$
\begin{array}{ccc}
\dfrac{p^2}{2m}\Psi & + \quad V(x)\Psi \quad = & E\Psi \\
\downarrow & \downarrow & \downarrow \\
-\dfrac{\hbar^2}{2m}\dfrac{\partial^2\Psi}{\partial x^2} & + \quad V(x)\Psi \quad = & i\hbar\dfrac{\partial\Psi}{\partial t}
\end{array}
$$

- Thus we arrive at $\quad -\dfrac{\hbar^2}{2m}\dfrac{\partial^2\Psi}{\partial x^2} + V(x)\Psi = i\hbar\dfrac{\partial\Psi}{\partial t}\quad$ which is the famous time dependent

Schrödinger wave equation.

Some comments on the Schrödinger equation

- The solution to the Schrödinger equation describes how the wave function changes as a function of space and time.

- But it does not tell us how a particle moves through space.

    - Newton's equations tell us the position and velocity of a particle as it moves through space

    - Schrödinger's equation tells us how *the information about the particle* changes with time.

- Though called a wave equation, it does not always have wave-like solutions.

    - If the potential is attractive, i.e. tends to pull particles together, such as a Coulomb force pulling an electron towards an atomic nucleus, then the wave function is not a wave at all: these are called *bound states.*

    - In other cases, the particle is free to move anywhere in space: these are called *unbound or scattering* states.

- There is a whole industry built around solving the Schrödinger equation — in principle all of chemistry flows from solving the Schrödinger equation.

- We will concentrate on one part of solving the Schrödinger equation: obtaining the wave function for a particle of a given energy E.

- We saw that for the particle in an infinitely deep potential well that for a particle of energy E, the solution looked like

$$\Psi(x, t) = \sqrt{\frac{2}{L}} \sin(kx) e^{-iEt/\hbar} = \psi(x) e^{-iEt/\hbar}$$

where the space and time parts of the wave function occur as separate factors.

- This suggests trying a solution like this for the Schrödinger wave equation, i.e. putting

$$\Psi(x, t) = \psi(x) e^{-iEt/\hbar}$$

- If we substitute this trial solution into the Schrödinger wave equation, and make use of the meaning of partial derivatives, we get:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} e^{-iEt/\hbar} + V(x)\psi(x)e^{-iEt/\hbar} = i\hbar. - iE/\hbar e^{-iEt/\hbar}\psi(x) = E\psi(x)e^{-iEt/\hbar}.$$

- The factor $\exp[-iEt/\hbar]$ cancels from both sides of the equation, giving

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

- After rearranging terms:

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

  which is the *time independent Schrödinger equation*.

- Note that the quantity E — the energy of the particle — is a free parameter in this equation.

  - I.e. we can freely choose a value for E and solve the equation.

  - Can emphasize this by writing the solution as $\psi_E(x)$.

- It appears that we would get a solution for any energy we choose, but it is not as simple as that . . .

The nature of the solutions

- The solutions to the Schrödinger equation assume two different forms:

  - Those for 'bound states', i.e. where the particle is trapped by an attractive potential, e.g. the electron in a hydrogen atom is bound to the proton by an attractive Coulomb potential.

    - The wave function must vanish as $x \to \pm\infty$.

    - This leads to the quantization of energy.

  - Those for 'scattering states' where the particle is free to move through space, though its behaviour is influenced by the presence of some potential, e.g. an alpha particle scattering off a gold nucleus as in the original experiments by Rutherford.

    - The wave function does not vanish as $x \to \pm\infty$: in fact it looks something like $e^{i(kx-\omega t)}$.

    - Have to be careful (creative?) with the probability interpretation of Ψ.

  - In addition, there is a technical requirement: $\psi(x)$ and $\psi'(x)$ must be continuous.

    - This is to guarantee that probability and the 'flow of probability' behave as they should.

- We will illustrate the two kinds of solutions in two important examples:

  - Harmonic oscillator

  - Scattering by a potential barrier.

The harmonic oscillator
Schrödinger equation

- The quantum harmonic oscillator is one of the most important solved problems in quantum mechanics. It is the basis of the description of

    - Molecular vibrations.

    - Sound propagation in solids (phonons).

    - The quantum theory of the electromagnetic field.

    - The theory of the particles known as bosons.

- A *classical* harmonic oscillator consists of a particle of mass m subject to a restoring force proportional to the displacement of the particle, i.e. $F = -kx$.

    - It undergoes simple harmonic motion $x = A\cos(\omega t + \phi)$ of frequency $\omega = \sqrt{k/m}$.

- To determine the properties of a quantum simple harmonic oscillator, we need the potential energy of such an oscillator. This is just $V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2$.

- The quantum mechanical simple harmonic oscillator of energy E is then described by the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi$$

Allowed energies of the quantum harmonic oscillator

- Recall that E is a free parameter that we can choose as we like.

- Unfortunately, for almost all choices of E we run into an awkward problem: the solution looks like

$$\psi(x) \approx \pm e^{\frac{1}{2}(x/a)^2} \quad \text{for} \quad x \to \pm\infty \quad a = \sqrt{\frac{\hbar}{m\omega}},$$

  i.e. it diverges.

  - We shall see an example shortly.

- So, what's wrong with that?

  - Recall that the solution must be normalized to unity, i.e. we must have

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

  and that can only happen if $\psi(x) \to 0$ as $x \to \pm\infty$.

- Only if the energy is chosen to be

$$E_n = (n + \tfrac{1}{2})\hbar\omega \quad n = 0, 1, 2, \ldots$$

do we get solutions that vanish as $x \to \pm\infty$.

Unacceptable solutions of SHO Schrödinger equation

- We can illustrate this by plotting the solutions as a function of E, starting at E less than $\frac{5}{2}\hbar\omega$ and slowly increasing until E reaches $\frac{5}{2}\hbar\omega$ (i.e. $n = 2$).

  - The solutions initially diverge to $-\infty$ for $x \to \pm\infty$ but as E approaches $\frac{5}{2}\hbar\omega$, the solution tends to extend along the x axis, ultimately asymptoting to zero along the x axis.

Comparison of quantum and classical energies.

- Once again, we see that the energy is quantized

$$E_n = (n + \tfrac{1}{2})\hbar\omega,$$

  and the lowest energy, $E_0 = \tfrac{1}{2}\hbar\omega$ is > 0.

  - This is the same situation as found with the particle in the infinite potential well.

  - Classically, the lowest energy would be zero, but once again, because of the uncertainty relation $\Delta x \Delta p \geq \tfrac{1}{2}\hbar$, the lowest energy is *not* zero.

- Suppose we had a *classical* oscillator of total energy $\tfrac{1}{2}\hbar\omega$.

- The amplitude a of oscillation of such an oscillator will be given by

$$\tfrac{1}{2}m\omega^2 a^2 = \tfrac{1}{2}\hbar\omega$$

  which we can solve to give $a = \sqrt{\dfrac{\hbar}{m\omega}}$.

- Later we will see that the quantum oscillator in its ground state can have an amplitude that is bigger than a!!!

The wave functions of a quantum SHO

- The wave functions for the allowed values of energy look like:

$$\psi_n(x) = \sqrt{\frac{1}{2^n n! a \sqrt{\pi}}} \, H_n(x/a) e^{-\frac{1}{2}(x/a)^2}$$

where $H_n(z)$ are known as the Hermite polynomials:

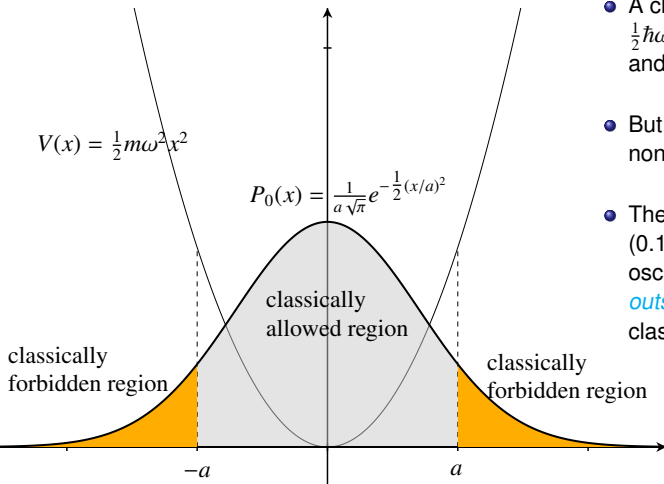$$H_0(z) = 1 \quad H_1(z) = z \quad H_2(z) = z^2 - 1 \quad \text{etc.}$$

- For $n = 0$, the solution is:

$$E_0 = \tfrac{1}{2}\hbar\omega \quad \psi_0(x) = \sqrt{\frac{1}{a\sqrt{\pi}}} e^{-\frac{1}{2}(x/a)^2} \quad P_0(x) = |\psi_0(x)|^2 = \frac{1}{a\sqrt{\pi}} e^{-(x/a)^2}.$$

- We can use this solution to show non-classical behaviour of a quantum harmonic oscillator.

Non-classical properties of quantum SHO

- The ground state probability distribution $P_0(x)$ and the potential $V(x)$ are plotted on the same figure:

$V(x) = \frac{1}{2}m\omega^2 x^2$

$P_0(x) = \frac{1}{a\sqrt{\pi}}e^{-\frac{1}{2}(x/a)^2}$

classically allowed region

classically forbidden region

classically forbidden region

$-a$

a

- A classical oscillator of energy $\frac{1}{2}\hbar\omega$ will oscillate between $-a$ and $+a$.

- But the wave function is non-zero for $x > a$ and $x < -a$.

- There is a non-zero probability (0.1573) of finding the oscillating mass in a region *outside* the allowed range of a classical oscillator.

Quantum scattering

- The other class of problems that can arise are so-called *scattering problems*

  - Scattering problems involve particles that are not bound by an attractive potential.

  - The wave function does not vanish at infinity so the usual probability interpretation is no longer valid, but we can still make sense of the solutions.

- Find that quantum mechanics allows particles to access regions in space that are classically forbidden.

  - I.e. according to classical physics, the particle does not have enough energy to get to some regions in space, but quantum mechanically, this has a non-zero probability of occurring.

  - Have already seen this occurring with the simple harmonic oscillator.

- The possibility of a particle being found in forbidden regions in space gives rise to barrier penetration and quantum tunnelling.

- Shall look at the first in detail, the latter in outline.

Scattering by a potential barrier
The classical version

- Shall consider a particle of energy E incident on a potential barrier V_0 with $E < V_0$.

- Consider the classical version of the problem:
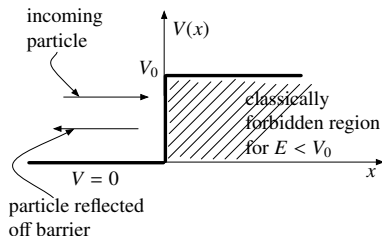
- The diagram shows a barrier defined by

$$V(x) = 0 \qquad x < 0$$
$$= V_0 \qquad x > 0$$

- For $x < 0$, as $V = 0$, the particle will have entirely kinetic energy $E = \dfrac{p^2}{2m}$.

- For $x > 0$ its energy will be $E = \dfrac{p'^2}{2m} + V_0$.

  - But $E < V_0 \;\Rightarrow\; \dfrac{p'^2}{2m} < 0$ i.e. it has *negative kinetic energy* which is impossible.

  - Thus the region $x > 0$ is classically forbidden, i.e. a particle cannot reach the region $x > 0$ as it does not have enough energy.

  - The particle must simply bounce off the barrier.

Schrödinger equation for potential barrier

- Recall that the time independent Schrödinger equation is given by

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

  for a particle of energy E moving in the presence of a potential $V(x)$.

- Here, the potential has two parts: $V = 0$ for $x < 0$ and $V = V_0$ for $x > 0$.

  - The Schrödinger equation will also have two parts (with $\frac{d^2\psi}{dx^2} = \psi''$):

$$-\frac{\hbar^2}{2m}\psi'' + 0.\psi = E\psi \qquad x < 0$$
$$-\frac{\hbar^2}{2m}\psi'' + V_0\psi = E\psi \qquad x > 0$$

- We have to solve both these equations, and then 'join the solutions together' so that $\psi(x)$ and $\psi'(x)$ are continuous.

- We do not get energy quantization, but we do get other strange results.

Solution of Schrödinger equation for potential barrier I

- We can rewrite these equations in the following way:

$$\psi'' + \frac{2mE}{\hbar^2}\psi = 0 \qquad x < 0$$

$$\psi'' - \frac{2m}{\hbar^2}(V_0 - E)\psi = 0 \qquad x > 0$$

- For $x < 0$, the energy is entirely kinetic as $V = 0$, so

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \qquad \text{using } p = \hbar k \;\Rightarrow\; k^2 = \frac{2mE}{\hbar^2}$$

- We will put $k = +\frac{\sqrt{2mE}}{\hbar}$ so the first equation becomes

$$\psi'' + k^2\psi = 0 \qquad x < 0$$

which has the general solution

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \qquad x < 0 \qquad A \text{ and } B \text{ are unknown constants.}$$

- This solution can be confirmed by substituting it back into the equation on the left hand side, and showing that the result equals the right hand side, i.e. $= 0$.
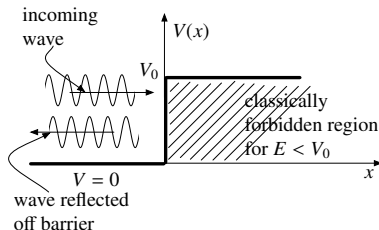
Solution of Schrödinger equation for potential barrier II

- The physical meaning of this solution is best found by putting back the time dependence.

  - Recall that the solution to the time dependent wave equation for a particle of energy E is

  $$\Psi(x, t) = \psi(x)e^{-iEt/\hbar} = \psi(x)e^{-i\omega t} \quad E = \hbar\omega$$

- In this case we have

$$
\begin{array}{ccccc}
\Psi(x, t) & = & Ae^{i(kx-\omega t)} & + & Be^{-i(kx+\omega t)} \\
 & & \downarrow & & \downarrow \\
 & = & \text{wave travelling to the right} & + & \text{reflected wave travelling to the left}
\end{array}
$$

Solution of Schrödinger equation for potential barrier III

- For the region $x > 0$, we have to solve

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

- We are interested in the case in which $E < V_0$, i.e. $V_0 - E > 0$

    - This is the case in which the particle has insufficient energy to cross over into $x > 0$.

- So we put

$$\alpha = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)} \quad \text{where } \alpha > 0$$

    to give

$$\psi'' - \alpha^2\psi = 0$$

    which has the solution

$$\psi(x) = Ce^{-\alpha x} + De^{\alpha x} \quad C \text{ and } D \text{ unknown constants.}$$

- We can check that this is indeed a solution by substituting the expression into the equation for $\psi(x)$.

Solution of Schrödinger equation for potential barrier IV

- There is a problem with this solution:

    - As $\alpha > 0$, the contribution $e^{\alpha x}$ will grow to infinity as $x \to \infty$.

    - This would mean that the probability of finding the particle at $x = \infty$ would be infinite, which is not physically acceptable.

        - This is a boundary condition once again.

    - So we must remove the $e^{\alpha x}$ contribution by putting $D = 0$ leaving:

        $$\psi(x) = Ce^{-\alpha x} \qquad x > 0.$$

- If we put the time dependence back in, we get

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

    which is NOT a travelling wave.

    - The particle is not 'moving' in the region $x > 0$.

Matching the two solutions

- Our overall solution so far is

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \qquad x < 0$$
$$\psi(x) = Ce^{-\alpha x} \qquad x > 0$$

- These solutions must join together smoothly at $x = 0$.

  - This requires $\psi(x)$ and $\psi'(x)$ to be continuous at $x = 0$.

- The first matching condition gives

$$\left(Ae^{ikx} + Be^{-ikx}\right)_{x=0} = \left(Ce^{-\alpha x}\right)_{x=0}$$

i.e. $\qquad\qquad A + B = C$

- The second matching condition gives

$$\left(Aike^{ikx} - Bike^{-ikx}\right)_{x=0} = \left(-\alpha Ce^{-\alpha x}\right)_{x=0}$$

i.e. $\qquad\qquad ik(A - B) = -\alpha C$

- These two equations can be easily solved for B and C in terms of A:

$$B = \frac{ik + \alpha}{ik - \alpha}A \qquad C = \frac{2ik}{ik - \alpha}A$$

Interpreting the solutions I

- We can write out the full solution as

$$\psi(x) = Ae^{ikx} + \frac{ik + \alpha}{ik - \alpha}Ae^{-ikx} \qquad x < 0$$

$$= A \cdot \frac{2ik}{ik - \alpha}e^{-\alpha x} \qquad x > 0.$$

- We have a bit of difficulty using the usual probability interpretation as we cannot normalize this solution.

  - I.e. there is no way for

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

  as the waves for $x < 0$ do not go to zero as $x \to -\infty$.

- But let's work out $|\psi(x)|^2$ anyway for these waves for $x < 0$ to see what they could mean:

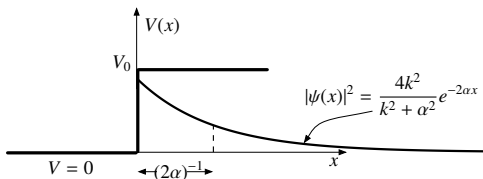$$|\psi(x)|^2 \text{ for incident waves } = |A|^2$$

$$|\psi(x)|^2 \text{ for reflected waves } = |A|^2 \cdot \left|\frac{ik + \alpha}{ik - \alpha}\right|^2 = |A|^2$$

Interpreting the solutions II

- If these were water waves, or sound waves, or light waves, this would mean that the waves are perfectly reflected at the barrier.

    - For our probability amplitude waves, this seems to mean that the particle has a 100% chance of bouncing off the barrier and heading back the other way.

    - Recall: the particle has an energy which is *less than* V_0, so we would expect that the particle would bounce off the barrier.

    - So this result is no surprise.

    - What we are actually doing here is calculating the 'particle flux' associated with the incident and reflected waves.

- But the wave function is *not zero* inside the barrier!

- For $x > 0$ we have

$$|\psi(x)|^2 = |A|^2 \cdot \left| \frac{2ik}{ik - \alpha} e^{-\alpha x} \right|^2 = |A|^2 \frac{4k^2}{\alpha^2 + k^2} e^{-2\alpha x}.$$

- This means that there is a non-zero probability of the particle being observed *inside the barrier*. This is the region which is *classically forbidden*.

- The particle will penetrate a distance $\sim 1/2\alpha$ into the wall.

The figure shows $V(x)$ with a potential step of height V_0 at $x = 0$, and $V = 0$ for $x < 0$. The probability density is labelled $|\psi(x)|^2 = \dfrac{4k^2}{k^2 + \alpha^2} e^{-2\alpha x}$, with the distance $(2\alpha)^{-1}$ marked on the x axis.

- Suppose we had a particle detector inside a solid wall and we fired a particle at the wall

  - But its energy is so low that it cannot penetrate through the wall.

- Nevertheless, in the region $x > 0$ inside the wall, there is a chance that the particle detector will register the arrival of the particle!!

  - If the particle is detected, then, of course, there is no reflected wave.

  - If the detector doesn't go off, then there is a reflected wave, i.e. the particle has bounced off the wall.

An example I

- Suppose a particle of energy E approaches a potential barrier of height $V_0 = 2E$.

  - The energy of the particle when it approaches the barrier is purely kinetic:

$$E = \frac{p^2}{2m} \Rightarrow p = \sqrt{2mE}$$

- Using the de Broglie relation $p = \hbar k$, we get as before $k = \dfrac{\sqrt{2mE}}{\hbar}$.

- For the $x > 0$ part of the wave function we have (using $V_0 = 2E$):

$$\alpha = \frac{\sqrt{2m(V_0 - E)}}{\hbar} = \frac{\sqrt{2mE}}{\hbar} = k$$

- Hence $\alpha^{-1} = k^{-1} = \dfrac{\lambda}{2\pi}$. The penetration depth is therefore $\dfrac{1}{2a} = \dfrac{\lambda}{4\pi}$.

- Thus, in this case of $E = \frac{1}{2}V_0$, the penetration depth is roughly the de Broglie wavelength of the incident waves. This gives a convenient estimate of the penetration depth in different cases.

An example II

- Consider two extreme cases:

    - The particle is an electron moving at 1 ms^{-1}, then the penetration depth turns out to be

        $$\frac{1}{2\alpha} = 0.06 \text{ mm} \quad \text{for an electron}$$

    - The particle is a 1 kgm mass also moving at 1ms^{-1}. The penetration depth is then

        $$\frac{1}{2\alpha} = 5.4 \times 10^{-32} \text{ m} \quad \text{for a 1 kg mass.}$$

- Clearly, the macroscopic object effectively shows no penetration into the barrier

    - Hence barrier penetration is unlikely to ever be observed in the macroscopic world.

- The microscopic particle penetrates a macroscopically measurable distance, and so there is likely to be observable consequences of this.

- Perhaps the most important is *quantum tunnelling*.

- If the barrier has only a finite width, then it is possible for the particle to emerge from the other side of the barrier: