Part 1: The Limits of Classical Physics

We start by discussing several situations or experiments that can not be understood using classical ideas. This will introduce the ideas of **quantization** and the important role of **probability**.

Blackbody radiation and the UV catastrophe

What are the properties of electromagnetic radiation in thermal equilibrium with matter at temperature T? Specifically, we would like to know the spectral energy density $u_\nu(T)$, where

$$u_\nu(T)d\nu$$

is the energy per unit volume in radiation with frequency between ν and $\nu + d\nu$. This question comes up when thinking about how electromagnetism and thermodynamics go together.

Exercise 1: What are the units of u_ν?

Let's start off with a reminder about electromagnetic waves and the wave equation in electromagnetism[1]. Maxwell's equations in vacuum $\Rightarrow$

$$\frac{1}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2} = \nabla^2 \mathbf{E}$$

a **wave equation** for the electric field **E** (can write the same thing for the magnetic field **B**). The **plane wave solutions** are[2]

$$\mathbf{E} \propto e^{i\mathbf{k}\cdot\mathbf{r}-i\omega t}$$

where

$$\mathbf{k} = \left(k_x, k_y, k_z\right)$$

is the **wavevector**. The **dispersion relation** is

$$\omega = 2\pi\nu = c\left|\mathbf{k}\right| = c\frac{2\pi}{\lambda}.$$

The wave propagates in the direction $\hat{\mathbf{k}}$.

Now think about electromagnetic waves in thermal equilibrium. How much energy is contained in the waves? A way to calculate this is to use the idea of **equipartition of energy** from classical thermodynamics. In thermal equilibrium, every degree of freedom gets $\frac{1}{2}k_BT$ of energy. For an oscillator, there are two degrees of freedom (kinetic plus potential energy, or here we have **E** and **B**), so the total is k_BT. Each EM wave gets k_BT of energy.

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[1] This is also useful because we'll see the same solutions come up when we solve the Schrödinger equation later.

[2] Recall that when we use complex notation and write the wave as $\propto e^{ikx}$ for example, we really mean $\mathcal{R}e\left(e^{ikx}\right) = \cos kx$. The real part gives the physical quantity.

To calculate the energy density, we just need to know the number of waves per unit volume for a given small frequency range between ν and $\nu + d\nu$. We get this by counting how many standing waves with that frequency fit in a box of volume V. In 1D, the standing waves are uniformly spaced in frequency (wavelength $\propto L/n$ where L is the length of the box, so that frequency $\propto n$). So for any frequency range ν to $\nu + d\nu$ we would get the same number of modes independent of the value of ν. But in 3D, we can distribute the nodes in different ways between the x, y, or z directions,

$$k^2 = k_x^2 + k_y^2 + k_z^2 \propto n_x^2 + n_y^2 + n_z^2$$

where $k^2 = (2\pi\nu)^2/c^2$ is fixed. I'm going to leave the details to the Appendix, and just quote the result here. The number of modes with frequency between ν and $\nu + d\nu$ is

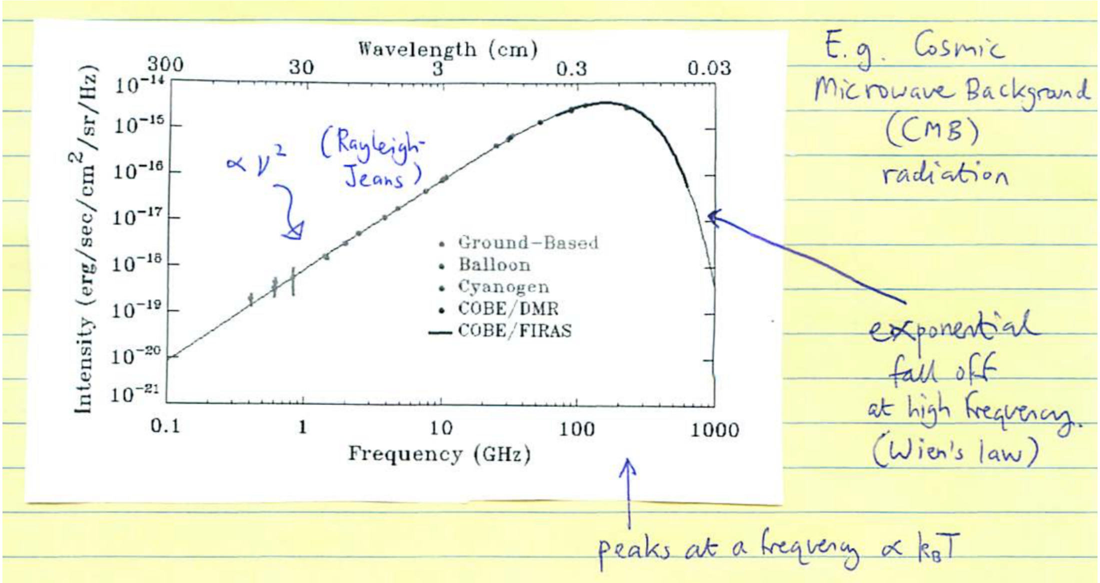
$$\frac{8\pi\nu^2 d\nu}{c^3} V. \tag{1}$$

Note that this is $\propto \nu^2$. As you go to higher frequency/shorter wavelength, there are many more combinations of k_x, k_y and k_z that give the same frequency $\nu = c\,|\mathbf{k}|\,/2\pi$.

If we give each of the standing wave modes $k_B T$ of energy, we get the **Rayleigh-Jeans law**

$$u_\nu(T) = \frac{8\pi\nu^2}{c^3} k_B T. \tag{2}$$

This is the classical equation for the spectral energy density of thermal radiation. It has two major problems! First, observed thermal radiation does show $u_\nu \propto \nu^2$ at low frequency, but sharply turns over at high frequencies:



Second, even just looking at equation (2), we can tell something is wrong. Imagine calculating the total energy density in radiation $U = \int_0^\infty d\nu\; u_\nu$. Because $u_\nu \propto \nu^2$ the integrand diverges at high frequency, and $U \to \infty$! This is called the **ultraviolet (UV) catastrophe**.

Planck's solution

Planck solved this problem by making a simple suggestion, that each mode is **quantized**. At each frequency ν, the energy can only take the discrete values

$$E = nh\nu \qquad\qquad n = 0, 1, 2, ...(\text{integer}).$$

The constant h is **Planck's constant** and has a value

$$h = 6.626 \times 10^{-34}\ \text{Js}.$$

[We will also often use the quantity $\hbar$ ("h-bar")

$$\hbar = 1.055 \times 10^{-34}\ \text{Js}$$

where then the energy is $E = n\hbar\omega$.]

How does this solve the problem? There are two different limits you can imagine. For low frequencies, the spacing between energy levels $h\nu$ is much smaller than the thermal energy $k_B T$. Then the energy $k_B T$ that we want to put into that frequency can easily be accommodated by choosing the right value of n, ie. the value of n closest to $k_b T/h\nu$. For $k_B T \gg h\nu$, we won't notice the slight difference between the actual value of $k_B T/h\nu$ and the nearest integer. This is the **classical limit**.

But in the other limit, at high frequencies where $h\nu \gg k_B T$, the energy required even for $n = 1$ is way more than we have available in thermal energy. You don't then expect those frequencies to have any energy. This is why u_ν turns over at high frequency. This is the **quantum limit**.

Exercise 2: Use the figure on the previous page to estimate the temperature of the cosmic microwave background.

Even when $h\nu > k_B T$, there is always some chance that the mode will have some energy because of thermal fluctuations – the probability that the mode with frequency ν has energy $nh\nu$ is given by a Boltzmann factor $\text{Prob}(n) \propto e^{-nh\nu/k_B T}$. Use this in the following exercise:[3]

Exercise 3: Use this probability to calculate the average energy in the mode with frequency ν at temperature T. Check the limits of your expression when $h\nu \gg k_B T$ and $h\nu \ll k_B T$. Are they what you expect?
You can use the result:

$$\frac{\sum_{n=0}^{\infty} nxe^{-nx}}{\sum_{n=0}^{\infty} e^{-nx}} = \frac{x}{e^x - 1}.$$

What is your prediction for $u_\nu(T)$?

You should find the **Planck spectrum**

$$u_\nu(T) = \frac{8\pi\nu^2 d\nu}{c^3} \frac{h\nu}{e^{h\nu/k_B T} - 1}.$$

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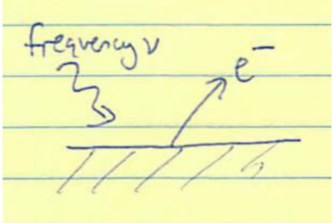
[3] Once again, I have an ulterior motive for asking you to do this, which is to practise using a probability distribution to calculate an average, we'll be doing this later with the wavefunction.

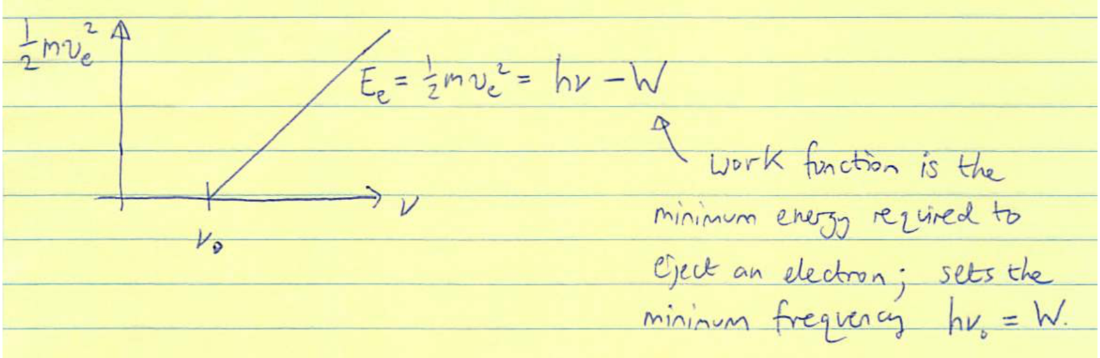
Photoelectric effect

The photoelectric effect is the ejection of electrons from the surface of a metal when illuminated with light.



It has the following properties:

- electrons are emitted only for frequencies larger than a critical value $\nu > \nu_0$
- whether or not electrons are emitted does not depend on the intensity of the radiation, only the frequency
- the current (rate at which electrons are ejected) *does* depend on the intensity
- the electron energy is $\propto \nu$ and independent of intensity



$$E_e = \frac{1}{2}mv_e^2 = h\nu - W$$

work function is the minimum energy required to eject an electron; sets the minimum frequency $h\nu_0 = W$.

> *Exercise 4:* Make sure you can explain why this provides direct evidence that light comes in individual quanta (photons) with energy $\propto \nu$.

Typically the work function is a few eV (1 eV $= 1.6 \times 10^{-19}$ J). Setting $h\nu_0 = 3$ eV gives $\nu_0 \approx 7 \times 10^{14}$ Hz or $\lambda \approx 0.4\ \mu$m. This corresponds to the blue end of optical light.

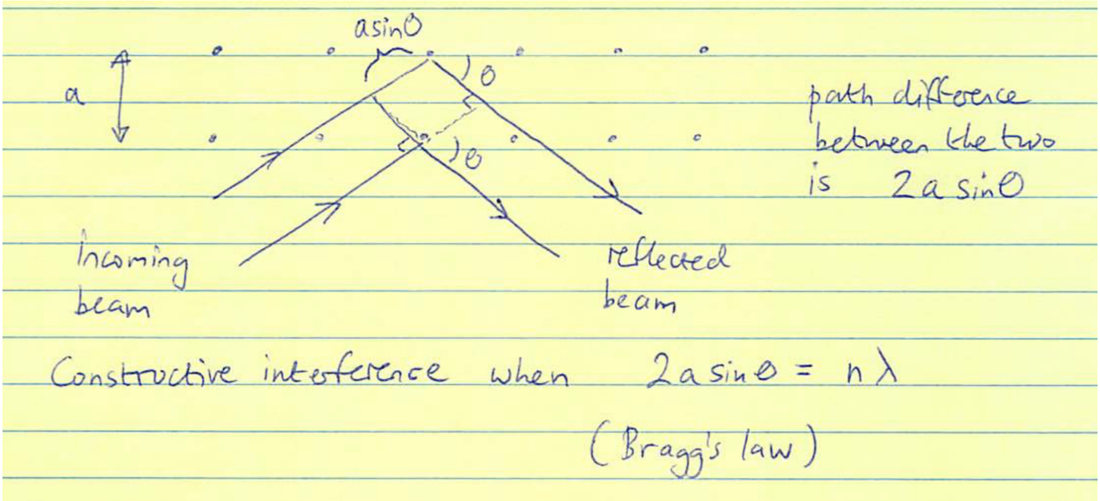
Wave-like nature of particles

De Broglie suggested that a particle with momentum p should have an associated wavelength

$$\lambda = \frac{h}{p},$$

the **de Broglie wavelength**, and that particles such as electrons will show wave character if some critical lengthscale in the system is $\lesssim \lambda$. This is **wave-particle duality**.

An example is electron or neutron diffraction used to study crystal structure:



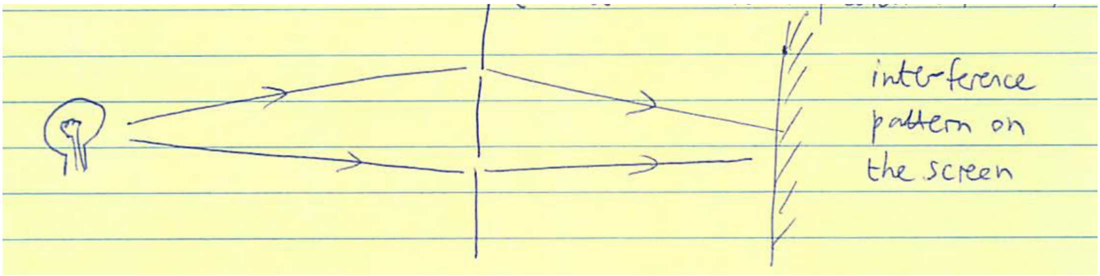
If the crystal spacing is $a \sim 10^{-10}$ m $= 1$Å, then the corresponding electron energy needed to see interference is

$$E_e \sim \frac{1}{2m_e}\left(\frac{h}{\lambda}\right)^2 \sim 3 \times 10^{-17}\ \mathrm{J} \sim 200\ \mathrm{eV}.$$

Exercise 5: What would the energy of neutrons have to be to see interference? Do you think it would be easy to make such a neutron source?

Double-slit experiment

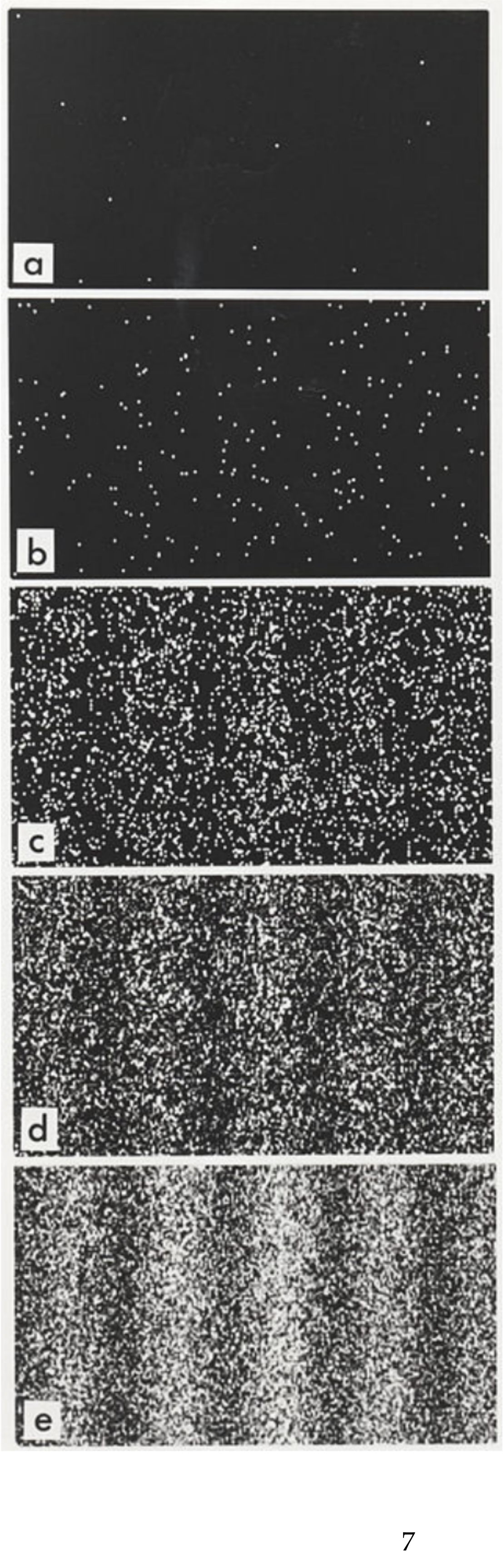
The double-slit experiment emphasizes the role of probability and the statistical nature of predictions in quantum mechanics. Here is the setup, you should know what to expect classically (treating the light as a wave):



Now think about photons. A useful thought experiment is to consider the limit of very low intensity, so that photons are going one by one through the apparatus. The arrival of individual photons can be detected at the screen. Gradually the interference pattern builds up — the wave description is telling us the *probability* that a particle will arrive at any location on the screen. This is shown in the figure on the next page, which I took from wikipedia page on the double-slit experiment.

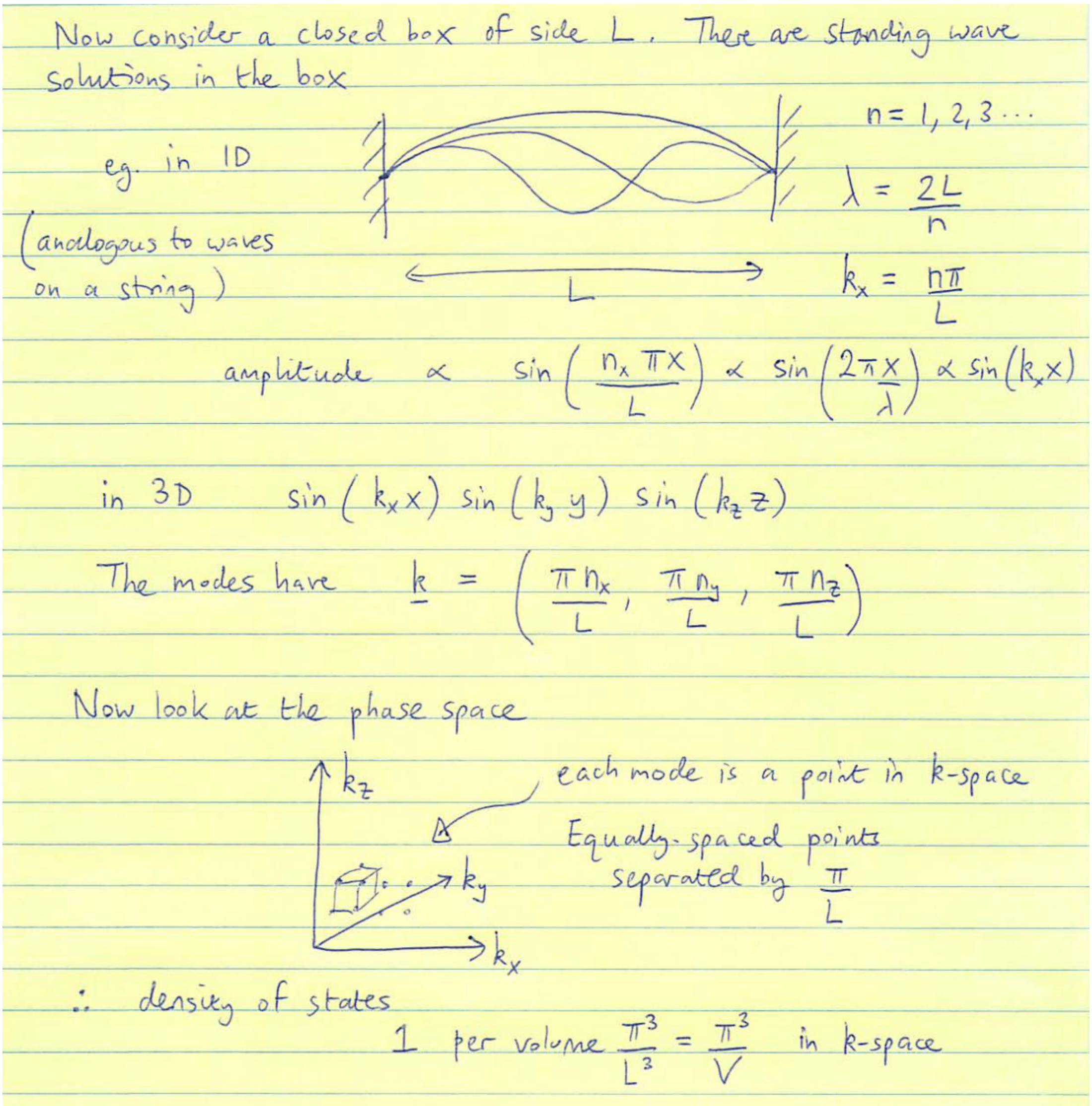
How do we describe this situation? In **wave mechanics**, we will be solving a wave equation (the **Schrödinger equation**) for a quantity Ψ (the **wave function**) that tells us the probability of a particle being in a particular location — uncertainty and probability are an intrinsic part of the theory.

This experiment also illustrates the critical role of the observer. If we install detectors that tell us whether the particle went through the top slit or bottom slit, the interference pattern goes away — as if we had run two separate one-slit experiments. Only when the slit that the particle went through has not been determined do both paths contribute to give an interference pattern. We'll come back to this idea, that measurement leads to "collapse of the wave function" – once we determine that the particle has passed through the upper slit for example, we know its trajectory, whereas without knowing which slit it went through, both possibilities are open and interfere. The act of observing changes the experiment.


a
b
c
d
e

APPENDIX: Calculation of density of states (eq. 1)

This something you might have seen already in a statistical mechanics course. It is not important for our class, so I include it here as an Appendix.



Now consider a closed box of side L. There are standing wave solutions in the box

eg. in 1D

(analogous to waves on a string)

$n = 1, 2, 3 \ldots$

$\lambda = \frac{2L}{n}$

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

$$\text{amplitude} \propto \sin\left(\frac{n_x \pi x}{L}\right) \propto \sin\left(\frac{2\pi x}{\lambda}\right) \propto \sin(k_x x)$$

in 3D $\sin(k_x x) \sin(k_y y) \sin(k_z z)$

The modes have $\underline{k} = \left(\frac{\pi n_x}{L}, \frac{\pi n_y}{L}, \frac{\pi n_z}{L}\right)$

Now look at the phase space

each mode is a point in k-space

Equally-spaced points separated by $\frac{\pi}{L}$

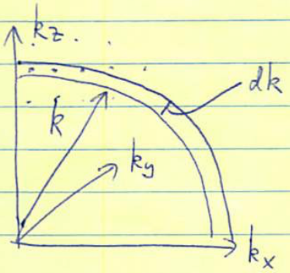
$\therefore$ density of states

1 per volume $\frac{\pi^3}{L^3} = \frac{\pi^3}{V}$ in k-space

We can use this to count how many modes there are at a particular wavelength λ or frequency ν. The k value corresponding to frequency ν is

$$k^2 = k_x^2 + k_y^2 + k_z^2 = \left(\frac{2\pi\nu}{c}\right)^2$$

these modes live on a spherical shell



modes in the shell is

$$\underbrace{\frac{4\pi k^2 dk}{8}}_{\text{volume of the shell}} \times \underbrace{\frac{V}{\pi^3}}_{\text{density of states}} \times \underbrace{2}_{\text{2 polarizations for photons}}$$

or in terms of frequency, the number of modes is

$$\left(k \rightarrow \frac{2\pi\nu}{c}\right) \qquad \boxed{\frac{8\pi\nu^2 d\nu}{c^3} V}$$

the number of modes in the box between ν and $\nu + d\nu$.

Part 2: Wave Mechanics and Free Particles

The Wavefunction and Schrödinger Equation

Consider a particle moving in a one-dimensional potential $V(x,t)$. Classically, it's equation of motion would be

$$\frac{dp}{dt} = -\frac{\partial V}{\partial x}$$

with a conserved total energy

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

In quantum mechanics, we describe the state of the particle by

the **wavefunction** $\Psi\,(x,t)$

where

$$|\Psi(x,t)|^2\,dx = \Psi^\star(x,t)\Psi(x,t)\,dx$$

is the probability of finding the particle between x and $x+dx$.

The wavefunction is **normalized**

$$\int_0^\infty |\Psi(x,t)|^2\,dx = 1$$

(the particle must be located somewhere!) and satisfies the **Schrödinger Equation**

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

a wave equation for Ψ.

The solution to the Schrödinger equation is deterministic in the sense that given initial conditions for Ψ we can solve to find Ψ for all future times. But the interpretation of Ψ is statistical in nature – we can't predict with certainty the position of a particle at a future time, all we know is the probability density function for its location, $|\Psi|^2$.

Exercise 6: Write down an expression for the average position of a particle $\langle x\rangle$ given the wavefunction $\Psi(x,t)$.

Exercise 7: Imagine a particle in a box of size L (the potential is $V=0$ for $0<x<L$ and $V=\infty$ otherwise). Is $\Psi=\sin(3\pi x/L)$ a valid wavefunction for the particle? If not, how would you fix it? Where is the particle most likely to be found?

Plane waves and the momentum operator

Since the Schrödinger equation is a wave equation, we could try a plane wave solution, i.e. $\Psi \propto e^{ikx-i\omega t}$. Substituting this into the Schrödinger equation gives

$$\hbar\omega\Psi = \frac{\hbar^2}{2m}k^2\Psi + V\Psi.$$

This equation is only satisfied everywhere if V is constant. For simplicity, let's set that constant to zero, $V = 0$, which is equivalent to thinking about a *free particle*. Then the plane wave solution works as long as

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

We already know from the de Broglie relation that

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

is the momentum, so the right hand side is $p^2/2m$. The left hand side is therefore the energy

$$E = \hbar\omega \Rightarrow \omega = \frac{E}{\hbar}.$$

Therefore the free particle wavefunction is

$$\Psi_p(x,t) \propto e^{ipx/\hbar}e^{-Et/\hbar},$$

and describes a particle moving with fixed momentum p in a constant potential, where $E = p^2/2m$.

Exercise 8: How is the wavefunction modified if $V \neq 0$?

Exercise 9: Where is the particle most likely to be found?

The kinetic energy term in Schrödinger's equation involves two derivatives and gives p^2. This suggests that if we want to find the momentum of a particle, we differentiate once, in particular

$$\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi_p = p\Psi_p.$$

We refer to $(\hbar/i)(\partial/\partial x)$ as the *momentum operator* which we write as $\hat{p}$. The momentum operator acts on the free particle wavefunction to return the momentum

$$\hat{p}\Psi_p = p\Psi_p.$$

We see that the free particle wavefunction Ψ_p is an eigenfunction of the momentum operator whose eigenvalue is the momentum p of that state.

Conservation of probability

The rate of change of the probability density $|\Psi|^2$ is

$$\frac{\partial |\Psi|^2}{\partial t} = \Psi^\star \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^\star}{\partial t}$$

$$= \frac{\Psi^\star}{i\hbar} \left[-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi \right] - \frac{\Psi}{i\hbar} \left[-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi^\star}{\partial x^2} + V\Psi^\star \right],$$

where we use Schrödinger's equation to substitute for $\partial\Psi/\partial t$ and $\partial\Psi^\star/\partial t$. The potential terms cancel, giving

$$\frac{\partial |\Psi|^2}{\partial t} = \frac{i\hbar}{2m} \left[\Psi^\star \frac{\partial^2 \Psi}{\partial x^2} - \Psi \frac{\partial^2 \Psi^\star}{\partial x^2} \right].$$

Now bring one of the derivatives outside:

$$\frac{\partial |\Psi|^2}{\partial t} = \frac{i\hbar}{2m} \frac{\partial}{\partial x} \left[\Psi^\star \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^\star}{\partial x} \right].$$

This equation is in *flux-conservative form*

$$\frac{\partial |\Psi|^2}{\partial t} = -\frac{\partial}{\partial x} J_\Psi$$

where

$$J_\Psi = \frac{i\hbar}{2m} \left[\Psi^\star \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^\star}{\partial x} \right]$$

is the probability flux.

This is the general form of a conservation law. To see this, integrate over a region from $x = a$ to $x = b$:

$$\frac{d}{dt} \int_a^b |\Psi|^2 \, dx = -\int_a^b dx \frac{\partial}{\partial x} J_\Psi = J_\Psi(x = a) - J_\Psi(x = b).$$

The probability of the particle being between $x = a$ and $x = b$ changes if there is a net flux of probability across the boundaries of the region.

For a wavefunction that has $\Psi \to 0$ at $x \to \pm\infty$ (i.e. normalizable), we see that

$$\frac{d}{dt} \int_\infty^\infty |\Psi|^2 \, dx = 0,$$

so that once normalized the wavefunction will remain normalized.

Expectation value of momentum

Now let's go back to think more about momentum. We earlier derived an expression for the mean position of the particle

$$\langle x \rangle = \int_{\infty}^{\infty} x \, |\Psi|^2 \, dx.$$

Now let's look at

$$\frac{d\langle x \rangle}{dt} = \int x \, dx \, \frac{\partial}{\partial t} \, |\Psi|^2 = -\int x \, dx \, \frac{\partial}{\partial x} J_\Psi.$$

Integrate by parts

$$\frac{\partial}{\partial x} \left(x \, J_\Psi \right) = J_\Psi + x \frac{\partial J_\Psi}{\partial x}$$

gives

$$\frac{d\langle x \rangle}{dt} = \int dx \, J_\Psi - \left[x J_\Psi \right].$$

The surface term vanishes if $J_\Psi \to 0$ at $x = \pm\infty$. Now put in the definition of J_Ψ

$$\frac{d\langle x \rangle}{dt} = -\int dx \frac{i\hbar}{2m} \left[\Psi^\star \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^\star}{\partial x} \right].$$

We again integrate the last term by parts. The derivative moves from the $\Psi^\star$ to the Ψ and the boundary term again vanishes, giving

$$\frac{d\langle x \rangle}{dt} = \frac{1}{m} \int dx \, \Psi^\star \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi.$$

We see the momentum operator has appeared. This suggests we write

$$m \frac{d\langle x \rangle}{dt} = \langle p \rangle = \int dx \, \Psi^\star \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi = \int dx \, \Psi^\star \hat{p} \Psi.$$

This is something we'll see many times over: the expectation value of a quantity is given by sandwiching the operator between $\Psi^\star$ and Ψ and integrating over all space. It applies to position also, if we think of x as the position operator $\hat{x}$ then the expectation value of position is

$$\langle x \rangle = \int_{\infty}^{\infty} dx \, \Psi^\star \hat{x} \Psi.$$

Exercise 10: If $\hat{x}$ is also an operator, it must have eigenstates, i.e. wavefunctions that represent particles with a definite position x_0. Write down the functional form of $\Psi_{x_0}(x)$ and show that it is an eigenfunction of $\hat{x}$ with eigenvalue x_0.

General solution using plane waves and the uncertainty principle

Since Schrödinger's equation is linear, we can construct any wavefunction $\Psi(x)$ as a sum of plane waves,

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, A(k)\, e^{i[kx-\omega(k)t]}, \tag{3}$$

where $A(k)$ is the amplitude of the wave with wavevector k (note that $A(k)$ is complex because the different k values can have different phases). Given an initial wavefunction at time $t = 0$, the amplitudes $A(k)$ are given by

$$A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, \Psi(x,0)\, e^{-ikx}.$$

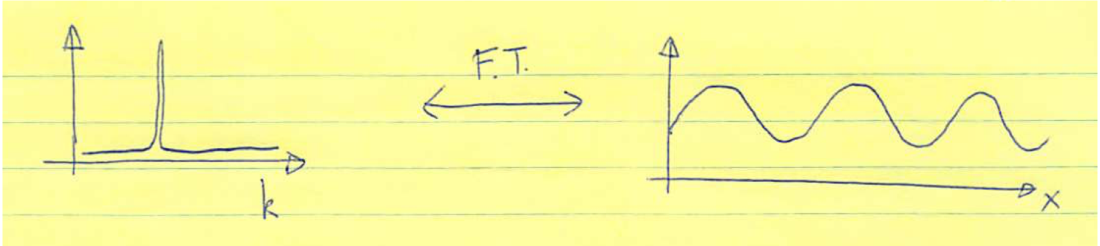
Because we know the time-dependence of each k, equation (3) then gives the time-dependent solution for Ψ.

You probably recognize that what we're doing here is taking a Fourier transform of $\Psi(x)$ to get $A(k)$ and vice versa. This Fourier transform gives rise to the *uncertainty principle*. The better we know position, the worse we know momentum, and vice versa.

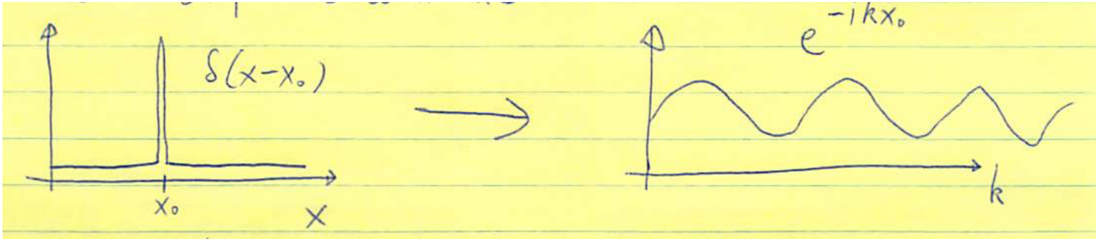
For example, to take the extreme cases, we already saw that if we know k precisely then we know nothing about the position of the particle. For example let's say that we know that $k = k_0$ so that $A(k) \propto \delta(k-k_0)$. Then Ψ is the Fourier transform of a delta function:

$$\Psi = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, \delta(k-k_0)\, e^{ikx} = \frac{1}{\sqrt{2\pi}} e^{ik_0x},$$

a plane wave with wavevector k_0. Then $|\Psi|^2$ is constant as we saw earlier.



The opposite case would be if we knew position precisely. Then $\Psi \propto \delta(x-x_0)$, and $A(k) = e^{-ikx_0}/\sqrt{2\pi}$. The amplitude of $A(k)$ is then independent of k, since $|A(k)|^2$ is constant.



Gaussian wavepacket

We'll show explicitly later that the best you can do in terms of knowing position and momentum at the same time is a *Gaussian wavepacket*,

$$\Psi(x) \propto \exp\left(-\frac{(x-x_0)^2}{2\sigma_x^2}\right).$$

The Fourier transform of a Gaussian is a Gaussian, so

$$A(k) \propto \exp\left(-\frac{(k-k_0)^2}{2\sigma_k^2}\right).$$

To relate σ_x and σ_k, carry out the Fourier transform:

$$\Psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, e^{ikx} \exp\left(-\frac{(k-k_0)^2}{2\sigma_k^2}\right).$$

Change variables $q = k - k_0$

$$\Psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dq\, e^{i(q+k_0)x} \exp\left(-\frac{q^2}{2\sigma_k^2}\right),$$

and then complete the square

$$\Psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dq\, e^{ik_0x} e^{-(q-ix\sigma_k^2)^2/2\sigma_k^2} e^{-x^2\sigma_k^2/2}.$$

Then using $\int \exp(-ax^2)dx = \sqrt{\pi/a}$,

$$\Psi(x) = \sigma_k e^{ik_0x} e^{-x^2\sigma_k^2/2}.$$

This shows that $\sigma_x = 1/\sigma_k$. Now we're actually interested in $|\Psi|^2$, which is also Gaussian but with width $\Delta x = \sigma_x/\sqrt{2}$, and similarly for k. Therefore $\Delta x = 1/\sqrt{2}\sigma_k = 1/2\Delta k$, and so

$$\Delta x \Delta k = \frac{1}{2}.$$

In terms of momentum,

$$\Delta x \Delta p = \frac{\hbar}{2}.$$

We'll prove later that the Gaussian wavepacket gives the minimum value of $\Delta x \Delta p$ – in general

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

the *uncertainty principle*.

Exercise 11: What would a wavefunction with $\Delta x \Delta p \gg \hbar/2$ look like?

Exercise 12: Imagine a Gaussian wavepacket at time $t = 0$. Without doing a detailed calculation, can you deduce what happens to $\Psi(x)$ over time? What happens to $A(k)$ over time?

Interpretation of $A(k)$: momentum representation

How should we interpret $A(k)$? First, consider $|\Psi|^2$ written in terms of $A(k)$:

$$|\Psi|^2 = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, A^\star(k)\, e^{-ikx} \int_{-\infty}^{\infty} dq\, A(q)\, e^{iqx}$$

(I've written it with two different integration variables k and q to separate the integrals)

$$|\Psi|^2 = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dq\, A^\star(k)\, A(q)\, e^{i(q-k)x}.$$

Now integrate this over x:

$$\begin{aligned}\int_{-\infty}^{\infty} dx\, |\Psi|^2 &= \int_{-\infty}^{\infty} dx\, \frac{1}{2\pi}\int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dq\, A^\star(k)\, A(q)\, e^{i(q-k)x} \\ &= \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dq\, A^\star(k)\, A(q)\, \frac{1}{2\pi}\int_{-\infty}^{\infty} dx\, e^{i(q-k)x} \\ &= \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dq\, A^\star(k)\, A(q)\, \delta(q-k) \\ &= \int_{-\infty}^{\infty} dk\, A^\star(k)\, A(k) = \int_{-\infty}^{\infty} dk\, |A|^2,\end{aligned}$$

where we used $\delta(k-q) = (1/2\pi)\int_{-\infty}^{\infty} e^{i(k-q)x}$.

You may have seen this result before in Fourier transforms as Parseval's theorem. If $\Psi(x)$ is a normalized wavefunction, $A(k)$ is also normalized. This suggests that we interpret $|A(k)|^2$ as a probability density for k, or the probability of measuring a momentum for the particle $p = \hbar k$. We can go further: $A(k)$ contains all the information that is contained in $\Psi(x)$ (they are just Fourier transforms of each other), so we can think of $A(k)$ as being the wavefunction of the particle, but written in momentum space. We call this the *momentum representation*.

To explore the momentum representation one step further, look at the momentum operator acting on Ψ:

$$\hat{p}\Psi = \frac{\hbar}{i}\frac{\partial}{\partial x}\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dk\, A(k)\, e^{ikx} = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dk\, \hbar k\, A(k)\, e^{ikx}.$$

Exercise 13: Use this to calculate $\langle p\rangle$ and show that

$$\langle p\rangle = \int_{\infty}^{\infty} dk\, A^\star(k)\, (\hbar k)\; A(k).$$

What do you deduce about the form of the momentum operator $\hat{p}$ when written in momentum space?

Momentum space or *k*-space?

I've been writing the momentum representation wavefunction in terms of k, as $A(k)$, so that the probability of the particle having k in the range k to $k + dk$ is $|A(k)|^2$. This corresponds to the probability the particle has momentum in the range $p = \hbar k$ to $p + dp = \hbar(k + dk)$.

We could alternatively define the wavefunction in terms of momentum $\tilde{A}(p)$ instead. Then $\left|\tilde{A}(p)\right|^2 dp$ is the probability of having momentum in the range p to $p + dp$.

The relation between the functions $A(k)$ and $\tilde{A}(p)$ is found by equating the probabilities:

$$\left|\tilde{A}(p)\right|^2 dp = \left|A\left(\frac{p}{\hbar}\right)\right|^2 \frac{dp}{\hbar} \Rightarrow \tilde{A}(p) = \frac{1}{\sqrt{\hbar}} A\left(\frac{p}{\hbar}\right).$$

Part 3: The Time-Independent Schrödinger Equation

Derivation, Hamiltonian operator, and stationary states

If the potential $V(x)$ is independent of time, the Schrödinger equation can be solved by separation of variables, i.e. there is a solution of the form $\Psi(x,t) = \psi(x)f(t)$ for some function of time $f(t)$. In fact, based on our experience of plane waves, we might guess that $f(t) \propto e^{-iEt/\hbar}$, so let's try a solution

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} \tag{4}$$

and see if it works. Substituting into Schrödinger's equation,

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

gives

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x), \tag{5}$$

or

$$\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = -\left[E - V(x)\right]\psi, \tag{6}$$

the **time-independent Schrödinger equation**.

We can write the right hand side of equation (5) in terms of the **Hamiltonian operator**

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x),$$

so that the time-independent Schrödinger equation is

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

The expectation value of the Hamiltonian is the energy

$$\int dx\, \Psi^\star \hat{H}\Psi = E.$$

We can solve equation (6) for any given potential $V(x)$. What we'll find is that solutions exist only for particular choices of E. These are the eigenvalues of the equation, and each eigenvalue E_n has a corresponding wavefunction $\psi_n(x)$. Often only discrete values of E are allowed (i.e. there is quantization) — for other choices of E, it is not possible to find a solution $\psi(x)$ that satisfies the boundary conditions. An example with a continuum of allowed E values is the free particle with $V = 0$ for which $\psi(x) = e^{ikx}$ and $E = \hbar^2k^2/2m$ for any k, but for a finite size system we'll see that the boundary conditions result in a discrete set of allowed energies E_n.

Once we have the solutions $\psi_n(x)$, we can construct a general solution

$$\Psi(x,t) = \sum_n a_n\psi_n(x)e^{-iE_nt/\hbar} \tag{7}$$

which is a linear combination of the states $\psi_n(x)$. Again this is the same as the free particle, except that we did an integral rather than a sum because E is continuous.

The solutions $\psi(x)$ are known as **stationary states** because $|\Psi|^2$ is time-independent for a solution of the form of equation (4).

Exercise 14: Show that the expectation value of an operator $\hat{Q}$ that is a function of position and momentum — $\hat{H}$ would be an example — is also independent of time.

Note that a combination of stationary states (i.e. a linear combination as in eq. 7) *does* depend on time. We'll see an example later.

Particle in a box: the infinite square well

The simplest example to consider is the particle in a box, i.e. $V = 0$ in the region $0 < x < a$ and $V = \infty$ for $x < 0$ and $x > a$.

Exercise 15: Solve the time-independent Schrödinger equation for this potential. Determine the eigenvalues E_n and normalized eigenfunctions $\psi_n(x)$.

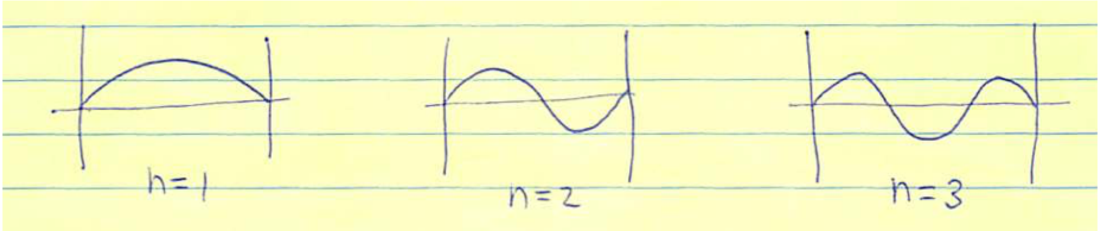
More on the infinite square well

In the exercise, you should have found

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) \qquad E_n = \frac{\hbar^2 n^2 \pi^2}{2ma^2}.$$

Points to note:

- The lowest energy state $n = 1$ is the *ground state* with $E = \hbar^2\pi^2/2ma^2$.
- The *excited states* with $n > 1$ have $E_n \propto n^2$.
- Each successive state has an extra node



- The states are alternately *odd* $\psi(-x) = -\psi(x)$ and *even* $\psi(-x) = \psi(x)$ about the center of the box.
- The states are *orthogonal*

$$\frac{2}{a}\int_0^a dx\,\sin\left(\frac{n\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right) = \delta_{nm},$$

or

$$\int_0^a dx\,\psi_n^\star(x)\psi_m(x) = \delta_{nm}.$$

Expanding in terms of stationary states

Any initial state can be expanded as a sum of the stationary states:

$$\Psi(x,0) = \sum_{n=1}^{\infty} c_n\psi_n(x).$$

To derive a formula for the coefficients c_n, multiply by $\psi_m(x)$ and integrate:

$$\int_0^a dx\,\psi_m(x)\Psi(x,0) = \sum_{n=1}^{\infty} c_n\int_0^a dx\,\psi_m(x)\psi_n(x) = \sum_{n=1}^{\infty} c_n\delta_{nm} = c_m.$$

The general time-dependent solution is then

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n\psi_n(x)e^{-iE_nt/\hbar}. \qquad (8)$$

Exercise 16: Show that the expectation value of the energy

$$\langle E \rangle = \int_0^a dx\, \Psi^\star \hat{H} \Psi$$

is

$$\langle E \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n.$$

What does this suggest about how to interpret $|c_n|^2$?

Exercise 17: Show that $\sum |c_n|^2 = 1$.

Mixtures of states

We mentioned already that time-dependence comes from mixtures of stationary states.

Exercise 18: Consider a particle initially in the state

$$\Psi(x,0) = \frac{1}{\sqrt{2}} \left(\psi_1(x) + \psi_2(x)\right),$$

a mixture of the ground state and first excited state of the infinite square well. Calculate Ψ, $|\Psi|^2$, $\langle x\rangle$, $\langle p\rangle$ and $\langle E\rangle$ at future times.

Exercise 19: Consider two different states

$$\Psi(x,0) = \frac{1}{\sqrt{2}} \left(\psi_1(x) + \psi_2(x)\right)$$

and

$$\Psi(x,0) = \frac{1}{\sqrt{2}} \left(\psi_1(x) + \psi_3(x)\right).$$

Which one evolves most rapidly with time?

The result for a mixture of two states can be generalized to an arbitrary mixture of states. If

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar},$$

you can show that

$$|\Psi|^2 = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_n c_m \psi_n(x) \psi_m(x) \cos\left(\frac{t(E_m - E_n)}{\hbar}\right).$$

This formula is implemented in the `mixed.py` python code which you can find on myCourses.

Measurement and collapse of the wavefunction

If we measure the energy of a particle in a mixture of stationary states (eq. [8]), we will measure one of the eigenvalues of the energy operator (Hamiltonian operator) $\hat{H}$, i.e. one of the energies of the stationary states E_1, E_2, E_3, etc. The probability of measuring energy E_n is given by $|c_n|^2$. Immediately after the measurement, we know the particle energy E_n — its wavefunction must then be the corresponding stationary state wavefunction $\Psi_n(x)$.

We saw something similar with position measurements. Before measuring the position of a particle, we know the probability of finding it at location x is $|\Psi(x)|^2$. When we measure the particle's position, the answer we get is one of the eigenvalues of the position operator, and the wavefunction then "collapses" to the equivalent eigenstate — i.e. a delta function located at the measured position. The same kind of "collapse of the wavefunction" happens with the energy measurement, but in energy space. Before the measurement, many different c_n's might be non-zero, but after the energy is measured to be E_m, only one of them is non-zero: $c_m = 1$, $c_{n\neq m} = 0$.

Exercise 20: You measure the position of a particle to be $x = x_1$. Some time later, you measure the position again. What value of x would you measure? Repeat the exercise for a measurement of energy. Why is your answer different?

For the infinite square well, the set of c_n's fully specifies the particle's state. We can think of this as an *energy representation* of the state Ψ. We're beginning to see a general pattern here: if we are interested in observable O, then we expand Ψ in terms of the eigenstates of the corresponding operator $\hat{O}$. When we measure O, we will measure one of the eigenvalues of the operator, with probability given by squaring the coefficients in the expansion.

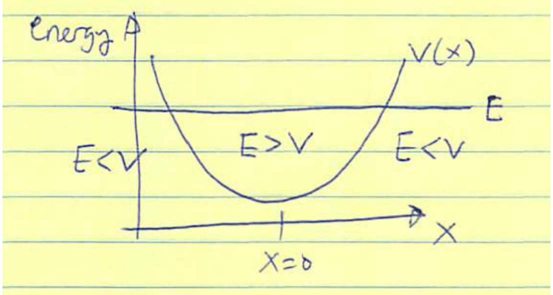
Harmonic oscillator

We're now going to go through a few different examples of time-independent potentials and the solution to the time-independent Schrödinger equation in these cases. We start with the harmonic oscillator which has a potential

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

where κ is the spring constant, and $\omega^2 = \kappa/m$ is the classical oscillation frequency for a particle of mass m.

We're going to solve for the wavefunction numerically, but before we do that let's think about what the stationary states will look like. First, note that in this problem for any given energy E, there are two regions, one where $E > V$ and one where $E < V$:



This has consequences for the shape of the solution. The time-independent Schrödinger equation is

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

When $E > V$,

$$\frac{d^2\psi}{dx^2} \propto -\psi$$

which gives wave-like solutions for ψ (as we saw for the infinite square well). For $E < V$,

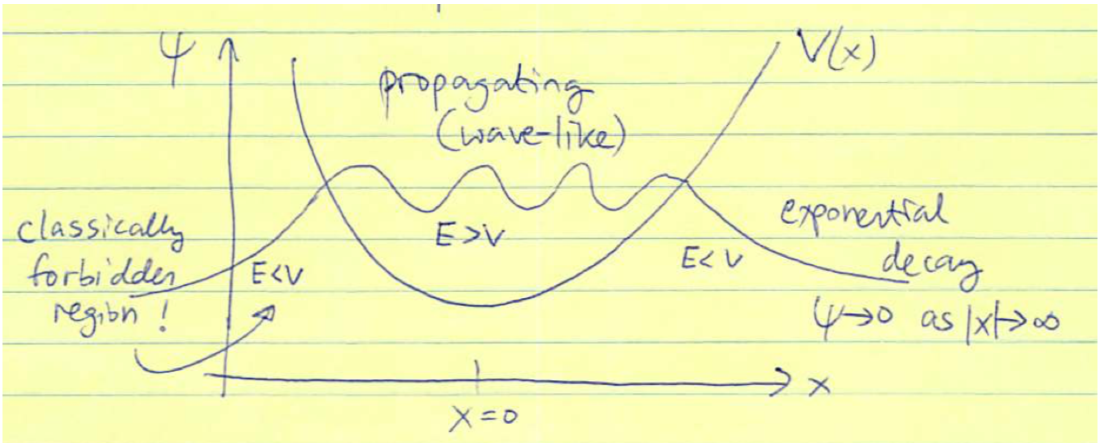
$$\frac{d^2\psi}{dx^2} \propto +\psi,$$

and the solution is then exponential. To see this, imagine V was a constant; the solution is then e^{ikx} with

$$k^2 = \frac{2m}{\hbar^2}(E - V)\,.$$

For $E > V$, k is real giving a propagating wave, but for $E < V$, k is imaginary $\Rightarrow \psi \propto e^{\pm|k|x}$, an evanescent solution. Notice that for either case, the value of $k \propto (E - V)^{1/2}$, so the lengthscale on which ψ changes (whether oscillating or decaying) depends on the difference in energy between the total energy and the potential at any given position.

This means that we might expect the solutions to look like



where the the number of nodes increases with increasing energy. The change from oscillating to decaying wavefunction happens at the *classical turning point* x_c. This is the location where a classical particle would turn around because all its kinetic energy had been converted to potential energy, ie. it is the place where $E = V = (1/2)\kappa x_c^2 \Rightarrow x_c = (2E/\kappa)^{1/2}$. Unlike the infinite square well, which has a fixed width, higher energy states in the harmonic oscillator are able to explore a larger range of x and so the well has a width which grows with energy. We'll see that, because of this, the energies of the states are $E_n \propto n$ rather than n^2 for the infinite square well. (See question 4 in homework 2).

Numerical solution for the harmonic oscillator

We will solve for the stationary states of the harmonic oscillator by numerically integrating the Schrödinger equation. We expect the states to have either odd or even symmetry about $x = 0$ (just like the infinite square well; in fact this is true for any potential $V(x)$ that is symmetric about the origin). We'll take advantage of this and start the integration at $x = 0$ and integrate to large x. The idea will be to try different values of E, and find those which give $\psi \to 0$ at large x. This technique is known as a *shooting method* for finding the eigenvalues. The boundary conditions at the origin are

$$\frac{d\psi}{dx} = 0 \qquad \psi = 1 \qquad \text{(even)}$$

$$\psi = 0 \qquad \frac{d\psi}{dx} = 1 \qquad \text{(odd)}.$$

(The value 1 is arbitrary, since the solutions are linear and will have to be normalized anyway. The important thing is that even solutions have vanishing gradient at the origin whereas odd solutions go through zero at the origin.)

The python code `harmonic.py` on myCourses carries out the integration. There are two "tricks" that are used:

1. the time-independent Schrödinger equation is reduced to two first order differential equations. The issue is that the numerical integrator needs the first derivative of ψ to take a step in x:

   $$\psi(x + \delta x) \approx \psi(x) + \delta x \left.\frac{d\psi}{dx}\right|_x + \ldots$$

   but the Schrödinger equation gives us the second derivative not the first. The solution is to define a new function

   $$\chi(x) = \frac{d\psi}{dx}$$

   and then the Schrödinger equation can be written as two first order ODEs:

   $$\begin{aligned} \frac{d\psi}{dx} &= \chi \\ \frac{d\chi}{dx} &= -\frac{2m}{\hbar^2}\,(E - V)\,\psi. \end{aligned}$$

   The boundary conditions on ψ and $d\psi/dx$ at $x = 0$ become conditions on ψ and χ instead.

2. it is simpler to use a dimensionless energy

   $$\tilde{E} = \frac{E}{\hbar\omega/2}$$

where $\omega^2 = \kappa/m$ is the classical oscillator frequency. The Schrödinger equation is then

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \left(\tilde{E}\frac{\hbar\omega}{2} - \frac{1}{2}\kappa x^2\right)\psi = \frac{\hbar\omega}{2}\left(\tilde{E} - \frac{\kappa}{\hbar\omega}x^2\right)\psi$$

or

$$-\frac{\hbar}{m\omega}\frac{d^2\psi}{dx^2} = \left(\tilde{E} - \frac{m\omega}{\hbar}x^2\right)\psi.$$

Now defining a rescaled coordinate

$$\tilde{x} = \sqrt{\frac{m\omega}{\hbar}}x,$$

we get

$$\frac{d^2\psi}{d\tilde{x}^2} = -\left(\tilde{E} - \tilde{x}^2\right)\psi$$

or

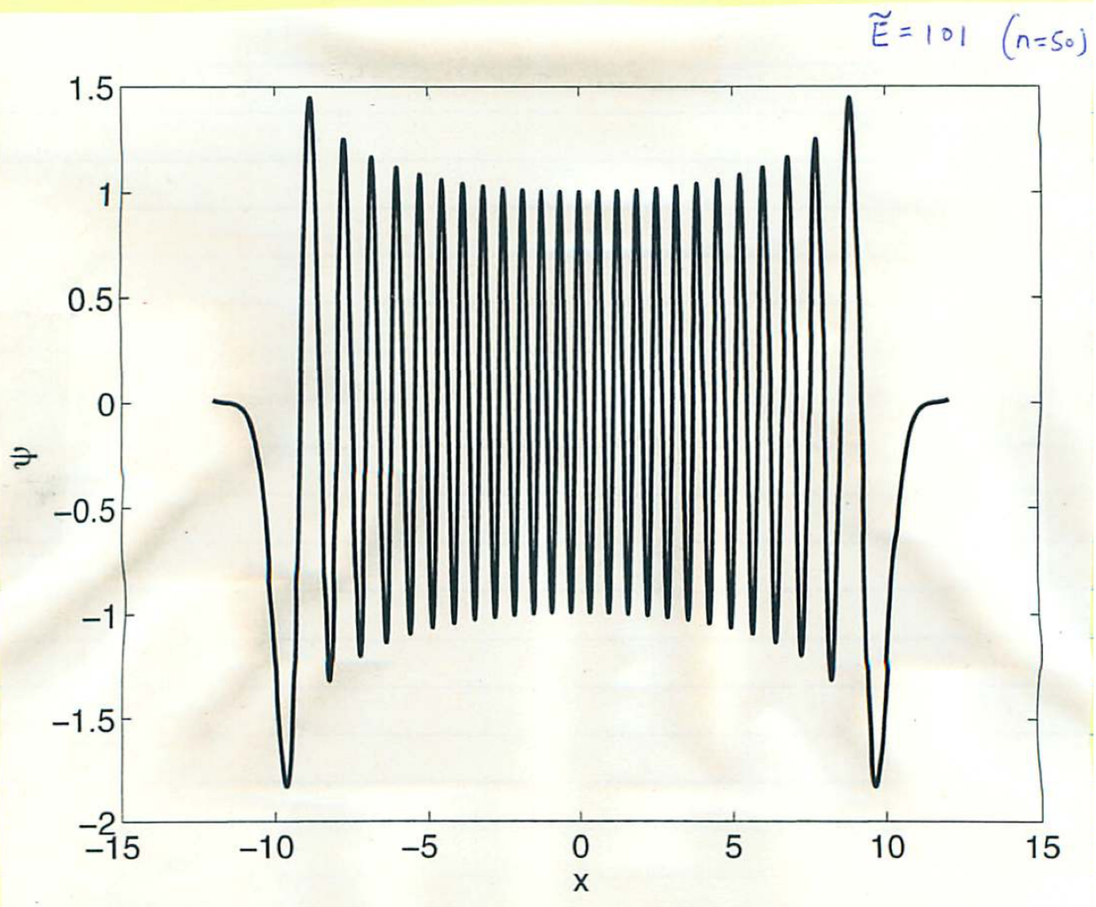
$$\begin{aligned} \frac{d\psi}{d\tilde{x}} &= \chi \\ \frac{d\chi}{d\tilde{x}} &= -\left(\tilde{E} - \tilde{x}^2\right)\psi. \end{aligned}$$

These are the equations that are integrated in the code.

Exercise 21: Run the code and find the allowed energies E_n and corresponding eigenfunctions $\psi_n(x)$ for the harmonic oscillator. Are the eigenfunctions as expected? Write a formula for E_n in terms of the oscillator frequency ω and n.

Some points to note:

- The allowed energies are
$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$
for $n = 0, 1, 2, 3....$ (This corresponds to $\tilde{E}$ being an odd number).
- The eigenfunctions are odd for odd n and even for even n.
- The wavefunction evanesces for $\tilde{x} > (\tilde{E})^{1/2} = \sqrt{2n+1}$ (the classical turning point).
- If you look at a high energy mode, you should see that both the amplitude of the oscillations and the separation between peaks in the wave increases with x out to the classical turning point.



$\tilde{E} = 101$ (n=50)

WKB approximation

The behaviour of the short wavelength solutions can be understood by using the *WKB approximation*. The idea is that when n is large, the wavelength is so short that the potential $V(x)$ is approximately constant over a wavelength. The solution is then approximately

$$\psi = A(x)e^{ik(x)x}$$

with

$$k(x)^2 = \frac{2m}{\hbar^2}\left(E - V(x)\right).$$

This explains why

- the solution is a wave inside the classical turning point where $E > V$ and $k^2 > 0$, but evanesces outside the classical turning point where $E < V$ and $k^2 < 0$.
- The wavelength of the wave $\lambda \propto 1/k \propto (E-V)^{1/2}$. As x increases, $E - V$ decreases $\Rightarrow \lambda$ increases.
- For a plane wave, the probability flux is (see question 3 in homework 1)

  $$J_\psi = A^2\frac{i\hbar k}{m} \propto \frac{A^2}{\lambda}.$$

  For a stationary solution, J_ψ has to be constant with x, implying that

  $$A \propto \lambda^{1/2} \propto \frac{1}{(E - V(x))^{1/4}}.$$

  The amplitude of the wave increases towards the classical turning point.

Applications of the harmonic oscillator

The harmonic oscillator has many applications across all areas of physics. Near the minimum of a potential $V = V_0$ at $x = x_0$, the first derivative $\partial V/\partial x$ vanishes. A Taylor expansion then gives

$$V \approx V_0 + \left.\frac{\partial^2 V}{\partial x^2}\right|_{x=x_0}(x - x_0)^2 + ...$$

for small distances $(x - x_0)$. The curvature of the potential sets the effective spring constant, $\kappa \sim \partial^2 V/\partial x^2$.

I'll just mention two applications here. The first is vibrations of molecules. Because the vibrations are quantized (in steps of $\hbar\omega$), molecules absorb or emit photons of particular energies when they transition between vibrational states. The photon energies are in the infrared, leading to infrared spectroscopy as a way to study molecules.

Infrared spectroscopy is a very direct way to observe the effects of quantization of vibrational energy levels. A second application which is more indirect is the heat capacity of solids at low temperatures. Classically, a solid with N atoms has N vibrational modes and, if each of them can accept thermal energy $k_B T$, the heat capacity of the solid should be $C = N k_B$. Measurements of heat capacity show that this holds well at high temperatures, but at low temperatures the lattice heat capacity drops dramatically, scaling as $C \propto T^3$ (Debye's law). The reason is that at low temperatures, the energy needed to exite a vibrational mode ($\hbar\omega/2$ for the ground state) becomes larger than $k_B T$. The high frequency modes are then no longer accessible, reducing the ability to absorb heat.

The Finite Square Well

The finite square well has

$$V(x) = \begin{cases} 0, & x < 0 \\ -V_0, & 0 < x < a \\ 0, & x > a, \end{cases}$$

where V_0 is positive and gives the depth of the well.

Exercise 22: By modifying the python code from last time, investigate the energy levels and eigenfunctions of this potential.

Boundary conditions for the Schrödinger Equation

In problems where the potential $V(x)$ is discontinuous, we need matching conditions on ψ and $d\psi/dx$ at the location of the discontinuity.

The first one is

$$\psi(x) \text{ is continuous}$$

at a boundary. This avoids having infinite gradients in ψ and therefore momentum $(\hbar/i)\partial\psi/\partial x$.

The second condition is

$$\frac{d\psi}{dx} \text{ is continuous}$$

at a boundary. To derive this, integrate the Schrödinger equation across the boundary from $x = -\epsilon$ to $+\epsilon$ and let $\epsilon \to 0$:

$$\int_{-\epsilon}^{\epsilon} \frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2}\, dx = \int_{-\epsilon}^{\epsilon} (E - V)\, \psi\, dx$$

$$\frac{-\hbar^2}{2m} \left[\frac{d\psi}{dx}\right]_{-\epsilon}^{\epsilon} = \int_{-\epsilon}^{\epsilon} (E - V)\, \psi\, dx$$

The right hand side vanishes as $\epsilon \to 0$, even if there is a discontinuity in $V(x)$ (eg. as in the square well). Therefore $d\psi/dx$ must have the same value on each side of the discontinuity.

Note that there is an exception to this rule. If $V(x)$ has a delta-function component,

$$V(x) = V_0 \delta(x)$$

then the integral on the right hand side does not vanish! Instead,

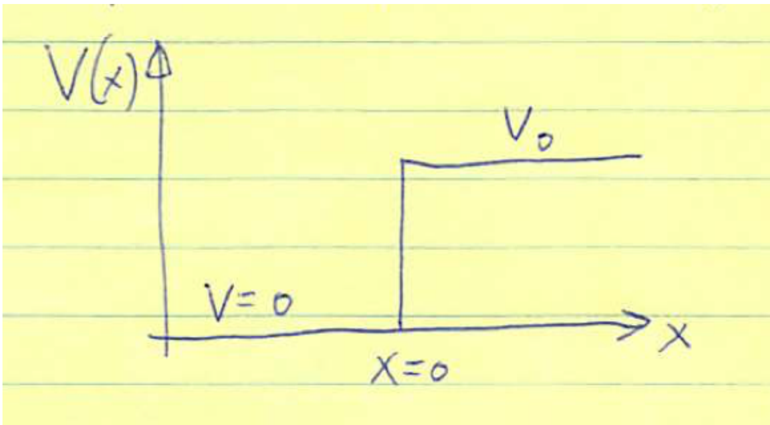
$$\left[\frac{d\psi}{dx}\right]_{-\epsilon}^{\epsilon} = \frac{2m}{\hbar^2} V_0 \psi(0).$$

You will put this to work in the homework.

Scattering at a potential jump

The infinite square well and harmonic oscillator only have *bound states* where the particle is confined by the potential ($\psi \to 0$ as $|x| \to \infty$). The finite square well has both bound states $E < 0$ and *scattering states* $E > 0$. The scattering states look like plane waves, with the amplitude and wavelength of the wave changing as the wave traverses the potential well. This leads us to consider incoming and outgoing waves in the presence of a localized potential feature – in other words *scattering*.

The simplest case is a step in the potential



A classical particle incident from the left will slow down on crossing $x = 0$ ($E > V_0$) or be reflected ($E < V_0$). In quantum mechanics, we'll see that there is a reflected wave even if $E > V_0$.

The wavefunction for $x < 0$ is

$$\psi(x) = e^{ikx} + re^{-ikx},$$

a sum of an incident wave and a reflected wave, where $k^2 = 2mE/\hbar^2$. For $x > 0$, the wavevector is given by $q^2 = (2m/\hbar^2)(E - V_0)$, and we assume that the particles are incident from the left, so that there is only a rightwards propagating wave

$$\psi(x) = te^{iqx}.$$

The coefficients r and t are determined by matching ψ and $d\psi/dx$ at $x = 0$:

$$1 + r = t$$

$$k(1 - r) = qt$$

$$\Rightarrow r = \frac{k - q}{k + q}$$

$$t = 1 + r = \frac{2k}{k + q}.$$

These are the amplitudes of the reflected and transmitted waves.

The probability flux in each component can be calculated using $J_\psi \propto k\,|A|^2$. This gives

$$R = \frac{\text{reflected prob flux}}{\text{incident prob flux}} = \frac{k\,|r|^2}{k} = \frac{(k-q)^2}{(k+q)^2}$$

$$T = \frac{\text{transmitted prob flux}}{\text{incident prob flux}} = \frac{q\,|t|^2}{k} = \frac{4kq}{(k+q)^2}.$$

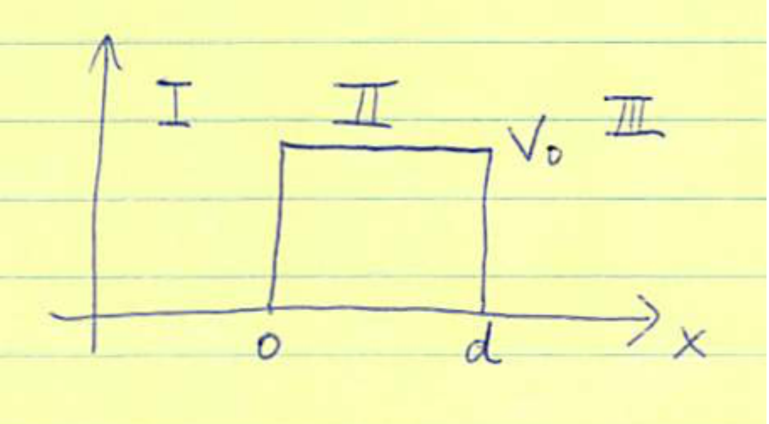
Note that $R + T = 1$ (conservation of probability). The interpretation is that if a beam of particles is incident on a potential step from the left, the probability of finding a particle outgoing on the right is T and probability of finding a particle reflected is R.

Exercise 23: Check the values of r, t, R and T in the two limits $E \gg V_0$ (particle energy well above the potential step) and $E \approx V_0$ (the particle energy is just above the potential step). (The situation where $E < V_0$ is left to the homework).

Exercise 24: What if V_0 was negative, so that the particle experiences a drop in potential rather than an increase in potential, what happens?

Tunnelling

We've already seen that the wavefunction is non-zero in regions with $E < V$ that would be classically forbidden. This leads to the phenomenon of *tunnelling*. The simplest example is to consider particles with energy $E < V_0$ incident on a barrier with a width d:



We need to write down the wavefunctions in the three regions

$$\begin{aligned} \text{I}: \quad & \psi = e^{ikx} + re^{-ikx} \\ \text{II}: \quad & \psi = ae^{qx} + be^{-qx} \\ \text{III}: \quad & \psi = te^{ikx} \end{aligned}$$

where $k^2 = 2mE/\hbar^2$ and $q^2 = (2m/\hbar^2)(V_0 - E)$.

The boundary conditions have to be applied at $x = 0$ and $x = d$. First, ψ continuous $\Rightarrow$

$$1 + r = a + b$$

$$ae^{qd} + be^{-qd} = te^{ikd}$$

then $d\psi/dx$ continuous $\Rightarrow$

$$ik(1 - r) = q(a - b)$$

$$aqe^{qd} - bqe^{-qd} = ikte^{ikd}.$$

These are four equations for the four unknowns a,b,r, and t. There's quite a bit of algebra to work through the get the answer. Here, I'll just give the answer for the transmission probability:

$$T = \frac{1}{1 + \left(\frac{k^2+q^2}{2kq}\right)^2 \sinh^2 qd}.$$

The probability is very sensitive to d as it controls how much ψ decays in the inside of the barrier, before it reaches the other side and can propagate again. For $qd \gg 1$

(barrier width is many times the particle wavelength)

$$T \approx \left(\frac{2kq}{k^2 + q^2} \right)^2 e^{-2qd}$$

or

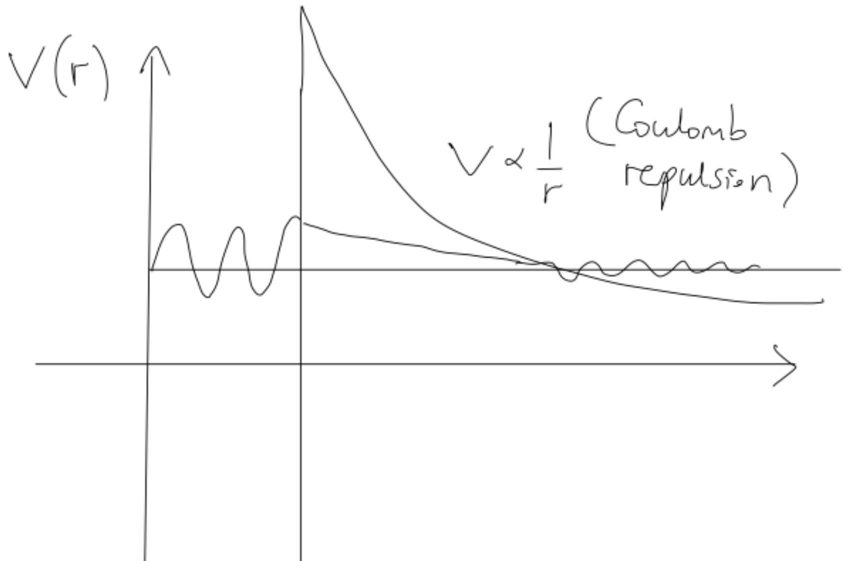
$$\ln T \approx -2qd + (\text{smaller logarithmic factor}) \,,$$

which can be used to estimate tunnelling probabilities (divide by 2.303 to get $\log_{10}$). Plugging in some numbers,

$$qd = \sqrt{\frac{2mE}{\hbar^2}} d \approx 5 \left(\frac{m}{m_e} \right)^{1/2} \left(\frac{E}{1 \text{ eV}} \right)^{1/2} \left(\frac{d}{\text{nm}} \right) .$$

This shows that tunnelling can be important on the scale of semiconductor devices for example. Tunnelling also is believed to play a role in some chemical reactions, e.g. enzyme reactions in biology.

A famous example of tunnelling is Gamow's theory of α-decay of nuclei, in which a nucleus ejects an α particle (helium nucleus). The α-particle and the daughter nucleus are both positively charged and repel each other strongly. Gamow showed that you can understand the decay rate based on quantum tunnelling through this potential. Here's an energy diagram:



The width of the barrier is approximately $d \propto 1/E$ and since $q \propto E^{1/2}$, then $qd \propto 1/E^{1/2}$. The tunnelling probability is

$$\exp\left(-\left(\frac{E_G}{E}\right)^{1/2}\right)$$

where E_G is a constant called the Gamow energy. This agrees beautifully with the data: a plot of the log of the lifetime of an unstable nucleus against the energy of the emitted alpha particle shows $\ln\tau \propto 1/E^{1/2}$. Nuclei that emit more energetic α's have shorter lifetimes because the α-particle can tunnel out more easily. The same tunnelling occurs in the inverse process of thermonuclear fusion (e.g. hydrogen fusion in the Sun) and sets the fusion rate as a function of temperature.

PART 4: BEYOND THE WAVEFUNCTION

Oct 24, 2016.

Dirac notation and Hilbert space

We've seen that our state of knowledge of a particle can be written in different ways:

wave function	$\psi(x)$	$\psi(x) = \int \delta(x)\psi(x')\,dx'$
mom. rep.	$\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} A(k)\, e^{ikx}\, dk$	$A(k) = \frac{1}{\sqrt{2\pi}}\int \psi(x) e^{-ikx} dx$
expansion in stationary states	$\sum c_n \psi_n$	$c_n = \int \psi_n(x)\psi(x)\,dx$

Suggests that we think of the state as an abstract concept that we can represent using whatever basis we choose – analogy with vectors

$$|\psi\rangle \longleftrightarrow \vec{A}$$

Dirac notation "ket"

$$\text{Basis} \quad |\psi_n\rangle \longleftrightarrow \vec{e}_i$$

eigenvectors of an operator

basis

eg position representation $\psi(x)$ $|x\rangle$

eigenfunction of position operator $\hat{x}|x\rangle = x|x\rangle$

mom. rep. $A(k)$ $|k\rangle$

$\hat{k}|k\rangle = k|k\rangle$

stationary states c_n $|\psi_n\rangle$

$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

these are the components of the vector

(A projection of $\vec{A}$ onto the ith axis)

$$A_i = \vec{e}_i \cdot \vec{A}$$

suggests we write

$$\psi(x) = \langle x|\psi\rangle$$
$$A(k) = \langle k|\psi\rangle$$
$$c_n = \langle \psi_n|\psi\rangle$$

where the dot product of two states is written as $\langle \phi|\psi\rangle$

"bra" "ket"

[Just like the dot product of two vectors, it takes the two states $|\phi\rangle$ and $|\psi\rangle$ and creates a (complex) scalar.]

To evaluate the dot product, we sum the product of the components $\vec{A} \cdot \vec{B} = \sum A_i B_i$

Do the same thing here

$$\langle \phi | \psi \rangle = \int_{-\infty}^{\infty} \phi^*(x)\, \psi(x)\, dx$$

only difference is we take the complex conjugate

Then

$$\psi(x) = \langle x | \psi \rangle$$

$$= \int \delta(x - x')\, \psi(x')\, dx' \quad \checkmark$$

$$A(k) = \langle k | \psi \rangle$$

$$= \int \frac{e^{-ikx}}{\sqrt{2\pi}}\, \psi(x)\, dx \quad \checkmark$$

$$c_n = \langle \psi_n | \psi \rangle$$

$$= \int \psi_n^*(x)\, \psi(x)\, dx \quad \checkmark$$ as before.

In the case where we evaluate the dot product using the eigenfunctions of the position operator as the basis, the dot product is an integral $\int_{-\infty}^{\infty}$ because there is a continuous infinite spectrum of eigenvalues of $\hat{x}$.

The vector $|\psi\rangle$ and the basis vectors $|x\rangle$ exist in an infinite-dimensional space <u>HILBERT SPACE</u>

A quick example of using this notation:

<u>Ex:</u> A particle is in a state $|\psi\rangle = \frac{1}{\sqrt{2}}(|\psi_1\rangle + |\psi_2\rangle)$

where $|\psi_1\rangle$ and $|\psi_2\rangle$ are the g.s. and 1st e.s. of HO.

Calculate Prob (measuring $E = E_2$)

$$|\langle\psi_2|\psi\rangle|^2 = \frac{1}{2}\Big|\underbrace{\langle\psi_2|\psi_1\rangle}_{0} + \underbrace{\langle\psi_1|\psi_1\rangle}_{1}\Big|^2$$

$$= \underline{\underline{\frac{1}{2}}}$$

Oct 26

Last time –

Dirac notation $|\psi\rangle$

Inner product $\langle \phi | \psi \rangle = \int_{-\infty}^{\infty} \phi^*(x)\, \psi(x)\, dx$

Exercise Write the following in Dirac notation:

a) the wavefunction is normalized

b) the probability of measuring position to be x

c) " " momentum " p

d) " " energy " E_n

e) the basis vectors are orthonormal

f) the expectation value of an operator $\hat{A}$

g) the Schrödinger equation.

Hermitian operators

What kinds of operators can represent observables?

First, introduce the idea of a Hermitian conjugate $\hat{A}^\dagger$ defined such that

$$\langle \hat{A}^\dagger \phi | \psi \rangle = \langle \phi | \hat{A} \psi \rangle$$

ie. $$\int (\hat{A}^\dagger \phi)^* \psi \, dx = \int \phi^* \hat{A} \psi \, dx$$

A Hermitian operator is its own Hermitian conjugate $\hat{A}^\dagger = \hat{A}$

$$\Rightarrow \quad \langle \hat{A} \psi | \psi \rangle = \langle \psi | \hat{A} \psi \rangle$$

or $$\int (\hat{A}\psi)^* \psi \, dx = \int \psi^* \hat{A} \psi \, dx$$

$$\overset{\parallel}{\left[\int \psi^* (\hat{A} \psi) \, dx \right]^*}$$

$$\Rightarrow \quad \left(\langle \psi | \hat{A} \psi \rangle \right)^* = \langle \psi | \hat{A} \psi \rangle$$

$$\Rightarrow \quad \langle A \rangle = \langle \psi | \hat{A} \psi \rangle \text{ is } \underline{\text{real}}$$

Since an observable must have a real expectation value, operators that correspond to observables must be Hermitian operators.

Ex: Prove that $(\hat{A}^{\dagger})^{\dagger} = \hat{A}$.

Ex: Prove that $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$ is Hermitian

We've seen the idea that we can expand a wavefunction as a linear combination of eigenfunctions of an operator.

eg. $$\psi(x) = \frac{1}{\sqrt{2\pi}} \int dk\, A(k)\, e^{ikx}$$

$$\psi(x) = \sum c_n \psi_n(x) = \sum c_n |\psi_n\rangle$$

This works because the eigenfunctions are orthogonal:

$$c_n = \int \psi_n^*(x)\, \psi(x)\, dx$$

$$
\left.
\begin{aligned}
c_n &= \langle \psi_n | \psi \rangle \\
|\psi\rangle &= \sum_m c_m |\psi_m\rangle \\
\langle \psi_n | \psi \rangle &= \sum_m c_m \langle \psi_n | \psi_m \rangle \\
&= \sum_m c_m \delta_{nm} \\
&= c_n .
\end{aligned}
\right\}
\begin{aligned}
&= \sum_m c_m \underbrace{\int \psi_n^* \psi_m \, dx}_{\delta_{nm}} \\
&= c_n \quad \checkmark
\end{aligned}
$$

or

$$
\begin{aligned}
A(k) &= \int \left(\frac{e^{ikx}}{\sqrt{2\pi}} \right)^* \psi(x) \, dx \\
&= \int \frac{e^{-ikx}}{\sqrt{2\pi}} \int dq \, A(q) \frac{e^{iqx}}{\sqrt{2\pi}} \, dx \\
&= \int dq \, A(q) \underbrace{\int dx \, \frac{e^{-ikx}}{\sqrt{2\pi}} \frac{e^{iqx}}{\sqrt{2\pi}}}_{\delta(q-k)} \\
&= A(k) \quad \checkmark
\end{aligned}
$$

$$
\begin{aligned}
|\psi\rangle &= \int dk \, A(k) \, |k\rangle \\
\langle q | \psi \rangle &= \int dk \, A(k) \, \langle q | k \rangle = \int dk \, A(k) \, \delta(q-k) \\
&= A(q).
\end{aligned}
$$

To prove that the eigenstates of a Hermitian operator are orthogonal:

Ex: Repeat this argument for a continuous spectrum of eigenvalues

Consider $\hat{A}\psi_1 = A_1\psi_1$

$$\hat{A}\psi_2 = A_2\psi_2$$

$$\langle\psi_2|\hat{A}|\psi_1\rangle = A_1\langle\psi_2|\psi_1\rangle$$

$$\langle\psi_2|\hat{A}\psi_1\rangle = \langle\hat{A}\psi_2|\psi_1\rangle = A_2\langle\psi_2|\psi_1\rangle$$

$$\Rightarrow \quad (A_1 - A_2)\langle\psi_2|\psi_1\rangle = 0$$

If $A_1 \neq A_2$ we see that $\boxed{\langle\psi_1|\psi_2\rangle = 0}$

the states are orthogonal.

What if $A_1 = A_2$? Then we can always choose linear combinations of ψ_1 and ψ_2 that are orthogonal:

$$\psi_\pm = \frac{1}{\sqrt{2}}(\psi_1 \pm \psi_2)$$

obey $\langle\psi_+|\psi_-\rangle = 0$

and so are valid states to use for our expansion.

Time-dependence of an observable

$$\frac{d\langle O\rangle}{dt} = \int_{-\infty}^{\infty} dx \left(\frac{\partial \psi^*}{\partial t}\hat{O}\psi + \psi^*\hat{O}\frac{\partial\psi}{\partial t} \right)$$

$$+ \int dx\, \psi^* \frac{\partial \hat{O}}{\partial t}\psi$$

the operator itself could have a specific time-dependence

Use the schrödinger equation $i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$

$$\frac{d\langle O\rangle}{dt} = \left\langle \frac{\partial\hat{O}}{\partial t}\right\rangle + \frac{1}{i\hbar}\int dx\left(-(\hat{H}\psi^*)\hat{O}\psi + \psi^*\hat{O}\hat{H}\psi \right)$$

but $\int dx\, (\hat{H}\psi^*)\hat{O}\psi = \int dx\, \psi^*\hat{H}\hat{O}\psi$

by the Hermitian property of $\hat{H}$.

$$\Rightarrow \frac{d\langle O\rangle}{dt} = \left\langle\frac{\partial\hat{O}}{\partial t}\right\rangle + \frac{1}{i\hbar}\int dx\, \psi^*[\hat{O},\hat{H}]\psi$$

$$\boxed{\frac{d\langle O\rangle}{dt} = \frac{1}{i\hbar}\langle[\hat{O},\hat{H}]\rangle + \left\langle\frac{\partial\hat{O}}{\partial t}\right\rangle}$$

eg. Consider $\hat{O} = \hat{x}$ with $\hat{H} = \frac{\hat{p}^2}{2m} + V$

$$[\hat{x}, \hat{H}] = \frac{1}{2m}[\hat{x}, \hat{p}^2] \qquad [\hat{p}, \hat{x}] = -i\hbar$$

$$= \frac{1}{2m}\left(\hat{x}\hat{p}\hat{p} - \hat{p}\hat{p}\hat{x}\right)$$

$$= \frac{1}{2m}\left(\hat{x}\hat{p}\hat{p} - \hat{p}\hat{x}\hat{p} + i\hbar\hat{p}\right)$$

$$= \frac{1}{2m}\left(i\hbar\hat{p} + i\hbar\hat{p}\right)$$

$$= \frac{i\hbar\hat{p}}{m}$$

$$\Rightarrow \quad \frac{d\langle x\rangle}{dt} = \frac{1}{i\hbar}\langle[\hat{p}, \hat{H}]\rangle$$

$$= \frac{1}{i\hbar}\left\langle \frac{i\hbar}{m}\hat{p}\right\rangle$$

$$\boxed{\frac{d\langle x\rangle}{dt} = \frac{\langle p\rangle}{m}}$$

Last time:

Commutator $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$

eg. $[\hat{p}, \hat{x}] = -i\hbar$

time-dependence of expectation value

$$\frac{d\langle A\rangle}{dt} = \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle + \frac{i}{\hbar}\langle [\hat{H}, \hat{A}]\rangle$$

eg. $$\frac{d\langle x\rangle}{dt} = \frac{i}{\hbar}\langle [\hat{H}, \hat{x}]\rangle$$

$$[\hat{H}, \hat{x}] = \frac{1}{2m}[\hat{p}^2, \hat{x}] = \frac{1}{2m}\left(\hat{p}\hat{p}x - \hat{p}\hat{x}\hat{p} + \hat{p}\hat{x}\hat{p} - \hat{x}\hat{p}\hat{p}\right)$$

$$= \frac{1}{2m}\left(\hat{p}[\hat{p}, \hat{x}] + [\hat{p}, \hat{x}]\hat{p}\right)$$

$$= \frac{1}{2m}\left(-i\hbar\hat{p} - i\hbar\hat{p}\right)$$

$$= -\frac{i\hbar}{m}\hat{p}$$

$$\Rightarrow \quad \underline{\underline{\frac{d\langle x\rangle}{dt} = \frac{\langle p\rangle}{m}}}$$

Commuting operators share the same eigenfunctions (but with different eigenvalues)

eg. if $\hat{A}|\psi\rangle = a|\psi\rangle$

and $\hat{B}|\psi\rangle = b|\psi\rangle$

for the same eigenstate $|\psi\rangle$

then $\hat{A}\hat{B}|\psi\rangle = \hat{A}(b|\psi\rangle) = b\hat{A}|\psi\rangle$

$= ba|\psi\rangle$

$\hat{B}\hat{A}|\psi\rangle = \hat{B}\left(\hat{A}|\psi\rangle\right) = \hat{B}(a|\psi\rangle)$

$= a\hat{B}|\psi\rangle = ab|\psi\rangle$

$\Rightarrow \underline{\underline{[\hat{A},\hat{B}] = 0}}$

eg. $\hat{p}$ and $\hat{H} = \frac{\hat{p}^2}{2m}$ (free particle Hamiltonian)

commute: $[\hat{p},\hat{H}]$

$\propto [\hat{p},\hat{p}^2] = 0$

and have eigenfunctions $e^{ipx/\hbar}$

(eigenvalues p and $p^2/2m$)

An operator with $[\hat{H}, \hat{A}] = 0$

must therefore have the same eigenstates

as $\hat{H}$ — the stationary states.

This explains why $\frac{d\langle A \rangle}{dt} \neq 0$

requires $[\hat{H}, \hat{A}] \neq 0$

so that the eigenfunctions of $\hat{A}$

are not stationary states.

Exercises with operators and Dirac notation

Prove that:

1) $\left(\langle \psi | \hat{A} | \phi \rangle \right)^* = \langle \phi | \hat{A} | \psi \rangle$

for Hermitian operator $\hat{A}$

2) $(AB)^\dagger = B^\dagger A^\dagger$

3) $[\hat{A}, \hat{B}]^\dagger = [\hat{B}, \hat{A}]$ (ie. the commutator is anti-Hermitian)

4) $(\hat{A}^\dagger)^\dagger = \hat{A}$

5) $\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$ is a Hermitian operator

6) Calculate $[\hat{p}, \hat{V}]$ for a potential $\hat{V} = V(x)$

Parity operator

We've seen that when $V(x)$ is symmetric about the origin $[V(-x) = V(x)]$ the stationary states are either odd or even

eg

To understand this we can define a parity operator $\hat{P}\psi(x) = \psi(-x)$

Even and odd wavefunctions are eigenstates of $\hat{P}$

EVEN $\hat{P}\psi(x) = \psi(-x) = \psi(x)$

eigenvalue $+1$

ODD $\hat{P}\psi(x) = \psi(-x) = -\psi(x)$

eigenvalue -1

The stationary states will be eignstates of $\hat{P}$ if $[\hat{P}, \hat{H}] = 0$.

What does this imply for H?

$$\hat{P}\,\hat{H}(x)\,\psi(x) = \hat{H}(-x)\,\psi(-x)$$
$$\hat{H}\,\hat{P}\,\psi(x) = \underbrace{\hat{H}(x)\,\psi(-x)}$$

for these to be the same, $\hat{H}(-x) = \hat{H}(x)$

or $V(-x) = V(x)$

If $V(-x) = V(x)$

then $[\hat{H}, \hat{P}] = 0$

$\Rightarrow$ stationary states are eigenstates of $\hat{P}$

$\Rightarrow$ stationary states are odd or even.

Exercise:

a) Show that $+1$ and -1 are the only possible eigenvalues of $\hat{\mathbb{P}}$.

b) Is $\hat{\mathbb{P}}$ a Hermitian operator?

Ladder operator for the harmonic oscillator

Another kind of operator is a LADDER OPERATOR.

The LOWERING OPERATOR $\hat{a}$ takes a state $|\psi_n\rangle$ and "lowers" it to $|\psi_{n-1}\rangle$.

$$\boxed{\hat{a}|\psi_n\rangle = \sqrt{n}\,|\psi_{n-1}\rangle}$$

Note that $\hat{a}|\psi_0\rangle = 0$ (can't lower the ground state)

The lowering operator is not Hermitian. To see this, consider

$$\langle\psi_{n-1}|\hat{a}|\psi_n\rangle = \sqrt{n}\,\langle\psi_{n-1}|\psi_{n-1}\rangle$$

$$= \sqrt{n}$$

Now act $\hat{a}$ to the left:

$$\left(\langle\psi_{n-1}|\hat{a}^{\dagger}\right)|\psi_n\rangle$$

this must give the same answer, $\sqrt{n}$

$\Rightarrow$ $\hat{a}^\dagger$ must be a RAISING OPERATOR

$$\boxed{\hat{a}^\dagger |\psi_{n-1}\rangle = \sqrt{n}\, |\psi_n\rangle}$$

We can make a Hermitian operator by combining $\hat{a}^\dagger$ and $\hat{a}$:

$$\hat{N} = \hat{a}^\dagger \hat{a}$$ is Hermitian ($\hat{N}^\dagger = \hat{N}$)

$\hat{N}$ is the NUMBER OPERATOR

$$\hat{N}|\psi_n\rangle = \hat{a}^\dagger \hat{a} |\psi_n\rangle = n |\psi_n\rangle.$$

The eigenfunctions of $\hat{N}$ are the stationary states, ie. $[\hat{N}, \hat{H}] = 0$

This makes sense (and is the reason this all works) because recall that the harmonic oscillator energy levels are

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

So that if $\hat{N}$ is the number operator, we must be able to write

$$\hat{H} = (\hat{N} + \tfrac{1}{2})\hbar\omega = (\hat{a}^\dagger \hat{a} + \tfrac{1}{2})\hbar\omega$$

(then $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$).

To see that we can write $\hat{H}$ in this way, start with

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$$

Complete the square:

$$\hat{H} = \hbar\omega\left[\frac{\hat{p}^2}{2m\hbar\omega} + \frac{m\omega}{2\hbar}\hat{x}^2\right]$$

$$= \hbar\omega\Bigg[\left(\sqrt{\frac{m\omega}{2\hbar}}\,\hat{x} - \frac{i\hat{p}}{\sqrt{2m\hbar\omega}}\right)$$

$$\times\left(\sqrt{\frac{m\omega}{2\hbar}}\,\hat{x} + \frac{i\hat{p}}{\sqrt{2m\hbar\omega}}\right)$$

$$\frac{+i}{2\hbar}[\hat{p},\hat{x}]\Bigg]$$

$$\Rightarrow \quad \hat{H} = \hbar\omega\left(\hat{a}^\dagger \hat{a} + \frac{1}{2}\right)$$

if we identify

$$\hat{a} \equiv \sqrt{\frac{m\omega}{2\hbar}}\,\hat{x} + i\frac{\hat{p}}{\sqrt{2m\hbar\omega}} .$$

Harmonic oscillator wavefunctions

[Exercise: now find $\psi_1(x)$]

We can use $\hat{a}|\psi_0\rangle = 0$ to get $\psi_0(x)$

$$\text{ie. } \left(\sqrt{\frac{m\omega}{2\hbar}}\,x + \frac{i}{\sqrt{2m\hbar\omega}}\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\psi_0(x) = 0$$

$$\left(m\omega x + \hbar\frac{\partial}{\partial x}\right)\psi_0 = 0$$

$$\frac{\partial \psi_0}{\partial x} = -\frac{m\omega}{\hbar}x\,\psi_0$$

$$\Rightarrow \boxed{\psi_0 \propto e^{-\frac{x^2 m\omega}{2\hbar}}}$$

Gaussian, just as we found numerically

The uncertainty principle

We've seen already that if two operators commute $[\hat{A},\hat{B}]=0$ then an eigenfunction of $\hat{A}$ is also an eigenfunction of $\hat{B}$. This implies that a measurement of A will also tell us B, ie. we can have complete certainty about the values of A and B. An example is the energy and momentum of a free particle.

This implies that the uncertainty principle must depend on whether two operators commute.

We measure uncertainty by the standard deviation of an observable ΔA where

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

$$= \langle (A^2 - 2A\langle A \rangle + \langle A \rangle^2) \rangle$$

$$= \langle A^2 \rangle - \langle A \rangle^2$$

$$= \langle \psi | \hat{A}^2 | \psi \rangle - \langle \psi | \hat{A} | \psi \rangle^2$$

In part 2 of the course, we wrote down the uncertainty relation for Δx and Δp:

$$\Delta x \, \Delta p \geq \hbar/2$$

(see page 4a of part 2 notes)

This is one particular example of a general uncertainty relation for two observables A and B with corresponding operators $\hat{A}$ and $\hat{B}$:

$$\boxed{(\Delta A)^2 (\Delta B)^2 \geq \left(\frac{\langle [\hat{A}, \hat{B}] \rangle}{2i} \right)^2} \quad \text{—} (*)$$

eg. for momentum and position, $\langle [\hat{x}, \hat{p}] \rangle = i\hbar$

$$\Rightarrow \quad (\Delta x)^2 (\Delta p)^2 \geq \left(\frac{i\hbar}{2i} \right)^2$$

$$\text{or} \qquad \underline{\Delta x \, \Delta p \geq \hbar/2}$$

as we had seen previously. Also, as we suspected two operators that commute can have $\Delta A \, \Delta B = 0$, so that we can know both quantities precisely.

The proof of $(*)$ is a bit long, so I'll include it separately (see page 22a).

Proof of generalized uncertainty relation

(this is the argument from Griffiths 3.5)

To prove equation (*) we need two results:

1) Schwarz inequality

$$\langle f|f\rangle\langle g|g\rangle \geqslant |\langle f|g\rangle|^2$$

eg. for two 3D vectors $\vec{A}, \vec{B}$ $\quad |\vec{A}|^2|\vec{B}|^2 \geqslant (\vec{A}\cdot\vec{B})^2$

since $\dfrac{\vec{A}\cdot\vec{B}}{\sqrt{|\vec{A}|^2|\vec{B}|^2}} = \cos\theta$ with θ the angle between the two vectors.

2) For any complex number z, $\quad |z|^2 \geqslant \mathrm{Im}(z)^2$

$$\geqslant \left[\frac{z-z^*}{2i}\right]^2$$

Then define two ~~operators $\hat{f}^*$~~ states

$$|f\rangle = (\hat{A}-\langle A\rangle)|\psi\rangle$$
$$|g\rangle = (\hat{B}-\langle B\rangle)|\psi\rangle$$

so that $(\Delta A)^2 = \langle\psi|(\hat{A}-\langle A\rangle)^2|\psi\rangle =$ [illegible]

$$= \langle f|f\rangle$$

and similarly $\langle g|g\rangle = (\Delta B)^2$.

The cross product is

$$\langle f|g\rangle = \langle\hat{A}\hat{B}\rangle - \langle A\rangle\langle B\rangle$$
$$\langle g|f\rangle = \langle\hat{B}\hat{A}\rangle - \langle A\rangle\langle B\rangle$$

Now combine (1) and (2): $\quad \langle f|f\rangle\langle g|g\rangle \geqslant \left[\dfrac{\langle f|g\rangle - \langle g|f\rangle}{2i}\right]^2$

$$\Rightarrow \quad (\Delta A)^2 (\Delta B)^2 \geq \left[\frac{\langle [\hat{A}, \hat{B}] \rangle}{2i} \right]^2$$

which is equation (*).

In section 2 of the course, we found that a Gaussian wavepacket had the minimum uncertainty $\Delta x \Delta p \underset{\uparrow \text{ equals sign.}}{=} \hbar/2$

We can prove that here by setting the inequalities (1) and (2) to equalities, which means that $|f\rangle \propto |g\rangle$

$$\text{and} \quad \mathrm{Re}(z) = 0 = \mathrm{Re}(\langle f | g \rangle)$$

$$\Rightarrow \quad \boxed{|g\rangle = i\underset{\uparrow \text{ real constant } a}{a} |f\rangle} \quad \text{defines minimum uncertainty state}$$

for momentum - position

we have $\left(\frac{\hbar}{i} \frac{\partial}{\partial x} - \langle p \rangle \right) \psi = i a \left(x - \langle x \rangle \right) \psi$

$$\Rightarrow \quad \boxed{\psi(x) = A\, e^{-a(x - \langle x \rangle)^2 / 2\hbar}\, e^{i \langle p \rangle x / \hbar}}$$

The minimum uncertainty wavepacket.

Matrix elements

Once we have chosen a basis $|\psi_i\rangle$ we can represent any operator $\hat{A}$ as a matrix A_{mn} where

$$\boxed{A_{mn} = \langle \psi_m | \hat{A} | \psi_n \rangle.}$$

MATRIX ELEMENTS OF OPERATOR $\hat{A}$.

Then, for exaple if we have a state $|\psi\rangle$ and we want to compute the expectation value of $\hat{A}$

$$\langle A \rangle = \langle \psi | \hat{A} | \psi \rangle$$

we can write this as a matrix operation by expanding

$$|\psi\rangle = \sum c_n |\psi_n\rangle$$

Then

$$\langle A \rangle = \sum c_m^* \langle \psi_n | \hat{A} \sum c_n |\psi_n\rangle$$

$$\boxed{\langle A \rangle = \sum_{m,n} c_m^* A_{mn} c_n}.$$

A Hermitian operator satisfies

$$\langle \psi_m | \hat{A} | \psi_n \rangle^*$$

$$= \langle \psi_n | \hat{A}^\dagger | \psi_m \rangle$$

$$= \langle \psi_n | \hat{A} | \psi_m \rangle$$

(you should make sure you understand what I am doing here – if not write everything out in terms of integrals)

$$\text{or} \quad A_{mn}^* = A_{nm}$$

The matrix is invariant under transpose + complex conjugate.

Such matrices are known as <u>Hermitian matrices</u>.

For example, consider the ladder operators for the harmonic oscillator. Use the stationary states as a basis $|\psi_n\rangle$.

Then $\langle \psi_m | \hat{a} | \psi_n \rangle = \sqrt{\hbar}\sqrt{n} \, \langle \psi_m | \psi_{n-1} \rangle$

$$(\hat{a})_{mn} = \sqrt{\hbar}\sqrt{n} \; \delta_{m,n-1}$$

$$\Rightarrow \quad (\hat{a})_{mn} = \begin{pmatrix} 0 & \sqrt{1} & & & & \\ & 0 & \sqrt{2} & & \bigcirc & \\ & & 0 & \sqrt{3} & & \\ & \bigcirc & & 0 & \sqrt{4} & \\ & & & & 0 & \sqrt{5} \\ & & & & & 0 \\ & & & & & & \ddots \end{pmatrix} \sqrt{\hbar}$$

(infinite matrix)

$$(\hat{a}^{\dagger})_{mn} = \begin{pmatrix} 0 & & & & & \\ \sqrt{1} & 0 & & & \bigcirc & \\ & \sqrt{2} & 0 & & & \\ & & \sqrt{3} & 0 & & \\ & \bigcirc & & \sqrt{4} & 0 & \\ & & & & \sqrt{5} & 0 \\ & & & & & & \ddots \end{pmatrix} \sqrt{\hbar}$$

Multiply these matrices, eg. truncate them at 3×3

$$\begin{pmatrix} 0 & \sqrt{1} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{1} & 0 & e \\ 0 & \sqrt{2} & 0 \end{pmatrix} = \begin{pmatrix} 1 & & \\ & 2 & \\ & & \ddots \end{pmatrix}$$

$\Rightarrow$ the Hamiltonian is $\hat{H} = \omega \hat{a} \hat{a}^{\dagger} - \frac{1}{2}\hbar\omega$

$$\Rightarrow \quad \hat{H} = \begin{pmatrix} \frac{1}{2} & & & & \\ & \frac{3}{2} & & 0 & \\ & & \frac{5}{2} & & \\ & 0 & & \frac{7}{2} & \\ & & & & \ddots \end{pmatrix} \hbar\omega$$

the Hamiltonian is diagonal in this basis as it must be — to see this calculate it directly:

$$H_{mn} = \langle \psi_m | \hat{H} | \psi_n \rangle = (n + \tfrac{1}{2}) \hbar\omega \; \delta_{nm}$$

Any operator expressed as matrix elements with a basis of its own eigenstates will be diagonal in that basis.

~~Such matrices are known as Hermitian matrices.~~

Example: neutrino oscillations

In the 1960s it was discovered that the number of electron neutrinos coming from the Sun was about 3 times smaller than predicted by solar models ("the solar neutrino problem"). We now know that the electron neutrinos change flavor into either mu or tau neutrinos on their way to Earth. A neutrino that starts off as an electron neutrino will change into a mu neutrino and back again as it propagates — this is referred to as "neutrino oscillations".

We now have enough quantum mechanics to be able to describe this. The neutrinos are produced in weak interactions in "flavor eigenstates" ie. as either e^-, μ, or τ neutrinos

$$|e^-\rangle,\ |\mu\rangle,\ \text{or } |\tau\rangle.$$

So we can imagine there's a flavor operator $\hat{F}$ that measures the neutrino flavor

$$\hat{F}|e^-\rangle = (\text{electron neutrino})\,|e^-\rangle$$

$$\hat{F}|\mu\rangle = (\text{mu neutrino})\,|\mu\rangle$$

This is what the neutrino detectors are doing because they use weak interactions to detect the neutrinos.

Neutrino oscillations arise because the flavor eigenstates are not eigenstates of the Hamitonian operator.

* The picture is that there are three neutrino particles with masses m_1, m_2, m_3. If I create one of these neutrinos with energy E and momentum p it is in an eigenstate of the Hamiltonian (a state with definite energy). But it turns out that that is not a flavor eigenstate — a measurement of the neutrino flavor (by a weak reaction) could give e, μ or τ with some probability.

Vice versa if I create a 100% electron neutrino it is not in a stationary state of the Hamiltonian – it is a mixture of the three particles 1, 2, and 3. Each of these evolves differently in time because they have different masses m_1, m_2, m_3, so even if the three components have the same energy E they have different momentum p and therefore different $k = p/\hbar$. (different wavelength).
As they propagate they become out of phase and the mixture no longer corresponds to a pure electron neutrino.

Mathematically what this means is that if we use the flavor eigenstates as a basis, the Hamiltonian is not a diagonal matrix. So what we'll do here is to try a simple mathematical model in which the Hamiltonian is not diagonal but has off-diagonal terms.

Imagine that there are only two neutrino flavors, and that the matrix elements of the Hamiltonian in the flavor basis are

$$\langle e|\hat{H}|e\rangle = h$$
$$\langle e|\hat{H}|\mu\rangle = g$$
$$\langle \mu|\hat{H}|\mu\rangle = h$$

(follow Griffiths notation on p 121 here)

ie. $\hat{H} = \begin{pmatrix} h & g \\ g & h \end{pmatrix}$ in the flavor basis

then as vectors $|e\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ $|\mu\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

Imagine we create an electron neutrino $|e\rangle$. What is its time-dependence? It cannot stay constant in time because it is not an eigenstate of the Hamiltonian. (stationary state)

We need to find the stationary states by solving $\hat{H}\psi = E\psi$ for the eigenvalues E and vectors ψ of $\hat{H}$.

$$\hat{H}\psi = E\psi$$
$$\Rightarrow (\hat{H} - E)\psi = 0$$

or as a matrix $\begin{pmatrix} h-E & g \\ g & h-E \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = 0$ — (*)

$\uparrow$ Components of the vector ψ in the flavor basis

For a non-trivial solution we need the determinant of the matrix $\underline{\underline{H}} - E\underline{\underline{I}}$ to vanish (why? make sure you know the answer!)

$$\det \begin{pmatrix} h-E & g \\ g & h-E \end{pmatrix} = 0$$

$$\Rightarrow \quad (h-E)^2 - g^2 = 0$$

$$\Rightarrow \quad E = h \pm g = E_\pm$$

there are two eigenvalues, ie. two stationary states with energies E_+ and E_-.

To find the eigenvectors, substitute back into (*)

$$\begin{pmatrix} h-E_+ & g \\ g & h-E_+ \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = 0$$

$$\Rightarrow \begin{pmatrix} -g & g \\ g & -g \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = 0$$

$$\Rightarrow \left. \begin{aligned} -g\psi_1 + g\psi_2 &= 0 \\ g\psi_1 - g\psi_2 &= 0 \end{aligned} \right\} \Rightarrow \psi_1 = \psi_2$$

$$\begin{pmatrix} h-E_- & g \\ g & h-E_- \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = 0 \Rightarrow \psi_1 + \psi_2 = 0 \Rightarrow \psi_1 = -\psi_2$$

$\Rightarrow$ the eigenstates are

$$|\psi_+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{energy } E_+$$

$$|\psi_-\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad E_-$$

Now imagine at $t=0$ we make an electron neutrino

$$|\psi(t=0)\rangle = |e\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}} \left(|\psi_+\rangle + |\psi_-\rangle \right)$$

It's time dependence is

$$|\psi\rangle(t) = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} e^{-iE_+t/\hbar} + \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix} e^{-iE_-t/\hbar}\right]$$

$$= \frac{1}{(\sqrt{2})^2}\begin{pmatrix} e^{-iE_+t/\hbar} + e^{-iE_-t/\hbar} \\ e^{-iE_+t/\hbar} - e^{-iE_-t/\hbar}\end{pmatrix}$$

$$= \frac{1}{(\sqrt{2})^2} e^{-iht/\hbar}\begin{pmatrix} e^{-igt/\hbar} + e^{igt/\hbar} \\ e^{-igt/\hbar} - e^{igt/\hbar}\end{pmatrix}$$

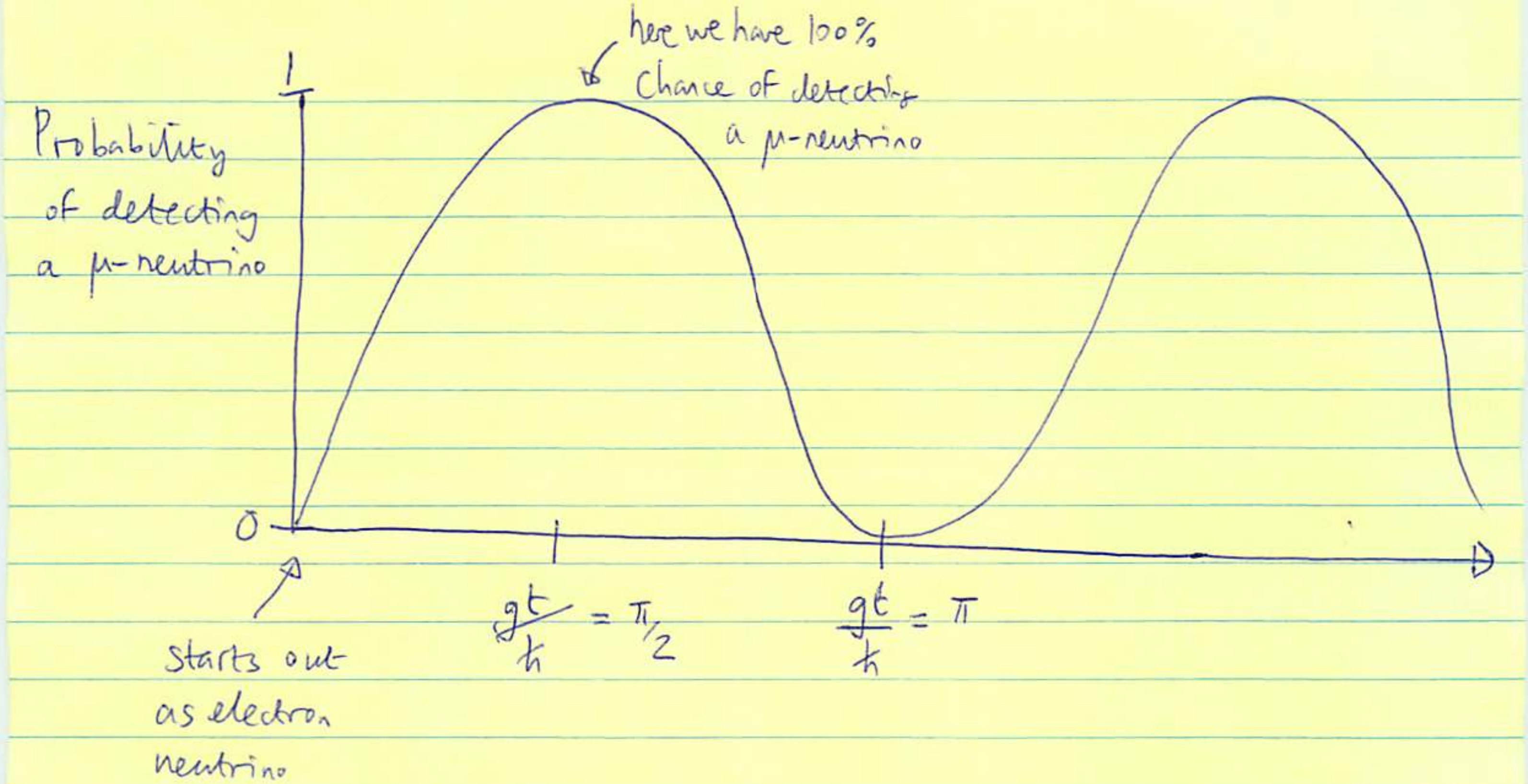
$$= \frac{1}{(\sqrt{2})^2} e^{-iht/\hbar}\begin{pmatrix} 2\cos gt/\hbar \\ -2i\sin gt/\hbar\end{pmatrix}$$

$$\boxed{|\psi\rangle(t) = e^{-iht/\hbar}\begin{pmatrix}\cos(gt/\hbar) \\ -i\sin\left(\frac{gt}{\hbar}\right)\end{pmatrix}}$$

Now imagine we build a detector that detects mu-neutrinos. What is the probability we will detect something?

$$|\langle\mu|\psi\rangle|^2 = \left|\begin{pmatrix}0\\1\end{pmatrix} \cdot e^{-iht/\hbar}\begin{pmatrix}\cos gt/\hbar \\ -i\sin gt/\hbar\end{pmatrix}\right|^2$$

$$= \sin^2\left(\frac{gt}{\hbar}\right).$$



here we have 100% chance of detecting a μ-neutrino

starts out as electron neutrino

The period of oscillation is $\frac{2\pi}{P} = g/\hbar = \frac{E_+ - E_-}{2\hbar}$

or $P = \frac{4\pi\hbar}{\Delta E}$

Here we considered only the time-dependence $e^{-iEt/\hbar}$ but if the neutrino is travelling through space then we should write $e^{-iEt/\hbar + ipx/\hbar}$

For a relativistic particle with $E \gg mc^2$, the velocity is $\simeq c$

$$\Rightarrow \quad Et - px = t(E - pc)$$

but $pc = \sqrt{E^2 - (mc^2)^2} \simeq E\left(1 - \frac{1}{2}\frac{(mc^2)^2}{E^2}\right)$

$$\Rightarrow \quad Et - px \simeq \frac{1}{2} t \left(\frac{mc^2}{E}\right)^2 E$$

In that case the same result as before applies but now

$$\frac{g}{\hbar} = \frac{(E_+ - p_+c) - (E_- - p_-c)}{2\hbar}$$

$$= \frac{1}{2\hbar}\,\Delta\left(\frac{m^2c^4}{2E}\right)$$

and $$P = \frac{2\pi\hbar}{g} = \frac{2\pi\;2\hbar\;2}{\Delta\left(m^2/E\right)\,c^4}$$

$$\boxed{P = \frac{4h}{c^4}\,\frac{1}{\Delta(m^2/E)}}$$

⇒ The neutrino oscillations tell us about the differences in m^2 between the neutrino types.

The neutrino oscillations tell us that neutrinos are not massless particles but they have a mass.

Part 5: Quantum Mechanics in 3D

The Schrödinger Equation and Momentum Operator in 3D

Everything we've done so far generalizes to 3D. The wavefunction depends on position $\mathbf{r} = (x, y, z)$, and the probability density is per unit volume, so that

$$|\Psi(\mathbf{r})|^2 \ d^3\mathbf{r}$$

is the probability of finding the particle in an infinitesimal volume at position $\mathbf{r}$. The normalization condition is then an integral over all space

$$\int |\Psi(\mathbf{r})|^2 \ d^3\mathbf{r} = 1.$$

The momentum operator is now a vector operator

$$\hat{\mathbf{p}} = \frac{\hbar}{i}\nabla$$

with components

$$p_x = \frac{\hbar}{i}\frac{\partial}{\partial x} \qquad p_y = \frac{\hbar}{i}\frac{\partial}{\partial y} \qquad p_z = \frac{\hbar}{i}\frac{\partial}{\partial z}.$$

The eigenstate of $\hat{\mathbf{p}}$ in 3D is the plane wave

$$\Psi_p \propto \exp\left(i\mathbf{k}\cdot\mathbf{r} - i\omega t\right).$$

The kinetic energy is

$$\frac{\hat{\mathbf{p}}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2$$

so that the Hamiltonian can be written

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

(the Schrödinger equation is $i\hbar\partial\Psi/\partial t = \hat{H}\Psi$ as usual).

An important point is that the position-momentum uncertainty relation applies in 3D, but only for position and momentum components in the same direction, i.e.

$$[\hat{x}, \hat{p}_x] = i\hbar \qquad [\hat{y}, \hat{p}_y] = i\hbar \qquad [\hat{z}, \hat{p}_z] = i\hbar$$

but $[\hat{x}, \hat{p}_y] = 0$ etc. A compact way to write this is

$$[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}.$$

Different components of $\hat{\mathbf{x}}$ commute and the same for $\hat{\mathbf{p}}$, e.g. $[\hat{x}, \hat{y}] = 0$, $[\hat{p}_x, \hat{p}_y] = 0$ etc.

Rotations and Angular Momentum

In 1D, we introduced the translation operator that translates the wavefunction in x

$$\hat{T}(\Delta x)\psi(x) = \psi(x - \Delta x)$$

and showed that for infinitesimal translations it can be written as

$$\hat{T}(dx) = 1 - \frac{i}{\hbar}\hat{p}\, dx.$$

If the Hamiltonian is translationally-invariant (it remains unchanged under the action of the translation operator) then it follows that $[\hat{H}, \hat{T}] = 0 \Rightarrow [\hat{H}, \hat{p}] = 0$ and therefore that the stationary states are also eigenstates of the momentum operator. Translational invariance of the potential implies that the stationary states have a definite momentum.

There is a similar connection in 3D between rotational invariance and angular momentum. To see this, we define a rotation operator which rotates the wavefunction about the z-axis by infinitesimal angle $d\phi$

$$\hat{R}(d\phi)\Psi(x,y,z) = \Psi(x + yd\phi,\, y - xd\phi,\, z).$$

Expanding in a Tayor series gives

$$\begin{aligned} \Psi(x + yd\phi,\, y - xd\phi,\, z) &\approx \Psi(x,y,z) + yd\phi\frac{\partial \Psi}{\partial x} - xd\phi\frac{\partial \Psi}{\partial y} \\ &\approx \left[1 - \frac{id\phi}{\hbar}\left(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x\right)\right]\Psi(x,y,z). \end{aligned}$$

That particular combination of position and momentum operators we recognize as the z-component of angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, ie. we can write an operator corresponding to the z-component of angular momentum

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x.$$

Comparing with the definition of the rotation operator, we see that

$$\hat{R}(d\phi) = 1 - \frac{id\phi}{\hbar}\hat{L}_z.$$

(Notice that the units work out: $\hbar$ has units of momentum times position which is angular momentum.)

We can now make the same symmetry argument as for translations. If the Hamiltonian is invariant under rotations about the z-axis, it follows that $[\hat{H}, \hat{R}] = 0$ and therefore $[\hat{H}, \hat{L}_z] = 0$, so that the stationary states have a definite angular momentum about the rotation axis.

Angular momentum commutation relations

What about the other components of angular momentum? Using the definition of angular momentum, it is straightforward to show that the commutation relations are non-vanishing:

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x$$

$$[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$$

(notice that these are cyclic permutations of each other).

The fact that the different components of the angular momentum operator do not commute means that we can only know one of them with certainty at any given time. This is different from linear momentum, where the components $\hat{p}_x$, $\hat{p}_y$, and $\hat{p}_z$ do commute and we are able to exactly specify the momentum vector $\hat{\mathbf{p}}$. The difference lies in the fact that translations commute, whereas rotations do not (try it!).

Exercise 25: Imagine if we knew that the angular momentum of a particle was $\mathbf{L} = (0, 0, L_z)$, i.e. purely in the z-direction. Show that this violates the momentum-position uncertainty principle. What if we knew that only one of L_x or L_y vanished instead of both of them?

The operator

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

gives the magnitude of the angular momentum. Unlike $\hat{L}_x$ and $\hat{L}_y$, $\hat{L}^2$ *does* commute with $\hat{L_z}$

$$[\hat{L}^2, \hat{L}_z] = 0.$$

Exercise 26: Use the commutation relations between $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ to show that $[\hat{L}^2, \hat{L}_z] = 0$.

This means that eigenstates of $\hat{L}_z$ are also eigenstates of $\hat{L}^2$, ie. there must be states $|\psi\rangle$ for which

$$\begin{aligned} \hat{L}_z |\psi\rangle &= m\hbar |\psi\rangle \\ \hat{L}^2 |\psi\rangle &= \lambda\hbar^2 |\psi\rangle . \end{aligned}$$

The factors of $\hbar$ are there to get the units right. In the next section, we'll use angular momentum ladder operators to work out the allowed values of m and λ.

Ladder operators and the spectrum of eigenvalues

The angular momentum ladder operators are

$$\begin{aligned}\hat{L}_+ &= \hat{L}_x + i\hat{L}_y \\ \hat{L}_- &= \hat{L}_x - i\hat{L}_y.\end{aligned}$$

They have commutation relations

$$\begin{aligned}[\hat{L}_z, \hat{L}_+] &= \hbar\hat{L}_+ \\ [\hat{L}_z, \hat{L}_-] &= -\hbar\hat{L}_-.\end{aligned}$$

You can see the ladder operator behaviour by looking at

$$\hat{L}_z\left(\hat{L}_+\left|\psi\right\rangle\right) = \hat{L}_+\hat{L}_z\left|\psi\right\rangle + \hbar\hat{L}_+\left|\psi\right\rangle = (m+1)\hbar\left(\hat{L}_+\left|\psi\right\rangle\right)$$

which shows that $\hat{L}_+$ acts to raise the eigenfunction with eigenvalue m to the eigenfunction with eigenvalue $m+1$.

Exercise 27: Use a similar argument to show that $\hat{L}_-$ is a lowering operator.

To explore the allowed values of m, consider the state for which m takes on the maximum allowed value, call it ℓ. Then

$$\hat{L}_+\left|\Psi(m=\ell)\right\rangle = 0.$$

Now consider

$$\hat{L}_-\hat{L}_+ = (\hat{L}_x - i\hat{L}_y)(\hat{L}_x + i\hat{L}_y) = \hat{L}_x^2 + \hat{L}_y^2 + i[\hat{L}_x, \hat{L}_y] = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z$$

operating on this maximal state

$$\hat{L}_-\hat{L}_+\left|\Psi(m=\ell)\right\rangle = 0 = (\lambda\hbar^2 - \ell^2\hbar^2 - \ell\hbar)\left|\Psi(m=\ell)\right\rangle$$

$$\Rightarrow \lambda = \ell(\ell+1).$$

This shows that if we write the eigenvalue of $\hat{L}^2$ as $\ell(\ell+1)\hbar^2$, then the eigenvalues of $\hat{L}_z$ can take on integer values m up to $m = \ell$.

Exercise 28: What about in the other direction? Use a similar argument to show that the minimal value of m is $m = -\ell$.

The angular momentum eigenstates

Now that we have the eigenvalue spectrum for angular momentum, we can write the states as $|\ell\ m\rangle$ which obey

$$\begin{aligned}\hat{L}_z\,|\ell\ m\rangle &= m\hbar\,|\ell\ m\rangle \\ \hat{L}^2\,|\ell\ m\rangle &= \ell(\ell+1)\hbar^2\,|\ell\ m\rangle\,.\end{aligned}$$

For a given value of $\ell = 0, 1, 2, ...$, the allowed values of m range from $-\ell$ to $+\ell$ in integer steps.

Exercise 29: Derive a formula for the number of m values at each ℓ.

Exercise 30: A particle with $\ell = 1$ is in the state

$$|\psi\rangle = \frac{1}{\sqrt{3}}\,|10\rangle + \sqrt{\frac{2}{3}}\,|11\rangle\,.$$

What possible values of m might you measure for the particle, and what are the probabilities of measuring each one?

Exercise 31: When $\ell = 0$, all components of angular momentum vanish. Is this consistent with the uncertainty principle?

The angular momentum eigenstates in position representation

We'll work in spherical coordinates (r, θ, ϕ), in which θ is the angle from the z-axis ($0 \leq \theta \leq \pi$), and ϕ is the azimuthal angle ($0 \leq \phi \leq 2\pi$).

First, write down the angular momentum operator in these coordinates

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = \frac{\hbar}{i} \hat{\mathbf{r}} \times \nabla,$$

where

$$\nabla = \left(\frac{\partial}{\partial r}, \frac{1}{r}\frac{\partial}{\partial \theta}, \frac{1}{r \sin\theta}\frac{\partial}{\partial \phi} \right).$$

The z-component of angular momentum is therefore ($r\sin\theta$ is the distance from the rotation axis)

$$\hat{L}_z = (r\sin\theta)\,\frac{\hbar}{i}\left(\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi} \right) = \frac{\hbar}{i}\frac{\partial}{\partial\phi}.$$

The operator $\hat{L}^2$ is more complicated to calculate. The details are not important (see Griffiths p168 if you'd like to see it), I'll just give the result here:

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial^2\phi} \right].$$

Let's write the wavefunction corresponding to $|\ell\ m\rangle$ as $\psi_{\ell m}(r, \theta, \phi)$. We know that

$$\hat{L}_z \psi_{\ell m} = m\hbar\psi_{\ell m} = \frac{\hbar}{i}\frac{\partial \psi_{\ell m}}{\partial\phi},$$

which tells us the ϕ-dependence:

$$\psi_{\ell m}(r, \theta, \phi) \propto e^{im\phi}.$$

To get the θ-dependence, we need to solve

$$\hat{L}^2 \psi_{\ell m} = \ell(\ell+1)\hbar^2 \psi_{\ell m},$$

or

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial\psi_{\ell m}}{\partial\theta} \right) + \frac{1}{\sin^2\theta}\frac{\partial^2 \psi_{\ell m}}{\partial^2\phi} + \ell(\ell+1)\psi_{\ell m} = 0.$$

Using the fact that $\partial\psi_{\ell m}/\partial\phi = im$, and changing variables to $\mu = \cos\theta$ gives

$$\frac{\partial}{\partial\mu}\left((1-\mu^2)\frac{\partial\psi_{\ell m}}{\partial\mu} \right) + \ell(\ell+1)\psi_{\ell m} - \frac{m^2}{1-\mu^2}\psi_{\ell m} = 0.$$

This is one of those classical ODEs whose solution is a named function, the *associated Legendre polynomials* $P_\ell^m(\mu)$. They are listed in Table 4.2 of Griffiths (included below). Because the angular momentum operators don't contain any r derivatives, the radial dependence of $\psi_{\ell m}$ can be anything. We see therefore that the angular momentum eigenfunctions must be of the form

$$\psi_{\ell m}(r, \theta, \phi) = A f(r) P_\ell^m(\cos\theta) e^{im\phi},$$

where A is a normalization constant and $f(r)$ is an arbitrary radial function. Notice that this is in the form of a separable solution (a product of functions of each variable).

The combination $P_\ell^m(\cos\theta)e^{im\phi}$ is called a *spherical harmonic* $Y_\ell^m(\theta,\phi)$, so that we can also write

$$\psi_{\ell m}(r,\theta,\phi) = A' f(r) Y_\ell^m(\theta,\phi)$$

for some other normalization constant A'. The spherical harmonics are normalized such that

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \, (Y_\ell^m)^* \, Y_{\ell'}^{m'} = \delta_{\ell'\ell}\delta_{m'm}.$$

Table 4.3 of Griffiths gives the first few Y_ℓ^m's (see below).

One way to think of these functions is as standing waves in the angular direction. The total angular momentum is determined by ℓ, and so ℓ sets the number of nodes or wiggles in the wavefunction overall; the z-component of angular momentum is determined by m and that sets how the nodes are partitioned between the ϕ and θ directions.

Stationary states of problems with rotational symmetry

As we mentioned earlier, if the Hamiltonian is rotationally invariant about some axis, $[\hat{H},\hat{L}_z] = 0$ and therefore $[\hat{H},\hat{L}^2] = 0$. The operators $\hat{L}_z$, $\hat{L}^2$ and $\hat{H}$ share eigenstates, and so the stationary states must be of the form $f(r)Y_\ell^m$. The form of $f(r)$ is determined by solving the Schrödinger equation for the particular potential of interest. This also determines the energies of the states. We'll do this next for the hydrogen atom.

TABLE 4.2: Some associated Legendre functions, $P_l^m(\cos\theta)$: (a) functional form, (b) graphs of $r = P_l^m(\cos\theta)$ (in these plots r tells you the magnitude of the function in the direction θ; each figure should be rotated about the z-axis).

$P_0^0 = 1$

$P_1^1 = \sin\theta$

$P_1^0 = \cos\theta$

$P_2^2 = 3\sin^2\theta$

$P_2^1 = 3\sin\theta\,\cos\theta$

$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$

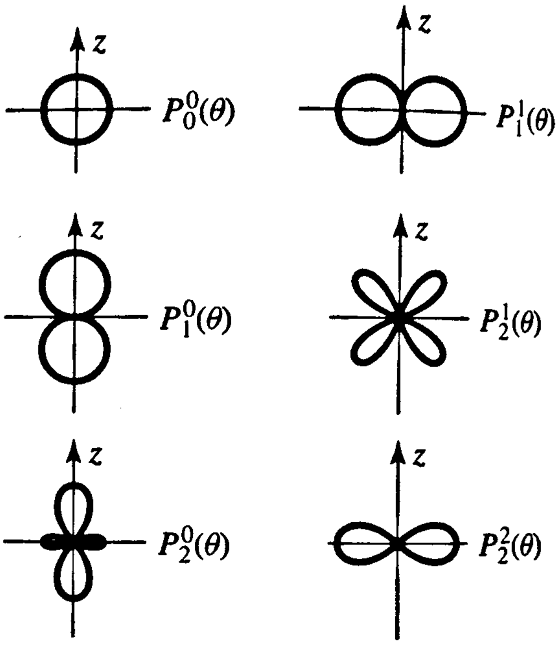
$P_3^3 = 15\sin\theta(1 - \cos^2\theta)$

$P_3^2 = 15\sin^2\theta\,\cos\theta$

$P_3^1 = \frac{3}{2}\sin\theta(5\cos^2\theta - 1)$

$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$

(a)



(b)

TABLE 4.3: The first few spherical harmonics, $Y_l^m(\theta, \phi)$.

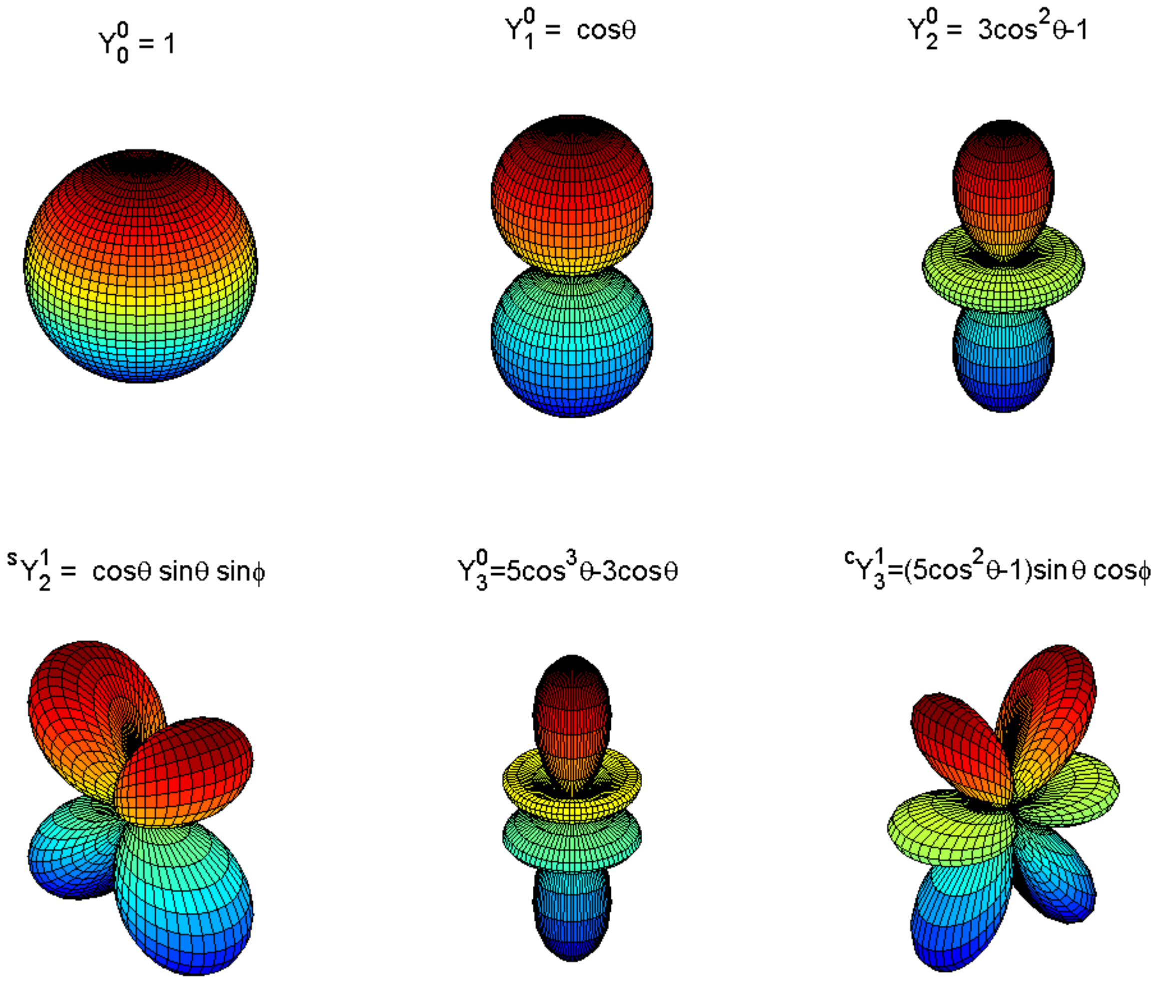
$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$	$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$
$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$
$Y_1^{\pm 1} = \mp \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$	$Y_3^{\pm 1} = \mp \left(\frac{21}{64\pi}\right)^{1/2} \sin\theta\,(5\cos^2\theta - 1) e^{\pm i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta \cos\theta e^{\pm 2i\phi}$
$Y_2^{\pm 1} = \mp \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta e^{\pm i\phi}$	$Y_3^{\pm 3} = \mp \left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$

The normalized angular wave functions[8] are called **spherical harmonics**:

$$\boxed{Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}}\, e^{im\phi}\, P_l^m(\cos\theta),} \qquad [4.32]$$

where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. As we shall prove later on, they are automatically orthogonal, so

$$\int_0^{2\pi} \int_0^{\pi} [Y_l^m(\theta, \phi)]^* [Y_{l'}^{m'}(\theta, \phi)] \sin\theta \, d\theta \, d\phi = \delta_{ll'} \delta_{mm'}, \qquad [4.33]$$


$Y_0^0 = 1$
$Y_1^0 = \cos\theta$
$Y_2^0 = 3\cos^2\theta - 1$
${}^sY_2^1 = \cos\theta \sin\theta \sin\phi$
$Y_3^0 = 5\cos^3\theta - 3\cos\theta$
${}^cY_3^1 = (5\cos^2\theta - 1)\sin\theta \cos\phi$

Stationary states of the hydrogen atom

We have all the ingredients we need now to solve the Schrödinger equation for the hydrogen atom. The proton is so much more massive than the electron, a good approximation is to assume the proton sits at rest at the origin and we need only solve for the electron wavefunction with a potential

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}.$$

The Schrödinger equation simplifies dramatically once we realise that in spherical coordinates, the Laplacian can be written in terms of the angular momentum operator,

$$\begin{aligned}\nabla^2 &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\phi^2} \\ &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hat{L}^2}{r^2\hbar^2},\end{aligned}$$

so that the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}.$$

Because the potential is spherically symmetric and therefore invariant under rotations, the angular momentum operators commute with the Hamiltonian and so the stationary states must look like

$$\psi(r,\theta,\phi) = f(r)Y_\ell^m(\theta,\phi).$$

Then writing $\hat{H}\psi = E\psi$ gives

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{df}{dr}\right) + \left[\frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}\right]f(r) = Ef(r).$$

The equation simplifies even more if we define a new function $g(r) = rf(r)$. Then after a bit of algebra we find

$$-\frac{\hbar^2}{2m}\frac{d^2g}{dr^2} + \left[\frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}\right]g(r) = Eg(r).$$

Points to note:

- The radial equation for $g(r)$ has the same form as the 1D Schrödinger equation we are used to solving, except for an extra term $\propto \ell(\ell+1)$ which we can think of as an additional potential term (centrifugal term).
- The eigenfunctions of the Hamiltonian are also eigenfunctions of $\hat{L}_z$ and $\hat{L}^2$, so they will be labelled by ℓ and m. There will also be a radial quantum number n that comes from solving the Schrödinger equation in the r direction and applying the boundary conditions (just as we did for the 1D potentials such as the infinite square well).

- Once we have $g(r)$, the full wavefunction is $\psi(r,\theta,\phi) = (g/r)Y_\ell^m(\theta,\phi)$.
- The equation for g doesn't have an m in it, so the energies will not depend on m. There is an ℓ in the equation, so in principle the energies could depend on the value of ℓ. However, we'll find for the $1/r$ potential of the hydrogen atom that the energies are independent of ℓ and depend only on the radial quantum number n.
- Boundary conditions: as $r \to \infty$, we need the normalization integral $\int r^2\, dr\, |\psi|^2$ to converge, so we must have $g(r) \to 0$ as $r \to \infty$. What about the origin? As $r \to 0$, the centrifugal term in the equation dominates, so for small r

  $$-\frac{\hbar^2}{2m}\frac{d^2 g}{dr^2} \approx -\frac{\hbar^2}{2mr^2}\ell(\ell+1)g.$$

  The solution is $g \propto r^{\ell+1}$ which is the boundary condition near the origin. (A solution $g \propto r^{-\ell}$ would also satisfy the equation but diverges as $r \to 0$). In terms of $f(r) = g(r)/r$ we need $f \propto r^\ell$ as $r \to 0$.

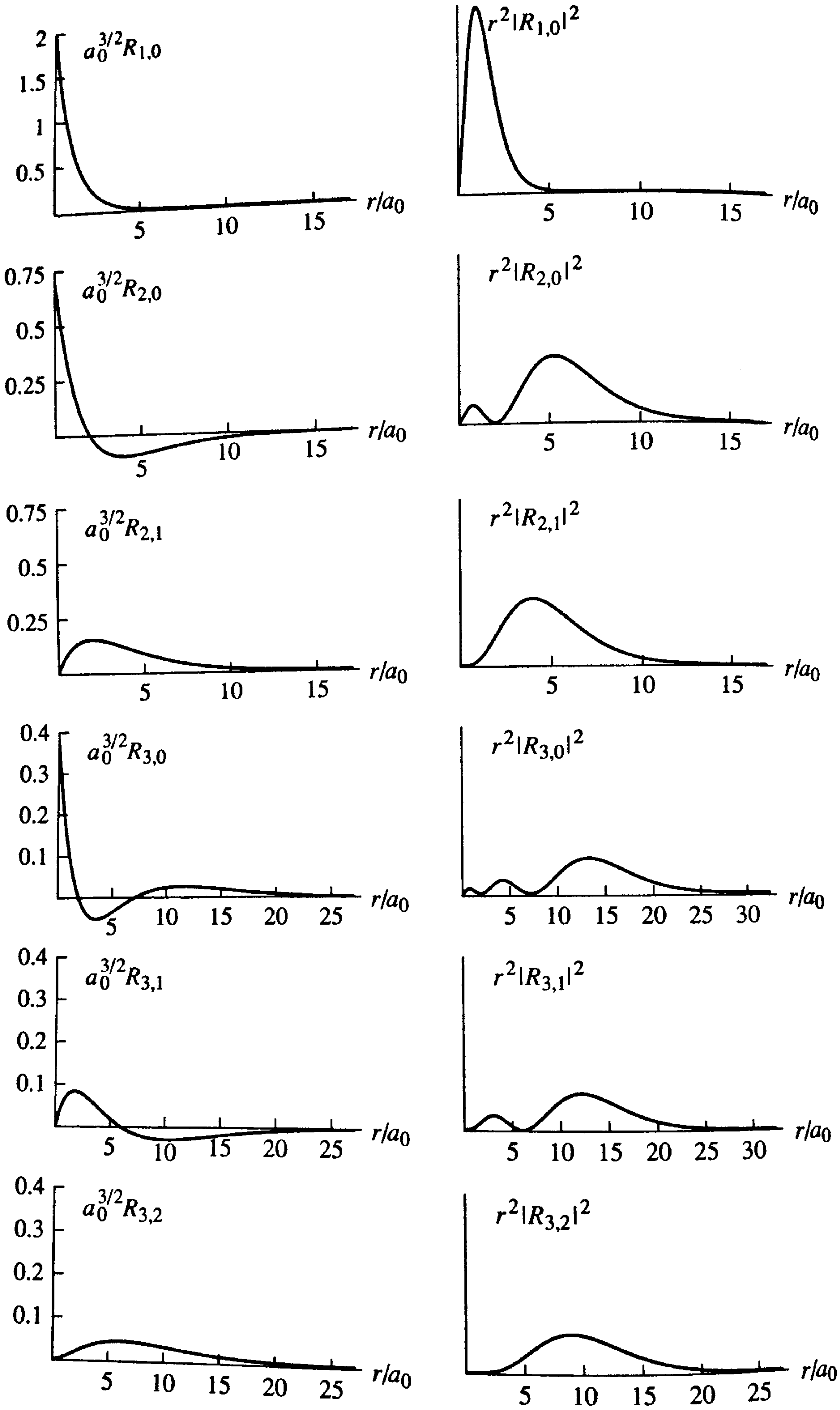


FIGURE 10.5

Plots of the radial wave function $R_{n,l}(r)$ and the radial probability density $r^2|R_{n,l}(r)|^2$ for the wave functions in (10.43), (10.44), and (10.45).

from Townsend "A Modern Approach to Quantum Mechanics" Chapter 10

The characteristic energy and size of the hydrogen atom

If you imagine numerically solving the radial Schrödinger equation, the first thing you might try to do is to choose a scale for energy and length that make the equation dimensionless (just as we did for the harmonic oscillator). A useful quantity for the atom is the *fine structure constant*

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}.$$

If we define

$$\tilde{E} = \frac{E}{\frac{1}{2}\alpha m c^2}$$

and

$$\tilde{r} = \frac{r}{\hbar/(\alpha m c)}$$

the equation for $g(r)$ becomes (after a bit of algebra – try it!)

$$-\frac{d^2 g}{d\tilde{r}^2} + g\left(-\frac{2}{\tilde{r}} + \frac{\ell(\ell+1)}{\tilde{r}^2}\right) = g\tilde{E},$$

which we can then solve numerically.

The energy scale is

$$\frac{1}{2}\alpha m c^2 = 13.6 \text{ eV}$$

which you might recognize as the ionization energy of hydrogen. The lengthscale is the *Bohr radius*

$$a_0 = \frac{\hbar}{\alpha m c} = 0.53\ \mathring{A},$$

the characteristic size of the atom.

Properties of the H atom wavefunctions

- The radial wavefunction depends on n and ℓ, so we can write it as $f_{nl}(r)$. The total wavefunction is therefore
$$\psi_{n\ell m}(r,\theta,\phi) = f_{nl}(r) Y_\ell^m(\theta,\phi).$$
- The energies of the stationary states depend only on n and not ℓ or m. They are
$$E_n = -\frac{13.6\ \mathrm{eV}}{n^2}.$$
Note that it in general, we'd expect the energies to depend on ℓ as well as n, since ℓ enters into the Schrödinger equation. The fact that the energies are independent of ℓ is a special property of the $1/r$ potential. (A similar result arises for a classical Keplerian orbit where the energy depends only on the semi-major axis, but the angular momentum depends on both semi-major axis and eccentricity.)
- The allowed values of ℓ are $\ell = 0, 1, ..., n-1$. For example, for $n = 1$ only $\ell = 0$ (s-orbital) is allowed; for $n = 2$, $\ell = 0$ or $\ell = 1$ (s- or p-orbitals) are allowed etc.
- The total degeneracy of level n is
$$\sum_{\ell=0}^{n-1} (2\ell + 1) = n^2$$
(where we sum over the allowed ℓ values, and use the fact that there are $2\ell + 1$ values of m at each ℓ). This means there are n^2 states with the same energy E_n.
- The radial wavefunctions have the form of a polynomial multiplied by e^{-r/na_0}. Here are the first few:
$$f_{10}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0}$$
$$f_{20}(r) = \frac{2}{(2a_0)^{3/2}} \left(1 - \frac{r}{a_0}\right) e^{-r/a_0}$$
$$f_{21}(r) = \frac{1}{\sqrt{3}} \frac{1}{(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}.$$
They have $n - \ell - 1$ nodes. The way to think about this is that the value of n sets the total energy, which determines how many nodes are needed in the wavefunction. At higher ℓ, more of these nodes go into the angular part of the wavefunction, so that the radial wavefunction is simplest for $\ell = n$ and has more nodes as ℓ decreases towards zero.
- The angular part is normalized such that
$$\int |Y_\ell^m|^2 \sin\theta\, d\theta\, d\phi = 1$$
so that the probability of finding an electron between r and $r + dr$ is
$$\int_{\theta,\phi} |\psi_{n\ell m}|^2\, r^2 \sin\theta\, d\theta\, d\phi\, dr = r^2\, |f_{n\ell}(r)|^2\, dr.$$

Spin and Pauli matrices

If you've looked at atomic structure before, you may know that each state of the atom $|n\ \ell\ m\rangle$ can be occupied by two electrons, one which is "spin up" and the other "spin down". The term "spin" refers to an intrinsic property of a particle that obeys the rules of angular momentum in quantum mechanics. The classical analogy is the spin angular momentum of a body, e.g. the spin of the Earth about its rotation axis, but it is not a straightforward comparison — in particular, because particles such as electrons are point-like and don't have a radial extent, but also because they can have half-integer spin values that are not possible for orbital angular momentum.

When we talk about spin, we use the same notation as for orbital angular momentum, but with $\ell \to s$, $\hat{L} \to \hat{S}$ etc. The states are $|s\ m\rangle$ with $m = -s, ... + s$, and

$$\hat{S}_z\,|s\ m\rangle = m\hbar\,|s\ m\rangle$$

$$\hat{S}^2\,|s\ m\rangle = s(s+1)\hbar^2\,|s\ m\rangle\,.$$

The reason that the electron in an atom can be "spin up" or "spin down" is that the electron is a *spin 1/2 particle*. It has $s = 1/2$ and therefore either $m = +1/2$ or $m = -1/2$. This is seen in the classic *Stern-Gerlach experiment*, in which a beam of electrons is passed between two magnetic poles. Each electron has a magnetic dipole moment proportional to its spin, and each electron feels a force which is proportional to the component of spin in the direction of the magnetic field. When this experiment is carried out, the beam splits into two indicating that there are only two possible values of the z-component of the spin.

When we are talking about the spin state of a particle, we therefore have a basis which has $2s+1$-dimensions. For example, for spin 1/2 particles, the $m = 1/2$ and $m = -1/2$ states, which we will write as $|\uparrow\rangle$ and $|\downarrow\rangle$ can be adopted as a basis. Using vector and matrix notation in this basis,

$$|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \hat{S}^2 = \frac{3\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

The ladder operators are

$$\hat{S}_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad \hat{S}_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}.$$

(Note that for $s = 1/2$ the coefficients in the ladder operators are 1).

By taking the sum and difference of the ladder operators, you can derive expressions for the other components of spin

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}.$$

The matrices that represent $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$ (usually written without the $\hbar/2$ factors) are known as *Pauli matrices*.

Exercise 32: Check that the Pauli matrices obey the commutation relations for angular momentum.

Multiple particles

We'll finish off the course by thinking about what happens when we want to put multiple particles into a quantum system. In an atom, we can only put one electron into each state (with quantum numbers n,ℓ,m and m_s) — why is that?

Start by thinking about two electrons. We'll assume that the electrons do not interact with each other, so we can write the Hamiltonian as $\hat{H} = \hat{H}_1 + \hat{H}_2$ where subscript 1 or 2 refers to particle 1 or particle 2. The state of the particle can then be written as a product of one-particle states, one for particle 1 and one for particle 2. For example, a possible spin state is

$$|\uparrow\uparrow\rangle = |\uparrow\rangle_1 \, |\uparrow\rangle_2 \, ,$$

in which both particles are "spin up".

The state $|\uparrow\uparrow\rangle$ has an important feature, that it is invariant under exchange of the two particles, i.e. if you swap the particle labels "1" and "2" you get the same state back. This is a requirement of a multi-particle state because the two electrons are identical particles — they are *indistinguishable*. [If you think about measuring the position of an electron, the wavefunction tells us the probability of measuring one of the electrons to be in a particular location, but we can't tell which one of the two electrons we've located, they are identical particles. This contrasts with classical physics, were the equations of motion allow us to track the coordinates of each particle precisely over time, and the particles are distinguishable.]

The state $|\downarrow\downarrow\rangle$, with both electrons being spin-down, is similarly invariant under exchange of particles. When it comes to a state with one particle up and one down, however, we have to be more careful. The state $|\uparrow\downarrow\rangle$ does not work, since it becomes $|\downarrow\uparrow\rangle$ when we swap the particle labels. The solution is to form a linear combination, either

$$\frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right)$$

or

$$\frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right) .$$

With the plus sign, swapping the particle labels gives the same state back. With the minus sign, swapping the particle labels gives the same state back but with a minus sign — it is said to be *antisymmetric* under interchange of particles. (Note that if you do a second swap you still get back to where you started, as you must.)

Exercise 33: Operate $\hat{S}_z$ and $\hat{S}^2$ on these four possible two-electron states. The total angular momentum $\hat{S}^2$ is a bit tricky because $(\hat{S}_1 + \hat{S}_2)^2$ has a cross-term $2\hat{S}_1 \cdot \hat{S}_2 = 2\hat{S}_{1x}\hat{S}_{2x} + 2\hat{S}_{1y}\hat{S}_{2y} + 2\hat{S}_{1z}\hat{S}_{2z}$. Using the ladder operators for spin 1 and spin 2 this can be rewritten as

$$\hat{S}^2 = \hat{S}_1^2 + \hat{S}_2^2 + \hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+} + 2\hat{S}_{1z}\hat{S}_{2z}.$$

What are the corresponding values of s and m for each of the four states?

You should find that the states form a $s = 0$ *singlet*

$$|0\,0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

and $s = 1$ *triplet*

$$\begin{aligned}|1\,1\rangle &= |\uparrow\uparrow\rangle \\ |1\,0\rangle &= \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) \\ |1\ \ -1\rangle &= |\downarrow\downarrow\rangle\,.\end{aligned}$$

As we might have guessed, adding two spin 1/2 particles gives an overall spin of either 1 or 0 (with corresponding m values).

In general, when you add angular momentum in quantum mechanics, e.g. add spin s to orbital angular momentum ℓ to get the total angular momentum, the possible values range from $\ell + s$ to $||\ell - s||$ in integer steps. The states can be written as linear combinations of products of the individual angular momentum states, with coefficients known as *Clebsch-Gordon coefficients*. For more details, you can look in Griffith's book.

Spin statistics theorem and Pauli exclusion principle

We've seen that for two spin 1/2 particles, the possible states are either symmetric under interchange of the two particles (the triplet states), or anti-symmetric under interchange (the singlet state). The spin statistics theorem is a connection between the symmetry under interchange and the spin of the particle:

- Particles with integer spins must have a symmetric wavefunction under interchange; these are known as *bosons*.
- Particles with half-integer spins must have an anti-symmetric wavefunction under interchange; these are known as *fermions*.

This leads to a lot of fun physics!

For fermions, the need to have an overall anti-symmetric wavefunction gives rise to the *Pauli exclusion principle*. As a simple example, ignore spin and consider putting two particles into a 1D harmonic oscillator, one in state m and one in state n. The wavefunction has to be anti-symmetric under interchange, so it must be

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}} \left[\psi_n(x_1)\psi_m(x_2) - \psi_n(x_2)\psi_m(x_1)\right]$$

where $\psi_n(x)$ is the single particle wavefunction for state n. We see that if $n = m$ the wavefunction vanishes! Two particles cannot be in the same state. This is the Pauli exclusion principle.

In an atom, we write the one-electron states as

$$|n\ \ell\ m\rangle \left|\frac{1}{2}\ m_s\right\rangle .$$

If two electrons have the same n, ℓ, and m, they must be in a singlet spin state so that the overall wavefunction is antisymmetric:

$$|\psi\rangle = |n\ \ell\ m\rangle_1 \, |n\ \ell\ m\rangle_2 \left(\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}\right) .$$

This is why the states of the atom are filled by two electrons with opposite spin.

Bosons are interesting because they have the opposite behavior — they *can* occupy the same state. In *Bose-Einstein condensation* a macroscopic number of particles occupy the same ground state. This idea underlies superfluids and superconductors.