The Limits of Classical Physics

We'll start by considering several situations or experiments that can not be understood using classical ideas. This will introduce the idea of QUANTIZATION, and the important role of PROBABILITY.

1) Blackbody radiation

What are the properties of electromagnetic radiation in thermal equilibrium with matter at temperature T? Specifically, what is the energy density $u_\nu(T)$?

where $u_\nu(T)\,d\nu$ is the energy per unit volume in radiation with frequency between ν and $\nu + d\nu$.

Before we try to answer this question, a reminder about EM waves and the wave equation in electromagnetism. Maxwell's equations in vacuum ⇒

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

a WAVE EQUATION for the electric field $\underline{E}$ (can write down the same thing for magnetic field $\underline{B}$)

Plane wave solutions: $\underline{E} \propto e^{i\underline{k}.\underline{r} - i\omega t}$

$\underline{k} = (k_x, k_y, k_z)$ is the wave vector

the wave propagates in the direction $\hat{\underline{k}}$

dispersion relation $\omega = c|\underline{k}| = c\frac{2\pi}{\lambda}$

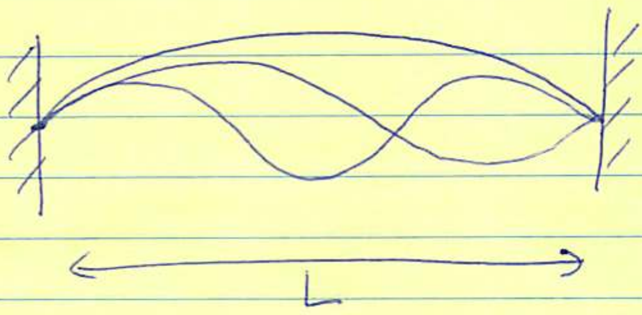
[Recall that when we use complex notation, writing the wave as $\propto e^{ik_x x}$, we really mean $\mathrm{Re}\left(e^{ikx}\right) = \cos kx$.

The real part gives the physical quantities.]

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)



$n = 1, 2, 3 \ldots$

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

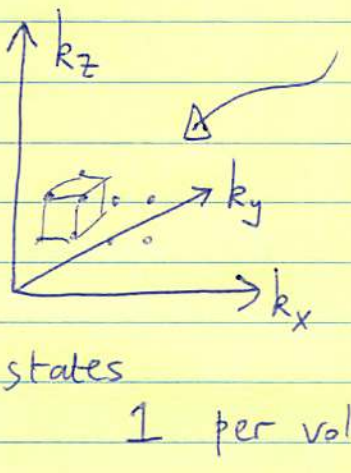
$$k_x = \frac{n\pi}{L}$$

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

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

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 $\frac{\pi}{L}$

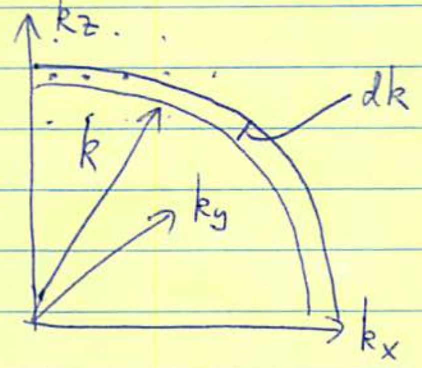
$\therefore$ density of states

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

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

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

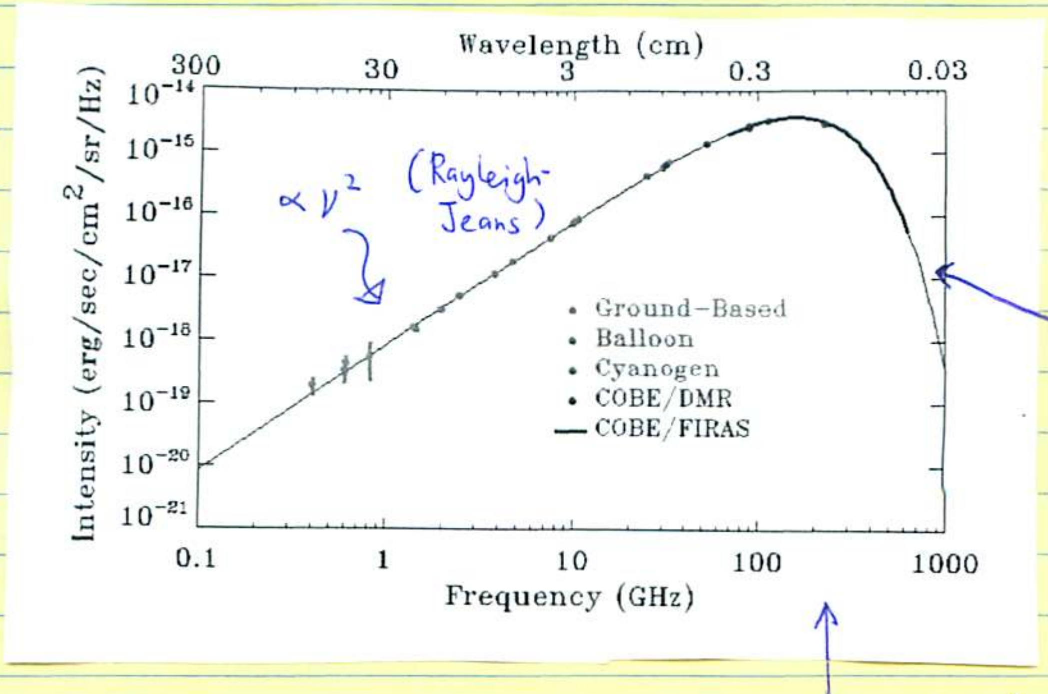
To get the energy, we use the idea of EQUIPARTITION OF ENERGY from classical thermodynamics. In thermal equilibrium, every degree of freedom gets $\frac{1}{2}k_BT$ of energy. For an oscillator there are 2 degrees of freedom (kinetic + potential energies or here $\underline{E}$ and $\underline{B}$), so the oscillator has an energy k_BT.

This suggests we give each mode in the box k_BT of energy, so that $\boxed{u_\nu(T) = \frac{8\pi\nu^2 k_B T}{c^3}}$ RAYLEIGH-JEANS LAW

This is the classical expectation for the spectral energy density of thermal radiation.

Two problems

— observed thermal radiation does show $u_\nu \propto \nu^2$ at low frequency, but sharply turns over at high frequencies



E.g. Cosmic Microwave Background (CMB) radiation

exponential fall off at high frequency. (Wien's law)

peaks at a frequency $\propto k_B T$

— In a sense, $u_\nu(T)$ has to fall off at high frequency because something is clearly wrong with the classical prediction

$u_\nu(T) \propto \nu^2 \Rightarrow$ energy density diverges at high frequency

"UV catastrophe"

Planck's solution:

At each frequency ν, the energy can take only discrete values

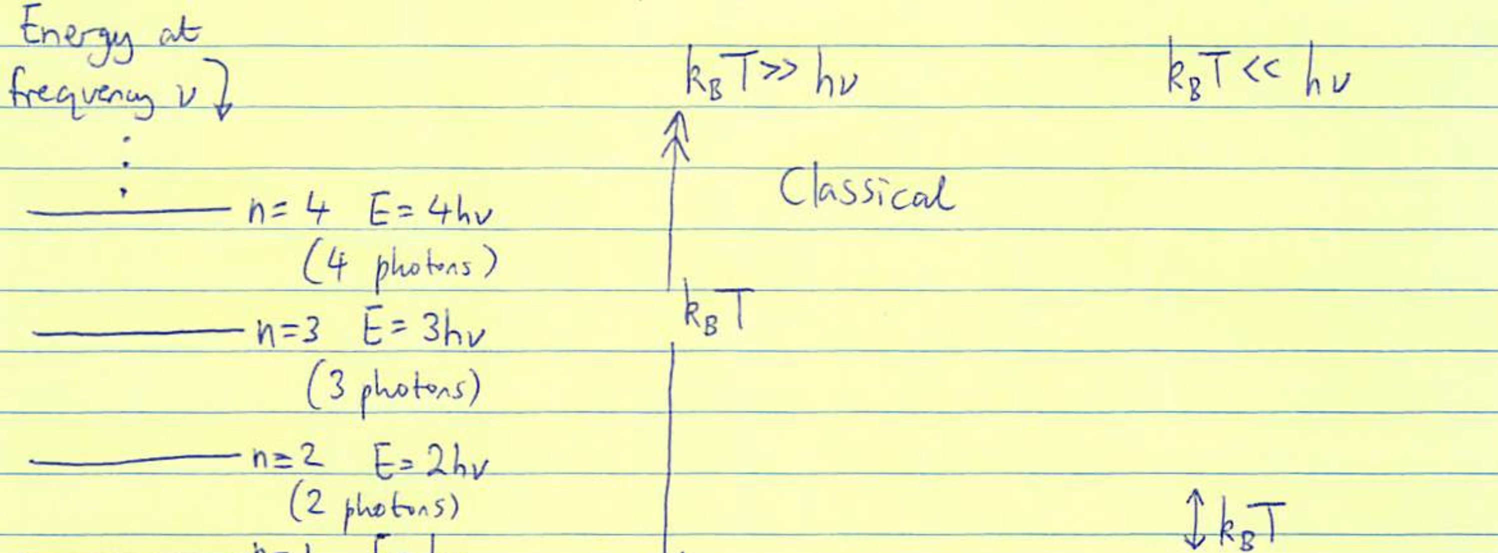
$$E = n h\nu \qquad n = 0, 1, 2 \ldots \quad (\text{integer})$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$ PLANCK'S CONSTANT

[We will often also use $\hbar = 1.055 \times 10^{-34}$ Js
"h-bar"

where $E = n \hbar\omega$]

Two limits are:



Quantum effects dominate —
care about the
spacing of levels

For any temperature, we can calculate the energy at frequency ν by summing over all levels and using BOLTZMANN'S LAW to calculate the probability that a given level is occupied

Probability $\propto e^{-E/k_BT}$

$\therefore$ the average energy at frequency ν is

$$\bar{E} = \frac{\sum_{n=0}^{\infty} nh\nu\, e^{-nh\nu/k_BT}}{\sum_{n=0}^{\infty} e^{-nh\nu/k_BT}}$$

$$= k_BT \frac{\sum_{n=0}^{\infty} nx\, e^{-nx}}{\sum_{n=0}^{\infty} e^{-nx}}$$

where

$$x = \frac{h\nu}{k_BT}$$

$$\Rightarrow \boxed{\bar{E} = k_BT \frac{x}{e^x - 1}} \quad - (*)$$

Check limits: $k_BT \gg h\nu$ $\quad x \ll 1$ $\quad \bar{E} \to k_BT$

Classical result: energy at frequency ν is k_BT

$k_BT \ll h\nu$ $\quad x \gg 1$ $\quad \bar{E} \to k_BT x e^{-x} = h\nu e^{-h\nu/kT}$

Energy at frequency ν is exponentially suppressed

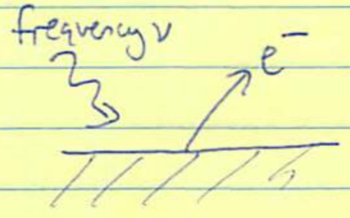
Now, follow previous argument but instead of giving k_BT to each mode, use equation (*) instead

$\Rightarrow$ PLANCK SPECTRUM

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

2) Photoelectric effect $\left\{ \begin{array}{l} \text{Direct evidence that light comes in individual} \\ \text{quanta (photons) with energy } \propto \nu. \end{array} \right.$

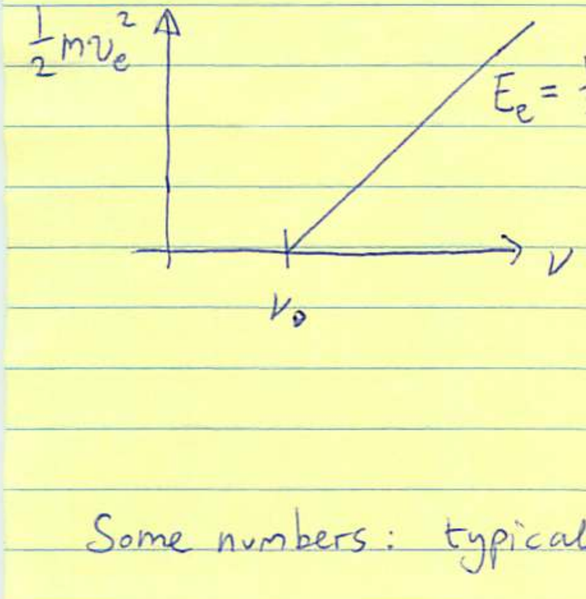
Ejection of electrons from the surface of a metal when illuminated with light



- 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 however.

- the electron energy $\propto \nu$ and independent of the 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 $h\nu_0 = W$.

Some numbers: typically W is a few eV

$$h\nu_0 = 3\,eV \Rightarrow \nu_0 = \frac{3 \times 1.6 \times 10^{-19}\,J}{6.63 \times 10^{-34}\,Js} \approx 7 \times 10^{14}\,Hz$$

$$\text{or } \lambda = \frac{c}{\nu} = 0.4\,\mu m$$

(blue end of optical light)

3) Wave-like nature of particles

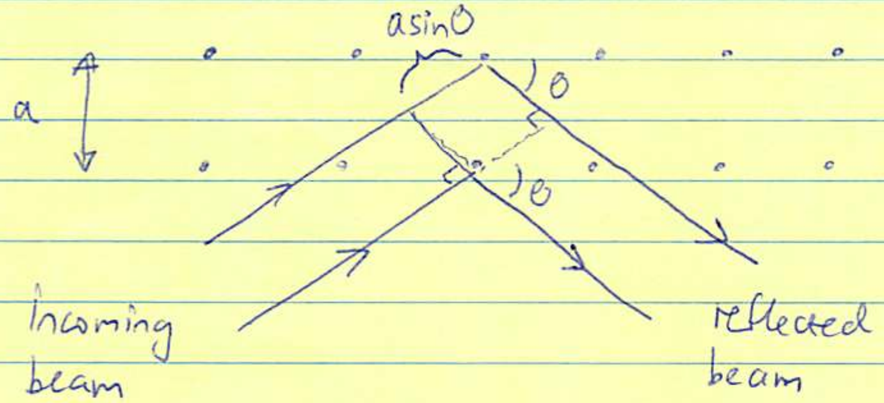
Wave-particle duality

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

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

DE BROGLIE WAVELENGTH

and that particles such as electrons will show wave character if some critical lengthscale in the system is $\lesssim \lambda$. Indeed this is observed – an example is electron or neutron diffraction used to study crystal structure.



path difference between the two is $2a\sin\theta$

Constructive interference when $2a\sin\theta = n\lambda$

(Bragg's law)

If the crystal spacing is $a \sim 10^{-10}\,\text{m} \sim 1\,\text{Å}$

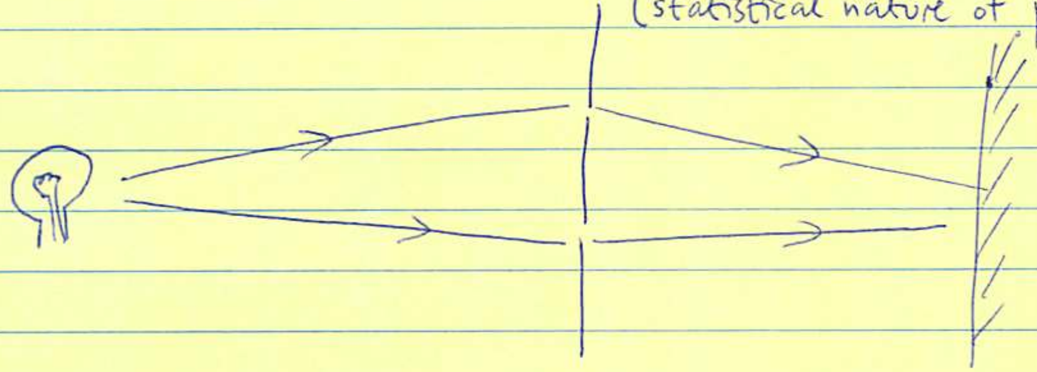
then the corresponding electron energy is

$$E_e \sim \left(\frac{h}{\lambda}\right)^2 \frac{1}{2m_e} \sim \left(\frac{6.63\times10^{-34}}{10^{-10}}\right)^2 \frac{1}{2\times10^{-30}}$$

$$\sim 3\times10^{-17}\,\text{J}$$

$$\sim 200\,\text{eV}.$$

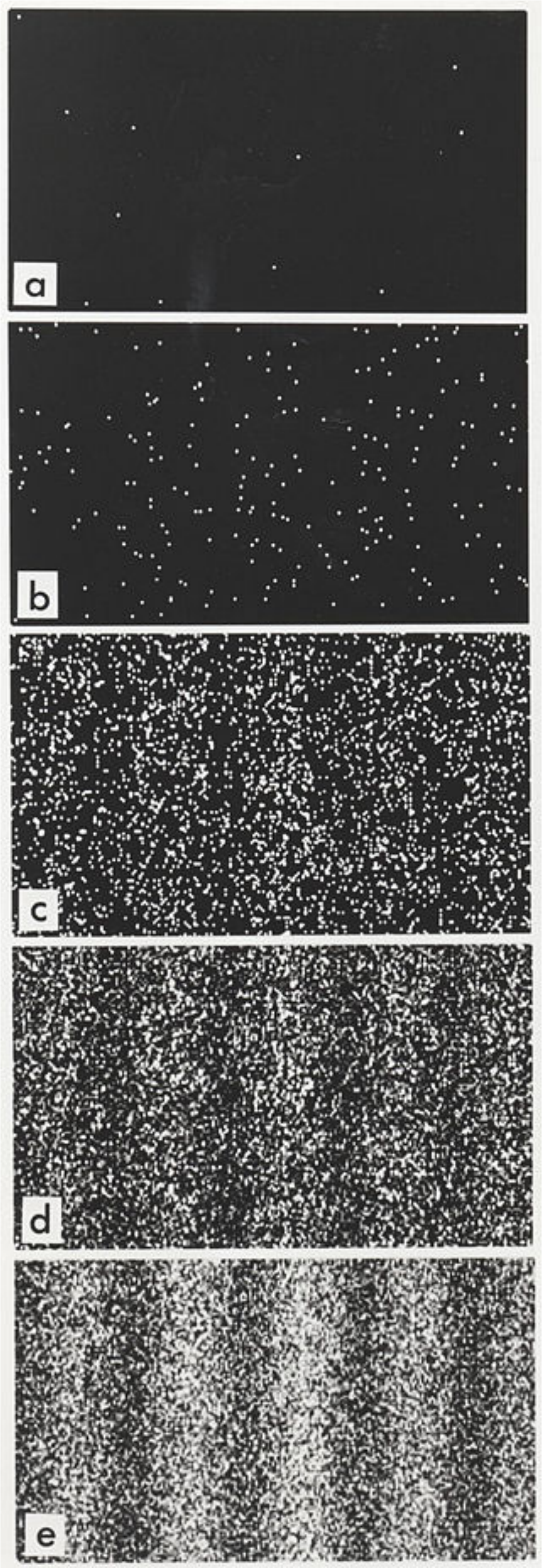
4) <u>Double-slit experiment</u> Emphasizes the role of probability (statistical nature of predictions in QM)



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 <u>probability</u> that a particle will arrive at any particular location on the screen.

Indeed we will be solving a wave equation (Schrödinger equation) for a quantity ψ (wave function) that tells us the probability of a particle being in a particular location — uncertainty and probability is an intrinsic part of the theory. "Wave mechanics"

This experiment also illustrates the critical role of the observer. If we install detectors that tell us whether the particle went through the top or bottom slit, the interference pattern goes away — as if we had run two seperate 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 wavefunction" — once we determine that the particle has passed through the upper slit we know its trajectory, whereas without knowing which slit, both possibilities are open and interfere. The act of observing changes the experiment.


a
b
c
d
e

[see Griffiths Chp 1]

Wave Mechanics: the Wave Function and Schrödinger Equation

Consider a particle moving in a one-dimensional potential $V(x,t)$ so that classically its equation of motion would be

$$\frac{dp}{dt} = -\frac{\partial V}{\partial x}, \quad \text{with (conserved) total energy} \quad E = \frac{p^2}{2m} + V.$$

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

$$\Psi(x,t) \qquad \text{WAVE FUNCTION}$$

where

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

= probability of finding the particle between x and $x+dx$

The wavefunction is normalized

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

(the particle must be located somewhere between $+\infty$ and $-\infty$)

and satisfies the SCHRÖDINGER EQUATION

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

(a wave equation for Ψ)

The evolution is deterministic in the sense that, given initial conditions for Ψ, we can solve for Ψ at all future times. But the interpretation of Ψ is statistical in nature — we cannot predict with certainty the position of the particle at a given time.

The Uncertainty Principle

A simple solution to the Schrödinger equation is

$$\Psi(x,t) = e^{ikx - i\omega t} \qquad \text{plane wave}$$

valid when $V(x,t) =$ constant (we'll set the constant to zero for simplicity). Substituting into (*) gives the required relation between ω and k:

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

this is $\frac{p^2}{2m}$ from the de Broglie relation $p = \hbar k$

$\Rightarrow$ the frequency is $\omega = E/\hbar$ or $E = \hbar\omega$. (as for photons)

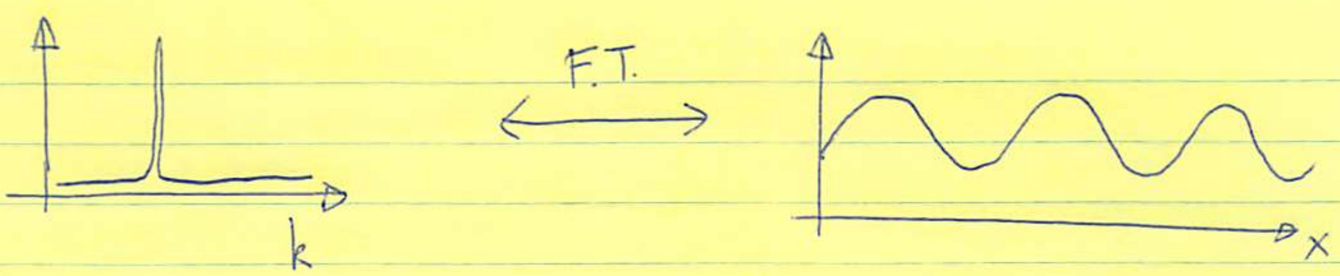
Therefore $\Psi(x,t) = e^{ipx/\hbar}\,e^{-iEt/\hbar}$

describes a particle moving with fixed momentum p in a constant potential, where E is the energy $E = \frac{p^2}{2m} + V_0$.

Note that $|\Psi(x,t)|^2 = 1 =$ constant

— there is equal probability of finding the particle at any position. Perfect knowledge of the momentum of the particle $\Rightarrow$ complete uncertainty about its location.

A useful way to think about this is in terms of Fourier transforms. You may recall that the Fourier transform of a delta-function is a sine-wave:



To see this mathematically, note that the Schrödinger equation is linear, so we can write a general solution

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk' \, e^{ik'x - i\omega(k')t} \, A(k') \Bigg\}$$

the Fourier Transform of A(k')

a sum of plane waves. Previously we took $A(k') \propto \delta(k-k')$

$$\Rightarrow \quad \Psi(x,t) = e^{ikx - i\omega(k)t}$$

What if, instead, we took $A(k') = e^{-ik'x_0}$ at $t=0$?

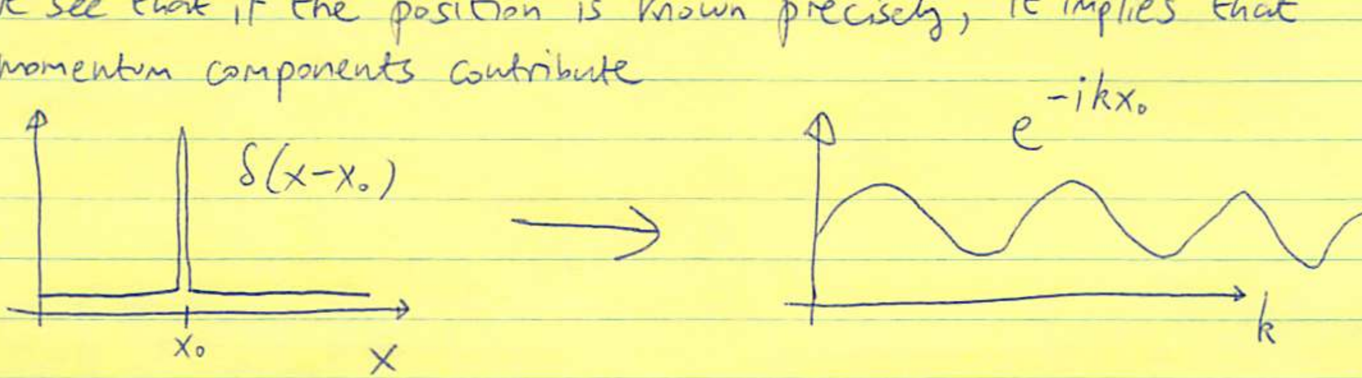
Then

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk' \, e^{ik'(x-x_0)}$$

$$= \cancel{2\pi} \, \delta(x-x_0) \, \sqrt{2\pi}$$

since $\boxed{\delta(x-x_0) = \frac{1}{2\pi} \int dk' \, e^{ik'(x-x_0)}}$

so we see that if the position is known precisely, it implies that all momentum components contribute



(but note that the time-dependence depends on k, so the wave packet is dispersive — the wave does not stay localized!)

This is a general principle - the UNCERTAINTY PRINCIPLE - that the more we know about the position of the particle, the less we know about its momentum and vice-versa.

As another example, consider a <u>Gaussian wave packet</u>

$$\Psi(x) \propto \exp\left(-\frac{(x-x_0)^2}{2\sigma_x^2}\right) \qquad (\text{at } t=0)$$

The Fourier trasform of a Gaussian is a Gaussian so the distribution in k will also be Gaussian:

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

They are related by

$$\Psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk' \, e^{ik'x} \, e^{-(k'-k_0)^2/2\sigma_k^2}$$

change variables $k'-k_0 \to k'$

$$\sqrt{2\pi}\, \Psi(x) = \int_{-\infty}^{\infty} dk' \, e^{i(k'+k_0)x} \, e^{-k'^2/2\sigma_k^2}$$

complete the square

$$= \int_{-\infty}^{\infty} dk' \, e^{ik_0x} \, e^{-(k'-ix\sigma_k^2)^2/2\sigma_k^2} \, e^{-\frac{x^2\sigma_k^2}{2}}$$

use $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$

$$\Rightarrow \underline{\Psi(x) = \frac{1}{\cancel{\sqrt{2\pi}}} \sqrt{\cancel{2\pi}\,\sigma_k^2} \; e^{ik_0x} \, e^{-x^2\sigma_k^2/2}}$$

$$\Rightarrow \quad \sigma_x = \frac{1}{\sigma_k}$$

widths in x and k-space are inversely proportional.

$$\text{or} \quad \boxed{\sigma_x \sigma_k = 1}$$

The general result is that $\boxed{\Delta x \, \Delta p \geq \hbar/2}$

We'll derive this in detail later.

We are actually interested in the uncertainty in the particle position, ie the width of $|\psi|^2 = \exp\left(-\frac{(x-x_0)^2}{\sigma_x^2}\right)$

writing this as $|\psi|^2 = e^{-(x-x_0)^2/2\Delta x^2}$

$$\Rightarrow \quad \Delta x = \sigma_x/\sqrt{2}$$

and similarly for k, $\Delta k = \sigma_k/\sqrt{2}$

$$\therefore \Delta x = \frac{\sigma_x}{\sqrt{2}} = \frac{1}{\sqrt{2}\sigma_k} = \frac{1}{2\Delta k}$$

$$\Rightarrow \quad \Delta x \Delta k = \frac{1}{2} \quad \text{or} \quad \underline{\Delta x \Delta p = \hbar/2}.$$

We'll show later that in general the result is

$$\boxed{\Delta x \Delta p \geq \hbar/2}$$

The Gaussian wavepacket gives the minimum value of $\Delta x \Delta p$.

[Question — what would a wavefunction with a much larger value of $\Delta x \Delta p$ look like?]

<u>A note on the normalization of $A(k)$</u>

We wrote the general solution

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk \, e^{ikx - i\omega t} A(k)$$

with a $1/\sqrt{2\pi}$ factor out front. This means that at $t=0$,

$$\int \psi^* \psi \, dx = \frac{1}{2\pi} \int_{-\infty}^{\infty} dx \int dk' dk \; e^{-ik'x} e^{ikx} A^*(k) A(k)$$

$$= \frac{1}{2\pi} \int dk \, dk' \; A^*(k') A(k) \; \delta(k-k')$$

$$= \int dk \; |A(k)|^2 . \qquad \left(\text{This is Parseval's theorem} \right)$$

If $\psi(x,0)$ is normalized $\int |\psi|^2 dx = 1$, then so is $A(k)$, $\int dk |A|^2 = 1$, so we can interpret $|A|^2$ as the probability density function in k space (and $A(k)$ as the wave function written in momentum space – more on that soon when we discuss the momentum operator).

Note that $|A(k)|^2$ is independent of time. To see that, Fourier transform $\psi(x,t)$ at some time $t > 0$:

$$A(k,t) = \frac{1}{\sqrt{2\pi}} \int dx \; e^{-ikx} \; \psi(x,t)$$

$$= \frac{1}{2\pi} \int dk' \; A(k',0) \; e^{-i\omega(k')t} \underbrace{\int dx \; e^{ik'x - ikx}}_{2\pi \; \delta(k-k')}$$

$$= A(k,0) \; e^{-i\omega(k)t}$$

So $A(k)$ develops a phase factor $e^{-i\omega t} = e^{-iEt/\hbar}$ but $|A|^2$ is constant in time. This means that the uncertainty in k or p is constant in time, unlike Δx which increases as the wavepacket broadens.

[This makes sense because for a free particle (constant background potential $V =$ constant) the velocity is constant in time, so $\langle v \rangle$ and $\langle v^2 \rangle$ must be constant. Therefore $(\Delta v)^2 = \langle (v - \langle v \rangle)^2 \rangle = \langle v^2 \rangle - \langle v \rangle^2$ is also constant.]

Conservation of probability

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

$$\frac{d}{dt}|\Psi|^2 = \Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t}$$

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

where we use the Schrödinger equation to substitute for $\partial\Psi/\partial t$ and $\partial\Psi^*/\partial t$. The potential terms cancel, leaving

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

Now bring one of the $\frac{\partial}{\partial x}$'s outside:

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

This equation is of the form

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

FLUX-CONSERVATIVE FORM

where J_Ψ is the <u>probability flux</u>

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

This is the general form of a conservation law. To see this, integrate over a region $x=a$ 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 into the region across the boundaries.

For a wave function that has $\Psi \to 0$ at $x \to \pm\infty$ (ie. is normalizable) we see that $\frac{d}{dt}\int_{-\infty}^{\infty} |\Psi|^2 dx = 0$

so that once normalized, the wave function will remain normalized.

Momentum operator

We already saw that for the plane wave the $-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2}$ term

in the Schrödinger equation $\to p^2/2m$, ie. taking the

spatial derivative of Ψ $\left(\partial\Psi/\partial x\right)$ gives information about the particle momentum.

Let's generalize this: first consider the mean position of the particle

$$\langle x \rangle = \int x\, |\Psi|^2\, dx. \quad \text{—(†)}$$

[Make sure you understand what we are writing down here — if we had an ensemble of systems in state $\Psi(x)$ and measured the position of each particle, the mean position would be $\langle x \rangle$ where the average is taken over the ensemble.]

Then $$\frac{d\langle x\rangle}{dt} = \int x\, dx \, \frac{\partial}{\partial t} |\Psi(x)|^2$$

$$= -\int x\, dx \, \frac{\partial}{\partial x} J_\Psi$$

Integrate by parts: $\frac{\partial}{\partial x}(x J_\Psi) = J_\Psi + x \frac{\partial J_\Psi}{\partial x}$

$$\Rightarrow \quad \frac{d\langle x\rangle}{dt} = \int dx\, J_\Psi - \underset{\uparrow}{[x J_\Psi]}$$

assume boundary term vanishes ($J_\Psi \to 0$ at $x = \pm\infty$)

$$\Rightarrow \quad \frac{d\langle x\rangle}{dt} = -\int dx\, \frac{i\hbar}{2m}\left(\Psi^* \frac{\partial \Psi}{\partial x} - \underbrace{\Psi \frac{\partial \Psi^*}{\partial x}} \right)$$

we can also integrate this term by parts, moving the derivative from the Ψ^* to the Ψ. Again, boundary term vanishes.

$$\Rightarrow \quad \boxed{\frac{d\langle x\rangle}{dt} = \frac{1}{m}\int \psi^* \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right) \Psi \, dx}$$

Another way to write this is

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

$$\text{or} \quad \boxed{\langle p\rangle = \int \Psi^* \hat{p}\, \Psi \, dx}$$

where $\hat{p} \equiv \frac{\hbar}{i}\frac{\partial}{\partial x}$ is the <u>momentum operator</u>.

Points to note:

- we have already met another operator, $\hat{x} \equiv x$, where we applied the same idea to find $\langle x \rangle$

$$\langle x \rangle = \int dx \; \Psi^* \hat{x} \Psi = \int dx \; x |\Psi|^2$$

(see equation †)

In general, $\langle O \rangle = \int dx \; \Psi^* \hat{O} \Psi$.

- you may find the identification $\frac{d\langle x \rangle}{dt} = \frac{\langle p \rangle}{m}$ not obvious.

One way to see that we may have the right answer is to write $\langle p \rangle$ in terms of the momentum (or k-space) representation $A(p)$

ie. $$\Psi(x) = \frac{1}{\sqrt{2\pi}} \int dp' \; e^{ip'x/\hbar} A(p')$$

then $$\hat{p}\Psi = \frac{\hbar}{i}\frac{\partial}{\partial x}\Psi = \frac{\hbar}{i}\int dp' \, A(p') \, \frac{ip'}{\hbar} \, e^{ip'x/\hbar}$$
$$= \int dp' \, A(p') \, p' \, e^{ip'x/\hbar}$$

and
$$\Psi^*(x) = \frac{1}{\sqrt{2\pi}} \int dp'' \; e^{-ip''x/\hbar} A^*(p'')$$

$$\Rightarrow \int dx \; \Psi^*(x) \, \hat{p} \, \Psi(x) = \int dx \int dp' \int dp'' \frac{1}{2\pi} e^{i(p'-p'')x/\hbar} A^*(p'') A(p') \, p'$$

the x-integration is $\int dx \; e^{ix(p'-p'')/\hbar} = 2\pi \, \delta(p'-p'')$

$$\Rightarrow \int dx \; \Psi^* \hat{p} \Psi = \cancel{2\pi} \underbrace{\int dp' \; A^*(p') \, p' \, A(p')}_{\int dp' \, A^* \hat{p} A \quad \text{with } \hat{p} \equiv p}$$

We see that if we use the momentum representation of the wavefunction $A(p)$, then the momentum operator takes the simple form $\hat{p} = p$.

[and one can show that $\hat{x} = i\hbar \frac{\partial}{\partial p}$].

- the equations for the expectation values are the classical equations for the particle, $\langle p \rangle = m \frac{d\langle x \rangle}{dt}$

also you can show that $\frac{d\langle p \rangle}{dt} = -\left\langle \frac{\partial V}{\partial x} \right\rangle$.

- if we go back to the Schrödinger equation, the term $-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2}$ on the right hand side is

$$\frac{\hat{p}^2}{2m}\Psi$$

we can write

$$i\hbar \frac{\partial \Psi}{\partial t} = \left(\frac{\hat{p}^2}{2m} + V \right) \Psi$$

$$\equiv \hat{H} \Psi$$

Hamiltonian operator gives the energy

- The $\hat{x}$ and $\hat{p}$ operators do not commute, ie. order matters. To see this, consider

$$[\hat{p}, \hat{x}]\Psi \equiv \hat{p}\hat{x}\Psi - \hat{x}\hat{p}\Psi = \frac{\hbar}{i}\frac{\partial}{\partial x}(x\Psi) - \frac{\hbar}{i} x \frac{\partial \Psi}{\partial x}$$

$$= \frac{\hbar}{i}\Psi$$

defines $[A, B]$ notation

We'll see later that this underpins the uncertainty relation between x and p.

Time-Independent Schrödinger Equation (Griffiths Chapter 2)

If the potential $V(x)$ is independent of time, the Schrödinger equation can be solved by separation of variables. In fact, we can already guess from the plane wave solution that the time-dependent part is $\exp\left(-i\frac{Et}{\hbar}\right)$, so let's try

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

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

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

the time-independent Schrödinger equation.

The left-hand-side is the Hamiltonian operator

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

whose expectation value is the energy $\int dx\, \psi^* \hat{H} \psi = E$

We can solve equation $(*)$ for the allowed enegies E_n and states $\psi_n(x)$ given a specified $V(x)$ and boundary conditions. Then we can construct a general solution

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

a linear combination of the states ψ_n. This is exactly the procedure we followed for the case of $V=0$ which had $\psi(x) = \exp(ikx)$ where $E = \frac{\hbar^2 k^2}{2m}$. One difference there is that there was a continuum of allowed values of E. In general for a finite-size system as we shall see in this section only a discrete set of energies E_n are allowed.

Note that the solutions to the Schrödinger equation when V is independent of time are stationary states in the sense that although Ψ depends on time $(\propto e^{-iEt/\hbar})$, $|\Psi|^2$ does not depend on time.
The same is true for any expectation value

$$\langle Q(x,p) \rangle = \int \Psi^* \hat{Q}\, \Psi \, dx$$

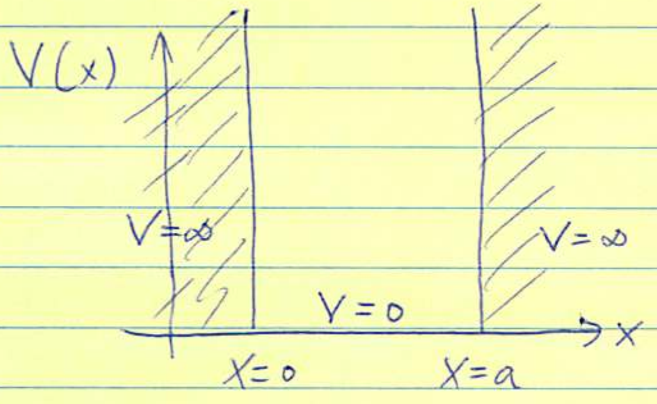
observable Q that depends on x or p.

$$= \int \psi^* e^{iEt/\hbar} \hat{Q}\, e^{-iEt/\hbar} \psi \, dx$$

$$= \int \psi^* \hat{Q} \psi \, dx$$ independent of time.

Infinite Square Well

It is easiest to dive into an example, a particle confined in a box with infinite walls



for $x<0$ or $x>a$, $V=\infty$
and $\psi = 0$
(particle cannot escape)

for $0<x<a$ $V=0$
ψ satisfies $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$

or we can write $\frac{d^2\psi}{dx^2} = -k^2\psi$ where $k^2 = \frac{2mE}{\hbar^2}$

Solution is $\psi = A \sin kx + B \cos kx$

but we need $\psi(0) = 0 \quad \psi(a) = 0$

$$\Rightarrow \quad \psi = A \sin\left(\frac{n\pi x}{a}\right) \qquad n = 1, 2, 3 \ldots$$

only particular values $k_n = \frac{n\pi}{a}$ can satisfy the b.c.'s

the corresponding energies are $E_n = \frac{\hbar^2}{2m}\frac{n^2\pi^2}{a^2}$

To set the constant A, normalize:

$$\int_0^a |A|^2 \sin^2(kx)\, dx = |A|^2 \frac{a}{2} = 1$$

(average value of $\sin^2$ is $\frac{1}{2}$)

$\Rightarrow$ we can take $A = \sqrt{\frac{2}{a}}$

∴ the allowed states are

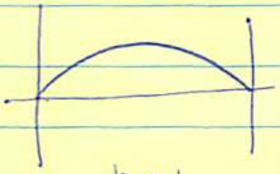
$$\boxed{\begin{aligned} \psi_n &= \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \\ E_n &= \frac{\hbar^2 n^2 \pi^2}{2ma^2} \end{aligned}}$$

Some properties of these solutions:

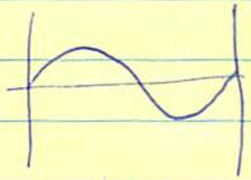
- the lowest energy state is the ground state with $n = 1$ $E = \frac{\hbar^2 \pi^2}{2ma^2}$

- the excited states with $n > 1$ have $E_n \propto n^2$

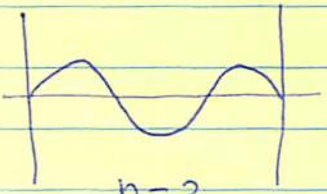
- each successive state has an extra node



$n=1$



$n=2$



$n=3$

and they are alternately odd $(\psi(x) = -\psi(-x))$
and even $(\psi(x) = +\psi(-x))$
about the centre of the box

- the states are orthogonal

$$\int_0^a dx \ \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) = 0 \text{ unless } n=m$$

we can write this as $$\boxed{\int_0^a dx \ \psi_n^*(x)\, \psi_m(x) = \delta_{nm}}$$

[the Kronecker delta is $\delta_{nm} = \begin{cases} 1 & n=m \\ 0 & n \neq m \end{cases}$]

Any initial wavefunction $\Psi(x,0)$ can be written as

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

Multiply by $\psi_m(x)$ and integrate

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

$$= c_m$$

$\Rightarrow$ the expansion coefficients are given by

$$\boxed{c_n = \int_0^a dx \sqrt{\frac{2}{a}}\ \sin\left(\frac{n\pi x}{a}\right) \Psi(x,0)}$$

and the general solution gives

$$\boxed{\Psi(x,t) = \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi x}{a}\right)\sqrt{\frac{2}{a}}\ e^{-it\hbar\pi^2 n^2/2ma^2}}$$

The expectation value of the energy is

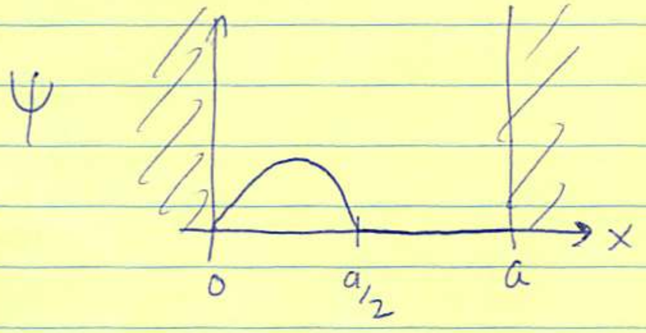
$$\langle H \rangle = \int \Psi^* \hat{H} \Psi\, dx = \sum_{n=1}^{\infty} |c_n|^2 E_n$$

which suggests the interpretation that $|c_n|^2$ gives the probability that a measurement of the energy will give a value E_n.

[Exercise: show that $\sum |c_n|^2 = 1$]

E.g. a particle is in the ground state of an infinite square well of width $a/2$. The square well is suddenly doubled in size, so that it extends from $x=0$ to $x=a$. What is the probability of finding the particle in the right hand side of the box as a function of time?

The initial state is $$\Psi(x,0) = \begin{cases} \sqrt{\frac{4}{a}} \sin\left(\frac{\pi x}{a/2}\right) & \text{for } x < a/2 \\ 0 & \text{for } x > a/2 \end{cases}$$



In the new box, $$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

$$C_n = \int_0^{a/2} dx \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \sqrt{\frac{4}{a}} \sin\left(\frac{2\pi x}{a}\right)$$

$$\theta = \frac{2\pi x}{a} \qquad C_n = \int_0^{\pi} \cancel{dx}\, \frac{2\sqrt{2}}{a} \sin\left(\frac{n\theta}{2}\right) \sin\theta \, \frac{a}{2\pi} \, d\theta$$

$$= \frac{\cancel{2}\sqrt{2}}{\pi} \int_0^{\pi} \sin\left(\frac{n\theta}{2}\right) \sin\theta \, d\theta$$

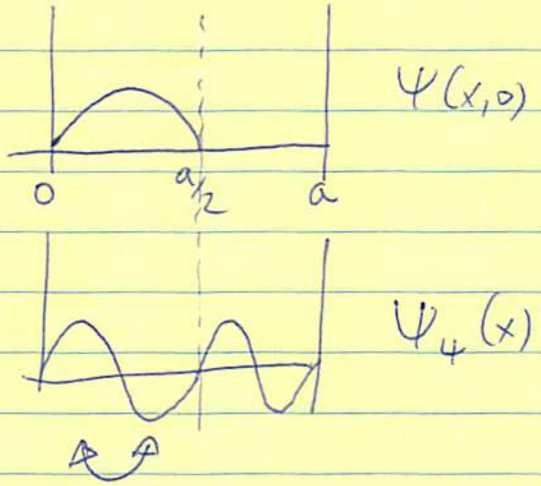
When $n=2$ we can do this:

$$C_2 = \sqrt{2} \underbrace{\frac{1}{\pi}\int_0^{\pi} \sin^2\theta \, d\theta}_{1/2} = \frac{1}{\sqrt{2}}$$

For arbitrary n, the integral is $\frac{\pi}{\sqrt{2}} c_n = \frac{-4\sin\left(\frac{n\pi}{2}\right)}{n^2-4}$ $(n \neq 2)$ (Mathematica)

Values are $\boxed{\begin{array}{llll} c_1 = +\frac{4}{3}\frac{\sqrt{2}}{\pi} & c_2 = \frac{1}{\sqrt{2}} & c_3 = +\frac{4}{5}\frac{\sqrt{2}}{\pi} & \\ c_4 = 0 & c_5 = \frac{-4}{21}\frac{\sqrt{2}}{\pi} & c_6 = 0 & \ldots \end{array}}$

Even n's give $c_n = 0$: we can understand this from the symmetry e.g.



equal and opposite contributions cancel

[Let's check the sum: for $n \geq 3$ we can write

$$\sum_{n=3}^{\infty} |c_n|^2 = \frac{2}{\pi^2}\sum_{m=0}^{\infty}\left(\frac{4}{(2m+3)^2-4}\right)^2$$

$$= \frac{2}{\pi^2}\sum_{m=0}^{\infty}\left(\frac{1}{m^2+3m+5/4}\right)^2$$

$$= \frac{2}{\pi^2}\left(\frac{\pi^2}{4} - \frac{16}{9}\right)$$

$$= \frac{1}{2} - \frac{2}{\pi^2}\frac{16}{9}$$

Add $c_1^2 + c_3^2$: $\sum_{n=1}^{\infty} |c_n|^2 = \frac{16}{9}\frac{2}{\pi^2} + \frac{1}{2} + \frac{1}{2} - \frac{2}{\pi^2}\frac{16}{9} = 1$ ✓]

This means that if we measure the particle energy, we will find

$$\text{energy} = \begin{cases} E_1 = \dfrac{\hbar^2\pi^2}{2ma^2} & \text{with probability } |c_1|^2 = \dfrac{16}{9}\dfrac{2}{\pi^2} \\ & = 0.36 \\ E_2 = \dfrac{\hbar^2\pi^2 2}{ma^2} & \text{" } \text{" } |c_2|^2 = \dfrac{1}{2} \\ \geqslant E_3 = \dfrac{9\hbar^2\pi^2}{2ma^2} & \text{" } \text{" } \sum_{n\geqslant 3}|c_n|^2 = \frac{1}{2} - 0.36 \\ & = 0.14 \end{cases}$$

The wavefunction is

$$\boxed{\Psi(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) e^{-iE_nt/\hbar}}$$

Probability particle is in right hand side of the box is

$$\int_{a/2}^{a} |\Psi|^2 dx = \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \int_{a/2}^{a} dx \, \frac{2}{a} \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) e^{-\frac{i\hbar^2\pi^2 t}{2ma^2\hbar}(n^2-m^2)} c_n c_m$$

We need $\displaystyle \frac{2}{a}\int_{a/2}^{a} dx \, \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right)$

$$\left[\theta = \frac{\pi x}{a}\right] \quad = \frac{2}{a}\frac{a}{\pi}\int_{\pi/2}^{\pi} d\theta \, \sin(n\theta)\sin(m\theta) \equiv I_{nm}$$

This is $\frac{1}{2}$ for $n = m$

$$\Rightarrow \int_{a/2}^{a} dx\, |\Psi|^2 = \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \underbrace{c_n c_m I_{nm}}_{\text{symmetric in } n,m}\, e^{-E_1 t/\hbar \underbrace{(n^2-m^2)}_{\text{antisymmetric in } n,m}}$$

arrange the terms in pairs and use $e^{i\theta} + e^{-i\theta} = 2\cos\theta$

$$\Rightarrow \int_{a/2}^{a} |\Psi|^2 dx = \underbrace{\sum_{n=1}^{\infty} |c_n|^2 \tfrac{1}{2}}_{\text{diagonal terms} = \frac{1}{2}} + \sum_{n=1}^{\infty}\sum_{m>n} 2 c_n c_m I_{nm} \cos\left(\frac{E_1 t}{\hbar}(n^2-m^2)\right)$$

The off-diagonal terms look complicated but recall that even c_n vanish for $n \geq 4$ and from symmetry I_{nm} is non-zero only if m is odd and n even or vice-versa.

Terms that survive are $n=1$ $m=2$ $\quad 2 c_1 c_2 I_{12}$

$$= 2\left(+\frac{4}{3}\frac{\sqrt{2}}{\pi}\right)\left(\frac{1}{\sqrt{2}}\right)\left(-\frac{4}{3\pi}\right)$$

$$= -\frac{32}{9\pi^2}$$

$n=2$ $\quad m = 3, 5, 7 \ldots$

$$I_{2m} = \frac{4\sin\left(\frac{m\pi}{2}\right)}{(m^2-4)\pi} \quad \text{(from mathematica)}$$

$$= -c_m/\sqrt{2}$$

$\Rightarrow \int_{a/2}^{a} |\Psi|^2 dx =$ ~~$\frac{1}{2} + \frac{32}{9\pi^2}\cos\left(\frac{3E_1 t}{\hbar}\right) + \sum_{n=3,5,7..} c_n^2 \cos\left(\frac{E_1 t}{\hbar}(n^2-4)\right)$~~

$$= \frac{1}{2} - \sum_{\substack{n \text{ odd} \\ (1,3,5..)}} c_n^2 \cos\left(\frac{E_1 t}{\hbar}(n^2-4)\right)$$

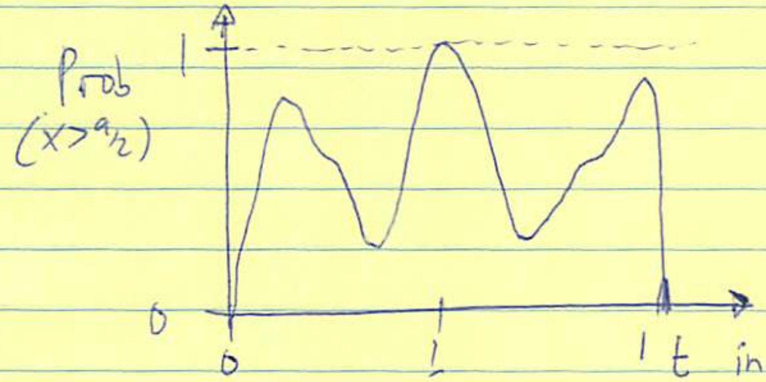
Recall that $c_2^2 = \frac{1}{2} \Rightarrow$ at $t=0$ the second term is

$$\sum_{n \text{ odd}} |c_n|^2 = \frac{1}{2}$$

so that at $t=0$ the probability of being in the right of the box vanishes as expected. ✓

Final answer:

$$\text{Prob}(x > a/2) = \frac{1}{2} - \sum_{n \text{ odd}} \frac{2}{\pi^2}\left(\frac{4}{4-n^2}\right)^2 \cos\left(\frac{E_1 t}{\hbar}(n^2-4)\right)$$



periodic in time

t in units of $\frac{2\pi\hbar}{E_1} = \frac{\hbar 2\pi}{\cancel{2\pi}} \frac{2ma^2}{\hbar^2\pi^2}$

$$= \frac{4ma^2}{\hbar^{\cancel{3}}\pi^{\cancel{3}}}$$

$$= \frac{8ma^2}{h}$$

As time progresses, the probability that the particle will be in the right hand side of the box oscillates between 0 and 1, with an average value of 1/2.

Evaluating $|\Psi|^2$ for a linear combination of stationary states

A common task is to evaluate $|\Psi|^2$ for Ψ of the form

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

then
$$|\Psi|^2 = \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} c_n^* c_m \psi_m^* \psi_n e^{-it(E_m-E_n)/\hbar}$$

The diagonal terms (where $n=m$) give $\sum_{n=1}^{\infty} |c_n|^2 |\psi_n|^2$

The terms where $n \neq m$ come in pairs

eg.
$$c_n^* c_m \psi_m^* \psi_n e^{-it(E_m-E_n)/\hbar}$$
$$+ \; c_m^* c_n \psi_n^* \psi_m e^{+it(E_m-E_n)/\hbar}$$

for c_n and ψ_n real, this is

$$c_n c_m \psi_m \psi_n \left(e^{it(E_m-E_n)/\hbar} + e^{-it(E_m-E_n)/\hbar} \right)$$

$$= 2 c_n c_m \psi_m \psi_n \cos\left(\frac{t(E_m-E_n)}{\hbar} \right)$$

we can split this in two pieces, one for each term and we are back to the double sum

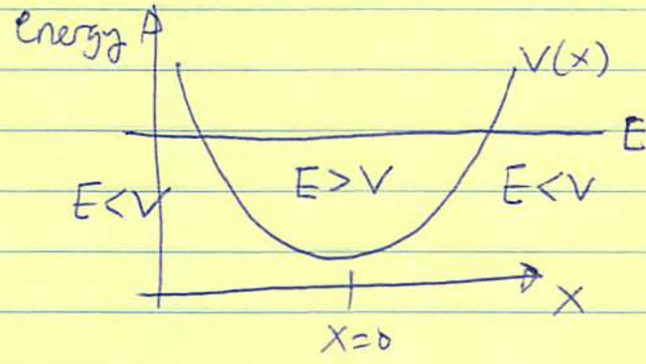
$$|\Psi|^2 = \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} c_n c_m \psi_n(x) \psi_m(x) \cos\left(\frac{t(E_m-E_n)}{\hbar} \right)$$

which also includes the diagonal terms correctly. HW2 Q1 gives an example.

Quantum harmonic oscillator

Next consider a potential $V(x) = \frac{1}{2}kx^2$

First note that there are two different kinds of behavior of the wavefunction, depending on whether $E<V$ or $E>V$



For $E>V$, $$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}(E-V)\psi < 0$$

$\Rightarrow$ wave-like solutions for ψ

but if $E<V$ $$\frac{d^2\psi}{dx^2} > 0$$

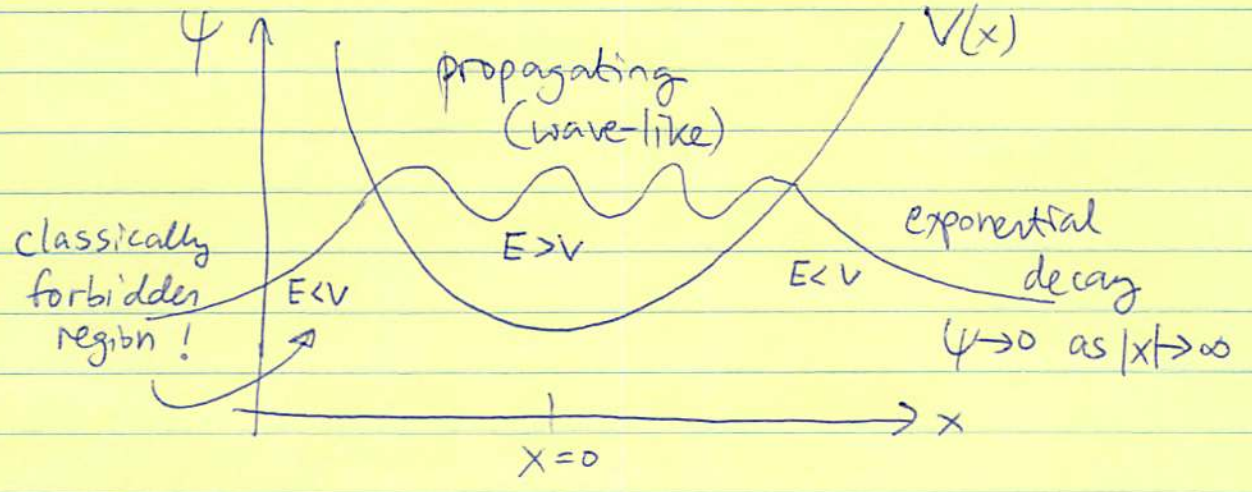
and the solution is exponential

[eg. if V was constant then e^{ikx} is a solution with $k^2 = \frac{2m}{\hbar^2}(E-V)$

$E>V \Rightarrow k$ real propagating wave e^{ikx}

$E<V \Rightarrow k$ imaginary evanescent solution $e^{-|k|x}$]

Therefore, we can expect the solutions to look like



with higher energy states having more nodes in the region where E>V.

The second point is that <u>ψ(x) will be either even or odd around x=0</u>. This is a general result when the potential is symmetric $V(x) = V(-x)$. To see this

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

$$x \to -x \qquad -\frac{\hbar^2}{2m}\frac{d^2\psi(-x)}{dx^2} = \big(E - V(-x)\big)\,\psi(-x)$$

$$= \big(E - V(x)\big)\,\psi(-x)$$

$\Rightarrow$ $\psi(-x)$ and $\psi(x)$ satisfy the same equation $\Rightarrow$ $\psi(-x)$ and $\psi(x)$ are the same up to a constant multiplier,

$$\psi(-x) = C\,\psi(x).$$

$$\frac{d\psi(-x)}{d(-x)} = -\frac{d\psi(-x)}{dx} = -C\,\frac{d\psi(x)}{dx}$$

but ψ must be continuous at $x=0$ and $d\psi/dx$ must be continuous at $x=0$.

Two ways to do it:

1) $\frac{d\psi}{dx} = 0$ at $x = 0$ and then $C = 1$

$$\psi(x) = +\psi(-x)$$ even function

or 2) $\psi = 0$ at $x = 0$ and then $C = -1$

so that $\frac{d\psi(x)}{dx} = -\frac{d\psi(-x)}{d(-x)}$ at $x = 0$

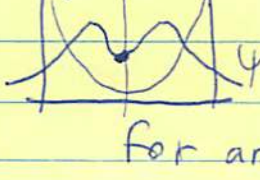
$$\Rightarrow \psi(x) = -\psi(-x)$$ odd function

(we'll see a much simpler way to arrive at this answer using the parity operator in a later part of the course)

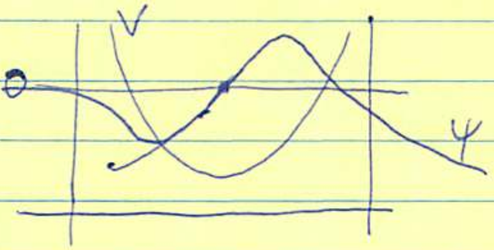
Numerical solution

Let's solve this problem with numerical integration. The idea will be to take advantage of the symmetry, and integrate from $x = 0$ to large x, finding the values of E for which $\psi \to 0$ at large x (the eigenvalues). This kind of method is known as a shooting method.

For an even solution, we will set $\psi = 1$ and $\frac{d\psi}{dx} = 0$ at $x = 0$



For an odd solution, we will set $\psi = 0$ and $\frac{d\psi}{dx} = 1$ at $x = 0$.



We will go through the numerical solution in class. Two "tricks" that we need are:

1) the integrator takes steps in x by using the derivative to calculate the value of ψ at the new x value based on ψ at the old x value:

$$\psi(x+\Delta x) \simeq \psi(x) + \Delta x \left.\frac{d\psi}{dx}\right|_x + \cdots$$

So it asks us to provide the first derivative $\frac{d\psi}{dx}$.

But the Schrödinger equation is 2nd order

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

The answer is to define a new function $\chi(x) = \frac{d\psi}{dx}$ and write the Schrödinger equation as two first order ODEs:

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

2) It is simpler to use a dimensionless energy $\tilde{E} = \frac{E}{\hbar\omega/2}$ where $\omega^2 = \frac{k}{m}$ is the classical oscillator frequency.

$k = m\omega^2$

The Schrödinger equation is then

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

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

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

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

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

or

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

This is what we will integrate numerically

b.c.'s are either $\psi = 1 \quad \chi = 0$ at $x = 0$ (even)
$\psi = 0 \quad \chi = 1$ at $x = 0$ (odd)

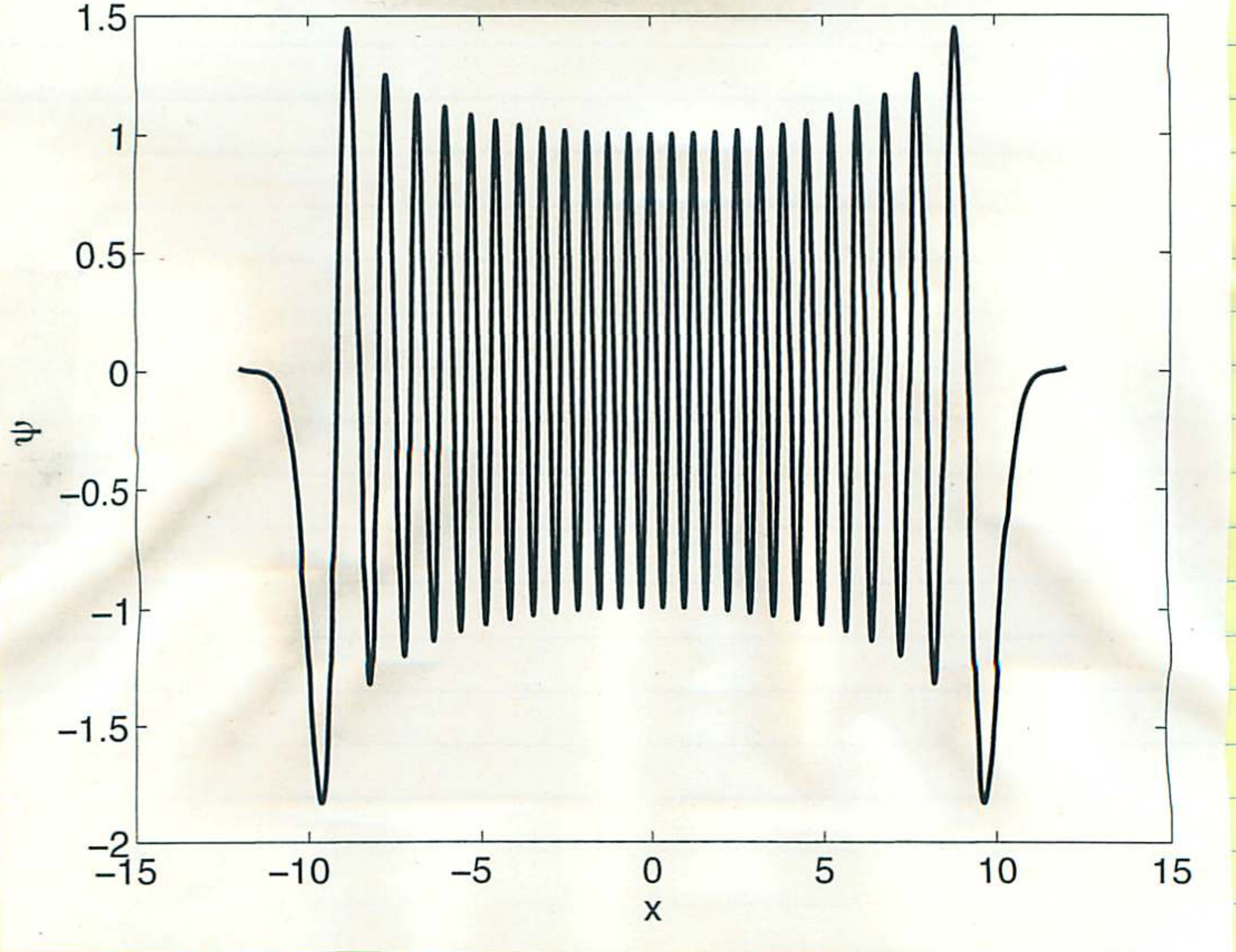
The numerical solution gives eigenvalues $\tilde{E} = 1, 3, 5, 7 \ldots$

or $\boxed{E = (n+\tfrac{1}{2})\hbar\omega}$ $\quad n = 0, 1, 2, 3 \ldots$

n even $\Rightarrow$ ψ_n is even
n odd $\Rightarrow$ ψ_n is odd

For large n, the solution looks like:

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



Notice that – the separation between peaks in the wave becomes larger as x increases

– the wave evanesces for $\tilde{x} \gtrsim \sqrt{\tilde{E}} = \sqrt{2n}$
where $E = V$ or $\tilde{E} = \tilde{x}^2$

– the amplitude of the propagating part of the solution increases towards the classical turning point

– there is a non-zero probability of finding the particle in the classically disallowed region! This is our first sign of <u>quantum tunnelling</u>!

We can understand these features with a "WKB" approach. We say that when n is large or the wavelength is very small, the potential V is locally constant. In other words $V(x)$ is changing on a lengthscale $\gg$ the wavelength of the wave. The solution is approximately the constant potential solution

$$\psi = A e^{ikx}$$

$$\text{with} \quad k^2 = \frac{2m}{\hbar^2}(E - V)$$

This explains:

1) As long as $E > V$ $k^2 > 0$ and the solution is a wave. Once $E < V$ the solution is evanescent. ✓

2) The wavelength of the wave $\lambda \propto \frac{1}{k} \propto \frac{1}{(E-V)^{1/2}}$

as x increases, V increases, $E-V$ decreases, λ increases ✓

3) For a plane wave the probability flux is (see HW 1 Q3)

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

for a stationary solution

$$\frac{\partial |\psi|^2}{\partial t} \propto \frac{\partial J_\psi}{\partial x} = 0$$

$$\Rightarrow \quad J_\psi = \text{constant}$$

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

the amplitude of the wave increases towards the classical turning point ✓

Boundary conditions for the Schrödinger equation

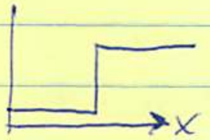
In problems where the potential $V(x)$ is discontinuous, we need matching conditions on ψ and $d\psi/dx$ at the location of the discontinuity.

The first is $\boxed{\psi \text{ is continuous}}$ at a boundary. This avoids infinite gradients in ψ and therefore momentum $\frac{\hbar}{i}\frac{\partial\psi}{\partial x}$.

The second is $\boxed{\frac{d\psi}{dx} \text{ is continuous}}$ at a boundary. To derive this, integrate the Schrödinger equation across the boundary from $x=-\varepsilon$ to $+\varepsilon$ and let $\varepsilon\to 0$.

$$\underbrace{\int_{-\varepsilon}^{\varepsilon} -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}\,dx}_{\text{this is } -\frac{\hbar^2}{2m}\left[\frac{d\psi}{dx}\right]_{-\varepsilon}^{\varepsilon}} = \underbrace{\int_{-\varepsilon}^{\varepsilon}(E-V)\,\psi\,dx}_{\substack{\text{this side vanishes for} \\ \varepsilon\to 0\text{, even if there is a} \\ \text{discontinuity in } V(x)}}$$

eg. $V(x)$



$$\Rightarrow \left[\frac{d\psi}{dx}\right]_{-\varepsilon}^{\varepsilon} = 0, \text{ or } \frac{d\psi}{dx} \text{ continuous.} \checkmark$$

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

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

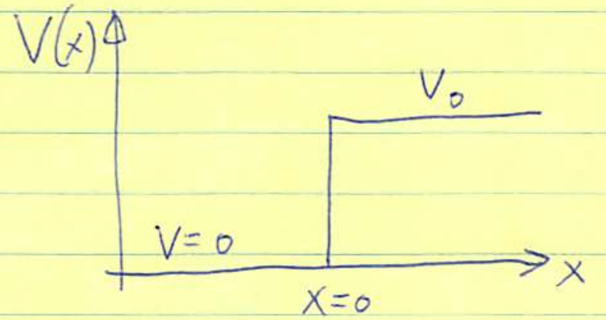
then the right-hand side does not vanish! Instead,

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

Scattering at a potential jump

The infinite square well and harmonic oscillator have only bound states - the particle is confined by the potential ($\psi \to 0$ at $|x| \to \infty$). Next we consider incoming and outgoing waves in the presence of a localized potential feature - in other words SCATTERING.

The simplest example 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, there is a reflected wave even when $E > V_0$.

The wavefunction for $x < 0$ is

$$\psi(x) = \underbrace{e^{ikx}}_{\substack{\text{incident} \\ \text{wave (travelling} \\ \text{in } +x \text{ direction)}}} + \underbrace{r e^{-ikx}}_{\substack{\text{reflected wave} \\ (-x \text{ direction})}}$$

where

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

For $x>0$, the wavevector is given by $q^2 = \frac{2m}{\hbar^2}(E-V_0)$

and there is only a rightwards travelling wave (since we assume particles are incident from the left)

$$\psi(x) = t\, e^{iqx}$$

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

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

$$\Rightarrow \quad 1+r = \frac{k}{q}(1-r)$$

$$r\left(1+k/q\right) = k/q - 1$$

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

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

As $V_0 \to 0$ $q \to k$ and $r \to 0$, $t \to 1$
$V_0 \to \infty$ $t \to 0$ $r \to -1$ (need to be a bit careful in the large V_0 limit because q is imaginary when $E < V_0$)

Its useful to look at the probability flux $J_\psi \propto k|A|^2$ (A = wave amplitude)

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

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

Note that $R+T=1$ (conservation of probability).

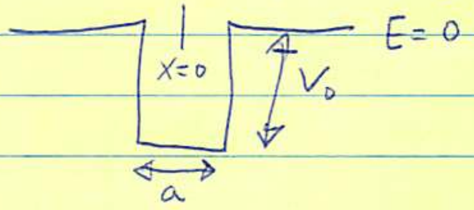
The interpretation is that if a beam of particles is incident on the potential step from the left, the probability of finding a particle outgoing on the right is T, and on the left (reflected) R.

[Exercise: think about what happens when $E < V_0$. What are the values of R and T?]

It's worth emphasizing the difference from a classical particle, for which T is either 1 $(E > V_0)$ or 0 $(E < V_0)$. In the quantum case, even a small potential jump gives some probability of reflection.

The delta-function potential

The potential $V(x) \propto -\delta(x)$ has both bound and scattering states. We can think of it as a limit of a square well whose depth has been taken to infinity keeping the product $V_0 a$ constant



as $V_0 \to \infty$ $a \to 0$

For this reason it is instructive to write it as $V(x) = -V_0 a\, \delta(x)$
Notice that this has the correct units because the units of $\delta(x)$ are $1/\text{length}$.

The bound state has $E < 0$, and $V = 0$ except at the origin,
$\Rightarrow$ the solution is

$$\psi = \begin{cases} e^{kx} & \text{for } x < 0 \\ e^{-kx} & \text{" } x > 0 \end{cases}$$

where we've chosen the solution that has $\psi \to 0$ as $|x| \to \infty$.
The prefactor is the same on both sides so that ψ is continuous at $x = 0$.

We showed previously that for a delta-function potential, there is a jump in $\frac{d\psi}{dx}$:

$$\left[\frac{d\psi}{dx}\right]_{-\varepsilon}^{\varepsilon} = -\frac{2mV_0 a}{\hbar^2}\psi(0)$$

$$\Rightarrow \quad -2k = -\frac{2mV_0 a}{\hbar^2} \quad \Rightarrow \quad k = \frac{maV_0}{\hbar^2} \,.\, //$$

Therefore there is a <u>bound state</u> <u>with energy</u> $\boxed{E = -\frac{\hbar^2 k^2}{2m} = -\frac{ma^2 V_0^2}{2\hbar^2}}$.

If we write $\psi = A e^{-k|x|}$

normalizing gives

$$1 = A^2\, 2\int_0^\infty e^{-2kx}\, dx$$

$$= \frac{2A^2}{-2k}\left[-1\right] \Rightarrow A = \sqrt{k}$$

$$= \frac{\sqrt{maV_0}}{\hbar}$$

$$\Rightarrow \quad \boxed{\psi = \frac{\sqrt{maV_0}}{\hbar}\, e^{-\sqrt{maV_0}\,|x|/\hbar}}$$

The scattering states have $E>0$. As for the potential step, write reflected and transmitted waves

$$x<0 \qquad \psi = e^{ikx} + r e^{-ikx} \qquad\qquad k^2 = \frac{2mE}{\hbar^2} > 0.$$

$$x>0 \qquad \psi = t\, e^{ikx}$$

then $\quad 1 + r = t$ as before

and

$$ikt - ik + ikr = -\frac{2mV_0 a}{\hbar^2}(1+r)$$

$$ik(1+r-1+r) = -\frac{2mV_0 a}{\hbar^2}(1+r)$$

$$\Rightarrow \quad r\left(2ik + \frac{2mV_0 a}{\hbar^2}\right) = -\frac{2mV_0 a}{\hbar^2}$$

$$r = -\frac{1}{1 + i\hbar^2 k/2mV_0 a} = -\frac{1}{1 + \frac{2iE}{V_0 k a}}$$

$$t = 1 + r = 1 - \frac{1}{1 + \frac{2iE}{V_0 ka}} = \frac{2iE/V_0 ka}{1 + 2iE/V_0 ka}$$

$$= \frac{1}{1 - iV_0 ka/2E}$$

reflected and transmitted flux fractions are

$$R = |r|^2 = \frac{1}{1 + 4E^2/V_0^2 (ka)^2}$$

$$T = |t|^2 = \frac{1}{1 + V_0^2 (ka)^2/4E^2}$$

(note that $R + T = 1$ ✓)

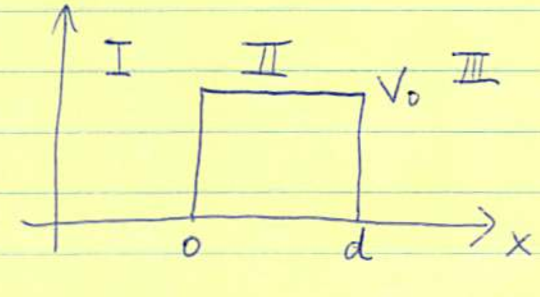
The critical parameter is $\frac{4E^2}{(ka)^2 V_0^2} = \frac{2\hbar^2 E}{\cancel{2} m a^2 V_0^2}$

Increasing E → more transmission, less reflection.

It is interesting to note that for a positive barrier $V(x) = +\delta(x)$ although the bound state is no longer present, the scattering coefficients t and r are the same (they depend on $(V_0 a)^2$ not the sign of V_0). The particle can tunnel through the infinitely high potential barrier!

Tunnelling

To see tunnelling in action, consider particles with energy $E < V_0$ incident on a barrier with finite width d



Now we have 3 regions

$$\text{I}: \quad \psi = e^{ikx} + r e^{-ikx}$$

$$\text{II}: \quad \psi = a e^{qx} + b e^{-qx}$$

$$\text{III}: \quad \psi = t e^{ikx}$$

$$k^2 = \frac{2mE}{\hbar^2} \qquad q^2 = \frac{2m}{\hbar^2}(V_0 - E)$$

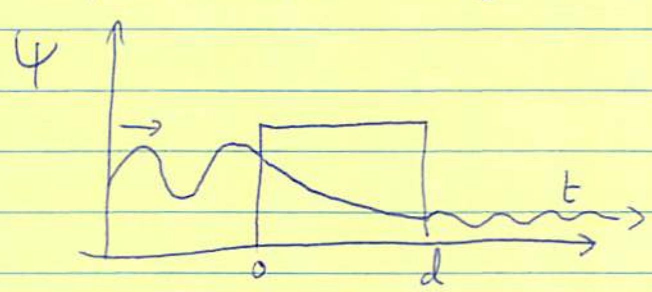
Now apply b.c.'s at $x = 0$ and $x = d$

$$\left.\begin{array}{ll} \psi \text{ cts:} & 1 + r = a + b \\ & a e^{qd} + b e^{-qd} = t e^{ikd} \\ \psi' \text{ cts} & ik(1 - r) = q(a - b) \\ & aq e^{qd} - bq e^{-qd} = ikt e^{ikd} \end{array}\right\} \begin{array}{l} \text{4 equations} \\ \text{can be} \\ \text{solved for} \\ a, b, t, r \end{array}$$

The solution involves some algebra to get a, b, t, r. Here, we'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 particle wavelengths)

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

and $\ln T \simeq -2qd + \left(\begin{matrix}\text{smaller logarithmic}\\ \text{factor}\end{matrix}\right)$

Just to put in some numbers,

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

Operators and Formalism

Hermitian operators

We noted earlier that for an observable O there is an operator $\hat{O}$ such that the expectation value of the observable is

$$\langle O \rangle = \int_{-\infty}^{\infty} \psi^*(x)\, \hat{O}\, \psi(x)\, dx \qquad \text{—(1)}$$

Examples that we've seen are

$\hat{x} \equiv x$ particle position

$\hat{p} \equiv \frac{\hbar}{i}\frac{\partial}{\partial x}$ " momentum

$\hat{H} \equiv i\hbar\frac{\partial}{\partial t}$ energy

$\frac{\hat{p}}{2m} \equiv -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$ Kinetic energy

The observable must be a real quantity, which implies particular properties for the operator $\hat{O}$. An operator with a real expectation value is known as a <u>HERMITIAN OPERATOR</u>.

The complex conjugate of (1) is

$$\langle O \rangle^* = \int [\hat{O}\psi]^*\, \psi\, dx$$

For real observables $\langle O \rangle = \langle O \rangle^*$

$$\Rightarrow \int \psi^*\, \hat{O}\psi\, dx = \int [\hat{O}\psi]^*\, \psi\, dx$$

Now we define the <u>hermitian conjugate operator</u> $O^\dagger$ by

$$\int dx\, \psi^*\, \hat{O}^\dagger \psi = \int [\hat{O}\psi]^*\, \psi\, dx.$$

For a real expectation value $\langle O \rangle = \langle O \rangle^*$

$$\Rightarrow \int \psi \hat{O} \psi \, dx = \int [\hat{O}\psi]^* \psi \, dx$$

$$= \int \psi^* \hat{O}^\dagger \psi \, dx$$

$$\Rightarrow \boxed{\hat{O} \equiv \hat{O}^\dagger}$$

A Hermitian operator is its own Hermitian conjugate.

eg. Consider momentum operator $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$

then $\int (\hat{p}\psi)^* \psi \, dx$

$$= \int \left(-\frac{\hbar}{i}\frac{\partial}{\partial x}\psi^*\right)\psi(x) \, dx$$

$$= \int \psi^*(x) \frac{\hbar}{i} \frac{\partial \psi(x)}{\partial x} \, dx \qquad \left(\text{integrating by parts}\right)$$

$$= \int \psi^* \hat{p}^\dagger \psi \, dx \quad \Rightarrow \quad \hat{p}^\dagger = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

and we see that $\hat{p} = \hat{p}^\dagger$ as expected. (because p is an observable).

$\langle p \rangle = \langle p \rangle^*$

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 $\hat{H}$.

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

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

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

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

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

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

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

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

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

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

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

The parity operator

The parity operator takes x → −x

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

An eigenfunction of the parity operator satisfies $\hat{P}\psi(x) = \lambda\psi(x)$ where λ is the eigenvalue. Now

$$\hat{P}^2\psi(x) = \hat{P}\psi(-x) = \psi(x) = \lambda^2\psi(x)$$

$\Rightarrow \lambda = \pm 1$

Two possibilities: $\lambda = +1$ $\quad \hat{P}\psi(x) = \psi(-x) = \psi(x)$

EVEN FUNCTION

$\lambda = -1$ $\quad \hat{P}\psi(x) = \psi(-x) = -\psi(x)$

ODD FUNCTION

If $[\hat{P}, \hat{H}] = 0$ then the parity will not change with time.
eg. harmonic oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2 = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2$$

does not change under x → −x

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

or $[\hat{H}, \hat{P}] = 0.$ $\qquad = \hat{H}(x)\,\psi(-x)$

$\therefore \quad \dfrac{d}{dt}\langle\hat{P}\rangle = 0$ Even eigenfunction will remain even, odd will remain odd.

Another way to say this is that when $[\hat{H}, \hat{P}] = 0$, the stationary states (eigenfunctions of $\hat{H}$) are also the eigenfunctions of $\hat{P}$. The stationary states have a definite parity.

In general if two operators have the same eigenfunctions they must commute.

eg. $\hat{A}\psi = a\psi$

and $\hat{B}\psi = b\psi$ for the same functions ψ

$$\Rightarrow \quad \hat{A}\hat{B}\psi = \hat{A}\, b\psi = ab\psi$$

$$= \hat{B}\hat{A}\psi = \hat{B}\, a\psi = ab\psi$$

an example is the state $\psi = A e^{ipx/\hbar}$ for a free particle which is an eigenstate of both $\hat{H}$ and $\hat{p}$,

$$\hat{H}\psi = \frac{p^2}{2m}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}$$

$$\hat{p}\,\psi = \frac{\hbar}{i}\frac{\partial\psi}{\partial x} = p\psi$$

because

$$[\hat{H}, \hat{p}] = [\frac{\hat{p}^2}{2m}, \hat{p}] = 0.$$

Ladder operators and the harmonic oscillator

There is an operator method to solve the harmonic oscillator. The idea is to complete the square in the Hamiltonian

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

(where the time-independent Schrödinger equation is $\hat{H}\psi = E\psi$).

We could try to complete the square by writing this as

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

[using $x^2 - y^2 = (x+y)(x-y)$]

$$= \underbrace{\omega \left(\frac{\hat{p}^2}{2m\omega} + \frac{m\omega}{2}\hat{x}^2 \right)}_{\substack{\text{this is what we want} \\ \hat{H}}} + \underbrace{\frac{i\omega}{2}\left(-\hat{x}\hat{p} + \hat{p}\hat{x} \right)}_{\substack{\text{there is an extra non-zero term –} \\ \text{the cross-terms do not vanish} \\ \text{because } \hat{x} \text{ and } \hat{p} \text{ do not} \\ \text{commute}}}$$

We showed earlier that $[\hat{x}, \hat{p}]\psi = (\hat{x}\hat{p} - \hat{p}\hat{x})\psi = i\hbar\psi$

So the extra term is $+\frac{\hbar\omega}{2}$.

Now define the <u>raising and lowering operators</u>

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

$$\hat{a}^{\dagger} = \sqrt{\frac{m\omega}{2}}\,\hat{x} - i\frac{\hat{p}}{\sqrt{2m\omega}}$$

Then $\hat{a}\hat{a}^{+}\omega = \hat{H} + \frac{\hbar\omega}{2}$

Similarly $\hat{a}^{+}\hat{a}\,\omega = \hat{H} - \frac{\hbar\omega}{2}$ because the change of order in $\hat{a}^{+}$ and $\hat{a}$ changes the sign of the cross term involving $[\hat{x},\hat{p}]$.

Therefore $\hat{a}$ and $\hat{a}^{+}$ do not commute:

$$\omega[\hat{a},\hat{a}^{+}] = \omega(\hat{a}\hat{a}^{+} - \hat{a}^{+}\hat{a}) = \hbar\omega$$

Now look at $[\hat{H},\hat{a}]$

$$\begin{aligned}
&= \hat{H}\hat{a} - \hat{a}\hat{H} \\
&= \hat{a}^{+}\hat{a}\hat{a}\,\omega + \frac{\hbar\omega}{2}\hat{a} - \hat{a}\hat{a}^{+}\hat{a}\,\omega - \frac{\hbar\omega}{2}\hat{a} \\
&= [\hat{a}^{+},\hat{a}]\,\hat{a}\,\omega \\
&= -\hat{a}\,\hbar\omega
\end{aligned}$$

We can use this to gain some insight into what these operators do when they act on the eigenstates of $\hat{H}$.

eg. $\hat{a}\hat{H}\psi = E\hat{a}\psi = \hat{H}\hat{a}\psi + \hbar\omega\hat{a}\psi$

$$\Rightarrow \quad \hat{H}(\hat{a}\psi) = (E - \hbar\omega)(\hat{a}\psi)$$

$\Rightarrow$ if ψ is an eigenstate of $\hat{H}$ with energy E

then $\hat{a}\psi$ is an eigenstate with energy $E \overset{-}{\cancel{+}} \hbar\omega$.

Similarly, $$[\hat{H}, \hat{a}^\dagger] = \hat{H}\hat{a}^\dagger - \hat{a}^\dagger\hat{H}$$
$$= \hat{a}^\dagger\hat{a}\hat{a}^\dagger \omega + \frac{\hbar\omega}{2}\hat{a}^\dagger$$
$$- \hat{a}^\dagger\hat{a}^\dagger\hat{a}\omega - \frac{\hbar\omega}{2}\hat{a}^\dagger$$
$$= \omega\hat{a}^\dagger[\hat{a}, \hat{a}^\dagger] = \hat{a}^\dagger\hbar\omega$$

So that
$$\hat{a}^\dagger\hat{H}\psi = \hat{a}^\dagger E\psi = \hat{H}\hat{a}^\dagger\psi - \hbar\omega\hat{a}^\dagger\psi$$

$$\Rightarrow \quad \hat{H}(\hat{a}^\dagger\psi) = (E + \hbar\omega)(\hat{a}^\dagger\psi)$$

$\Rightarrow$ $(\hat{a}^\dagger\psi)$ is an eigenstate of $\hat{H}$ with energy $E + \hbar\omega$.

This is the reason for referring to $\hat{a}^\dagger$ and $\hat{a}$ as raising and lowering operators, respectively. They are also known as ladder operators.

Every application of $\hat{a}$ gives a new stationary state with energy lower by $\hbar\omega$. Eventually this must stop when we reach the ground state ψ_0 :

$$\boxed{\hat{a}\psi_0 = 0}$$ cannot lower the ground state

The energy of the ground state is $$\hat{H}\psi_0 = \hat{a}^\dagger\cancelto{0}{\hat{a}\psi_0} + \frac{\hbar\omega}{2}\psi_0$$
$$= \frac{\hbar\omega}{2}\psi_0 = E_0\psi_0$$

$$\Rightarrow \boxed{\text{ground state energy } \hbar\omega/2}$$

Applying $a^\dagger$, we move to higher energy states

$$\hat{H}(a^\dagger \psi_0) = (E_0 + \hbar\omega)(a^\dagger\psi_0)$$

$$\Rightarrow \quad a^\dagger \psi_0 = \psi_1 \qquad \text{and} \qquad E_1 = E_0 + \hbar\omega$$

The energy spectrum is $\boxed{E_n = \hbar\omega\left(n+\tfrac{1}{2}\right)}$ $n = 0, 1, 2, \cdots$

Note that we derived this result without solving for $\psi(x)$. In fact the states ψ have been abstract quantities without any specific representation specified, whether in real space $\psi(x)$ or momentum space $A(p)$. More on this later.

We can use the ladder operators to solve for $\psi_n(x)$

$$\hat{a}\,\psi_0(x) = 0$$

$$\Rightarrow \quad \sqrt{\frac{m\omega}{2}}\,\hat{x}\,\psi_0(x) + \frac{i\,\hat{p}}{\sqrt{2m\omega}}\,\psi_0(x) = 0$$

$$\Rightarrow \quad \sqrt{\frac{m\omega}{2}}\,x\,\psi(x) + \frac{\hbar}{\sqrt{2m\omega}}\,\frac{d\psi_0}{dx} = 0$$

$$\Rightarrow \quad \frac{d\psi_0}{dx} = -\frac{m\omega}{\hbar}\,x\,\psi_0$$

which is satisfied by $\psi_0 = A e^{-m\omega x^2/2\hbar}$

The normalization factor is given by $\int_{-\infty}^{\infty} |\psi_0|^2\,dx = 1$

$$\Rightarrow \quad A = \left(\frac{m\omega}{\hbar\pi}\right)^{1/4}$$

which you can check for yourself using the integral

$$\int_{-\infty}^{\infty} e^{-ax^2}\,dx = \sqrt{\frac{\pi}{a}}.$$

The first excited state is given by $a^{\dagger}\psi_0 = \psi_1$

$$\Rightarrow \quad \psi_1(x) = \left(\sqrt{\frac{m\omega}{2}}\,x - \frac{\hbar}{\sqrt{2m\omega}}\frac{\partial}{\partial x}\right)\psi_0$$

$$= \left(\sqrt{\frac{m\omega}{2}}\,x - \frac{\hbar}{\sqrt{2m\omega}}\cdot\left(-\frac{m\omega}{\hbar}x\right)\right)\psi_0$$

$$\psi_1(x) = 2\sqrt{\frac{m\omega}{2}}\cdot\psi_0(x)\,x$$

$$\boxed{\psi_1(x) = \sqrt{2m\omega}\;x\;\psi_0(x)}$$

which is odd function as expected.

we can keep going: in general

$$\psi_n(x) = \frac{1}{\sqrt{n!}}\left(\sqrt{\frac{m\omega}{2}}\,x - \frac{\hbar}{\sqrt{2m\omega}}\frac{d}{dx}\right)^n \psi_0(x)$$

generates the eigenfunction n.

[I've inserted the correct normalization factor $\sqrt{n!}$, see page 20a]

Hilbert space and Dirac notation

There's an interesting analogy between what we've been doing and vector spaces that leads to the idea of Hilbert space.

We've seen that if we solve $\hat{H}\psi(x) = E\psi(x)$
we obtain the EIGENFUNCTIONS of $\hat{H}$, $\psi_E(x)$

with EIGENVALUES E.

The spectrum of eigenvalues may be continuous (eg. free particle)
or discrete (eg. harmonic oscillator)
or both (eg. finite square well)

The eigenfunctions $\psi_E(x)$ are ORTHONORMAL

$$\int \psi_n(x)\,\psi_m(x)\,dx = \delta_{nm} \qquad \text{(discrete)}$$

$$\int \psi_E(x)\,\psi_{E'}(x)\,dx = \delta(E-E') \qquad \text{(continuous)}$$

and we can expand any wavefunction $\psi(x)$ as

$$\psi(x) = \underbrace{\sum c_n \psi_n(x)}_{\text{discrete part}} + \underbrace{\int dE\; c(E)\,\psi_E(x)}_{\text{continuous part}} \qquad -(*)$$

Because the eigenfunctions of $\hat{H}$ (the stationary states) obey

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi = E\psi \Rightarrow \psi \propto e^{-iEt/\hbar}$$

this means that for any initial wavefunction $\Psi(x,0)$ the solution is

$$\Psi(x,t) = \sum c_n \psi_n(x) e^{-iE_nt/\hbar} + \int c(E)\, dE\, \psi_E(x) e^{-iEt/\hbar}$$

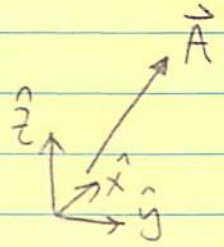
where

$$c_n = \int \psi_n(x)\, \Psi(x,0)\, dx$$

or $\quad C(E) = \int \psi_E(x)\, \Psi(x,0)\, dx$

which you can prove by multiplying (*) by either $\psi_n(x)$ or $\psi_E(x)$ and integrating.

There is an analogy here with vectors. Imagine we have the 3D vector $\vec{A}$



it has components A_x, A_y, A_z in a particular basis $\hat{x}, \hat{y}, \hat{z} \longleftarrow$ unit vectors

$$\vec{A} = A_x \hat{x} + A_y \hat{y} + A_z \hat{z}$$

We can extract the coefficients by taking a dot product

$$A_x = \hat{x} \cdot \vec{A}$$
$$A_y = \hat{y} \cdot \vec{A}$$
$$A_z = \hat{z} \cdot \vec{A}$$

because $\hat{x}, \hat{y}, \hat{z}$ are orthonormal $\quad \hat{x}\cdot\hat{x} = 1$
$\hat{x}\cdot\hat{y} = 0$
$\hat{x}\cdot\hat{z} = 0$.

In an N dimensional space, we can choose a basis $\hat{e}_i \quad i = 1..N$ and then

$$\vec{A} = \sum_{i=1}^{N} A_i \hat{e}_i \quad \text{with} \quad A_i = \hat{e}_i \cdot \vec{A}$$

because $\hat{e}_i \cdot \hat{e}_j = \delta_{ij}$. We can say that A_i is the PROJECTION of $\vec{A}$ along $\hat{e}_i$.

We've been doing something very similar which we can see more clearly if we define a dot product or SCALAR PRODUCT

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

analogous to the dot product of two vectors $\vec{A} \cdot \vec{B}$. The difference is that $\vec{A} \cdot \vec{B} = \sum A_i B_i$ involves a sum over N terms (in N-dimensional space) whereas $\langle \phi | \psi \rangle$ involves an infinite sum over the continuous label x.
In this sense we think of $\psi(x)$ as a vector in an infinite dimensional space, HILBERT SPACE, and we write it in a new notation $|\psi\rangle$

eg. for a discrete set of stationary states

$$\hat{H} |\psi_n\rangle = E_n |\psi_n\rangle \qquad \langle \psi_m | \psi_n \rangle = \delta_{nm}$$

and a general state $|\psi\rangle = \sum_n c_n |\psi_n\rangle$

where $c_m = \langle \psi_m | \psi \rangle$

because
$$\langle \psi_m | \psi \rangle = \sum c_n \langle \psi_m | \psi_n \rangle$$
$$= \sum c_n \delta_{nm} = c_m .$$

We can say that c_m is the projection of $|\psi\rangle$ on the basis state $|\psi_m\rangle$.

We also write for an operator $\hat{A}$

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

eg. $\langle p \rangle = \langle \psi | \hat{p} | \psi \rangle$ is the expectation value of momentum given state $|\psi\rangle$.

This notation is DIRAC NOTATION

$\langle \psi |$ is a "bra"

$|\psi\rangle$ is a "ket".

Probability of measuring an observable

We can take this a little further. Any operator $\hat{A}$ has a set of eigenvalues A_n and eigenfunctions $|\psi_{A,n}\rangle$ where

$$\hat{A} \, |\psi_{A,n}\rangle = A_n |\psi_{A,n}\rangle .$$

The eigenfunctions $|\psi_{A,n}\rangle$ form a complete basis and can be used to expand

$$|\psi\rangle = \sum a_n \, |\psi_{A,n}\rangle$$

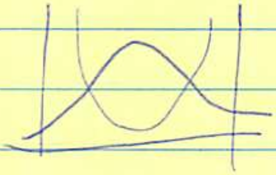
$$\text{where} \quad a_n = \langle \psi_{A,n} | \psi \rangle$$

Recall that when we expanded in terms of the eigenfunctions of the Hamiltonian, $|c_n|^2 = |\langle \psi_n | \psi \rangle|^2$ gave the probability that if we measured the energy of the particle we would measure an energy E_n.

Here, $|a_n|^2 = |\langle \psi_{A,n} | \psi \rangle|^2$ gives the probability that a measurement of A gives a value A_n.

eg. a particle is in the ground state of the harmonic oscillator;

$$|\psi_0\rangle = \psi_0(x)$$



What is the probability of measuring the particle momentum to be p ?

The eigenfunctions of the momentum operator are

$$|p\rangle = e^{ipx/\hbar}$$

because $\hat{p}|p\rangle = \frac{\hbar}{i}\frac{\partial}{\partial x} e^{ipx/\hbar} = p\,e^{ipx/\hbar}$

$$= p\,|p\rangle$$

$\Rightarrow$ the probability of measuring a particlelar value p of momentum is

$$|\langle p|\psi_0\rangle|^2$$

where $\langle p|\psi_0\rangle = \int_{-\infty}^{\infty} dx\, e^{-ipx/\hbar}\, \psi_0(x)$ —(1)

(this is actually a probability density since p is continuous.)

Notice that this is exactly what we wrote down at the beginning of the course when we expressed a wavefunction in terms of its plane wave components:

$$\psi(x) = \int dp\, e^{ipx/\hbar} A(p)$$

with $$A(p) = \int dx\ \psi(x)\ e^{-ipx/\hbar} \qquad \text{—(2)}$$

(See pages 4, 4a, 4b from part 2 of the notes).

We noted there that $A(p)$ is an alternative way to represent the wavefunction – it contains the same information as $\psi(x)$ and either one is enough to specify the state of the particle. We also showed there that the probability of measuring momentum p is $|A(p)|^2$.

We have the same result here: comparing (1) and (2)

$$\Rightarrow \quad \boxed{A(p) = \langle p | \psi_0 \rangle}$$

wavefunction written in terms of basis vectors $|p\rangle$ – "Momentum representation"

choice of basis vectors $|p\rangle$

state of particle $|\psi_0\rangle$ (abstract vector in Hilbert space)

This tells us a way to think of $\psi(x)$. Write the eigenfunctions of the position operator as $|x\rangle$
so that
$$\hat{x}\,|x\rangle = x\,|x\rangle$$

(these are states with definite particle position)

Probability of measuring particle location x is

$$|\langle x | \psi_0 \rangle|^2 \quad \text{which we usually write } |\psi(x)|^2$$

$$\Rightarrow \quad \boxed{\psi(x) = \langle x | \psi_0 \rangle}$$

The wavefunction $\psi(x)$ is the projection of the state $|\psi_0\rangle$ onto the basis $|x\rangle$.

More on Hermitian operators

We saw that Hermitian operators have real expectation values. Observables correspond to Hermitian operators since they must be real quantities. But not all operators that we've come across are Hermitian. For example the ladder operators are Hermitian conjugates of each other (as you might guess from the notation $\hat{a}$ and $\hat{a}^\dagger$).

For example, consider $\quad \hat{a}|\psi_n\rangle = |\psi_{n-1}\rangle$

if we take the scalar product with $|\psi_{n-1}\rangle$ we'll get a non-zero answer:

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

Now take the complex conjugate:

$$\left(\langle \psi_{n-1} | \hat{a} | \psi_n \rangle \right)^* = \left(\int \psi_{n-1}^* \, \hat{a} \psi_n \, dx \right)^*$$

$$= \int \psi_{n-1} (\hat{a}\psi_n)^* \, dx$$

$$= \int \psi_n^* \, \hat{a}^\dagger \psi_{n-1} \, dx$$

$\downarrow$ use definition of Hermitian conjugate

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

But for this to be equal to 1, we must have that $\hat{a}^\dagger|\psi_{n-1}\rangle = |\psi_n\rangle$

$\Rightarrow$ if $\hat{a}$ is a lowering operator
$\hat{a}^\dagger$ must be a raising operator.

We also see that for any operator $\hat{A}$,

$$\boxed{\langle\psi_1|\hat{A}|\psi_2\rangle^* = \langle\psi_2|\hat{A}^\dagger|\psi_1\rangle}$$

if $\hat{A}$ is Hermitian, then $\hat{A}^\dagger = \hat{A}$ and so

$$\boxed{\langle\psi_1|\hat{A}|\psi_2\rangle^* = \langle\psi_2|\hat{A}|\psi_1\rangle} \text{ for Hermitian } \hat{A}$$

Combinations of Hermitian operators are not necessarily Hermitian. For example consider two operators $\hat{A}, \hat{B}$:

$$\langle\psi_1|\hat{A}\hat{B}|\psi_2\rangle^* = \left(\int dx\ \psi_1^*\ \hat{A}(\hat{B}\psi_2)\right)^*$$

$$= \int dx\ \psi_1^{\cancel{*}}\left[\hat{A}(\hat{B}\psi_2)\right]^*$$

$$= \int dx\ (\hat{B}\psi_2)^*\ \hat{A}^\dagger\psi_1$$

$$= \int dx\ \psi_2^*\ \hat{B}^\dagger(A^\dagger\psi_1)$$

$$= \langle\psi_2|\hat{B}^\dagger\hat{A}^\dagger|\psi_1\rangle$$

So if we make an operator $\hat{C} = \hat{A}\hat{B}$
its Hermitian conjugate is $\hat{C}^\dagger = \hat{B}^\dagger\hat{A}^\dagger$.

If $\hat{A}$ and $\hat{B}$ are Hermitian, then
$$\hat{C}^\dagger = \hat{B}\hat{A}$$
$$= \hat{A}\hat{B} - [\hat{A}, \hat{B}]$$

Therefore the operator $\hat{A}\hat{B}$ is Hermitian only if $[\hat{A}, \hat{B}] = 0$.

Exercise: show that for two Hermitian operators $\hat{A}, \hat{B}$ the operator $\hat{C} = i[\hat{A}, \hat{B}]$ is Hermitian.

A note on the normalization of the ladder operators

On p18, we assumed that $\hat{a}|\psi_n\rangle = |\psi_{n-1}\rangle$. In fact, we can not write an equals sign in this expression. Our original argument on p8 showed only that $\hat{a}|\psi_n\rangle \propto |\psi_{n-1}\rangle$, so

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

and $$\hat{a}^\dagger|\psi_n\rangle = c_n^+\,|\psi_{n+1}\rangle$$

What are the values of c_n^- and c_n^+ ?
To find out, consider the expectation value of energy for a stationary state $|\psi_n\rangle$. The harmonic oscillator has energy levels $E_n = \hbar\omega(n+\frac{1}{2})$

$$\Rightarrow \qquad \langle\psi_n|\,\hat{H}\,|\psi_n\rangle = \hbar\omega\left(n+\tfrac{1}{2}\right)$$

But $\hat{H} = \omega\,\hat{a}^\dagger\hat{a} + \frac{\hbar\omega}{2}$

$$\begin{aligned}\Rightarrow \quad \langle\psi_n|\,\hat{H}\,|\psi_n\rangle &= \omega\langle\psi_n|\hat{a}^\dagger\hat{a}|\psi_n\rangle + \frac{\hbar\omega}{2}\langle\psi_n|\psi_n\rangle \\ &= \omega\langle\psi_{n-1}|\psi_{n-1}\rangle\,|c_n^-|^2 + \frac{\hbar\omega}{2}\langle\psi_n|\psi_n\rangle \\ &= \hbar\omega\left(\frac{|c_n^-|^2}{\hbar} + \frac{1}{2}\right)\end{aligned}$$

$$\Rightarrow \quad \underline{\underline{c_n^- = \sqrt{\hbar}\,\sqrt{n}}}$$

We can also write $\hat{H} = \omega\,\hat{a}\,\hat{a}^\dagger - \hbar\omega/2$

$$\begin{aligned}\Rightarrow \quad \langle\psi_n|\,\hat{H}\,|\psi_n\rangle &= \omega\langle\psi_n|\hat{a}\,\hat{a}^\dagger|\psi_n\rangle - \frac{\hbar\omega}{2}\langle\psi_n|\psi_n\rangle \\ &= \hbar\omega\left(\frac{|c_n^+|^2}{\hbar} - \frac{1}{2}\right)\end{aligned}$$

$$\Rightarrow \quad \frac{|C_n^+|^2}{\hbar} = n+1 \quad \Rightarrow \quad C_n^+ = \sqrt{\hbar}\,\sqrt{n+1}$$

Therefore,

$$\boxed{\begin{aligned} \hat{a}\,|\Psi_n\rangle &= \sqrt{\hbar}\,\sqrt{n}\,|\Psi_{n-1}\rangle \\ \hat{a}^+\,|\Psi_n\rangle &= \sqrt{\hbar}\,\sqrt{n+1}\,|\Psi_{n+1}\rangle \end{aligned}}$$

We can define a number operator $\boxed{\hat{N} = \frac{\hat{a}^+\hat{a}}{\hbar}}$ that returns the number of the state:

$$\hat{N}\,|\Psi_n\rangle = \frac{\hat{a}^+\hat{a}}{\hbar}\,|\Psi_n\rangle = n\,|\Psi_n\rangle$$

The Hamiltonian is $\boxed{\hat{H} = \hbar\omega\left(\hat{N} + \frac{1}{2}\right)}$.

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:

$$\Delta x \Delta p \geqslant \hbar/2$$

(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 $\hat{B}$:

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

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

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

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

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

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

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

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, $\quad |z|^2 \geq \mathrm{Im}(z)^2$

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

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): $\quad \langle f|f\rangle\langle g|g\rangle \geq \left[\dfrac{\langle f|g\rangle - \langle g|f\rangle}{2i}\right]^2$

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

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 <u>inequalities</u> (1) and (2) to <u>equalities</u>, which means that $|f\rangle \propto |g\rangle$

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

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

for momentum - position

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

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

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 example 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)

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

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

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

(infinite matrix)

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

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

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

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

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

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

↑ 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!)

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

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

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

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

To find the eigenvectors, substitute back into (*)

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

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

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

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

$\Rightarrow$ the eigenstates are

energy

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

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

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

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

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

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

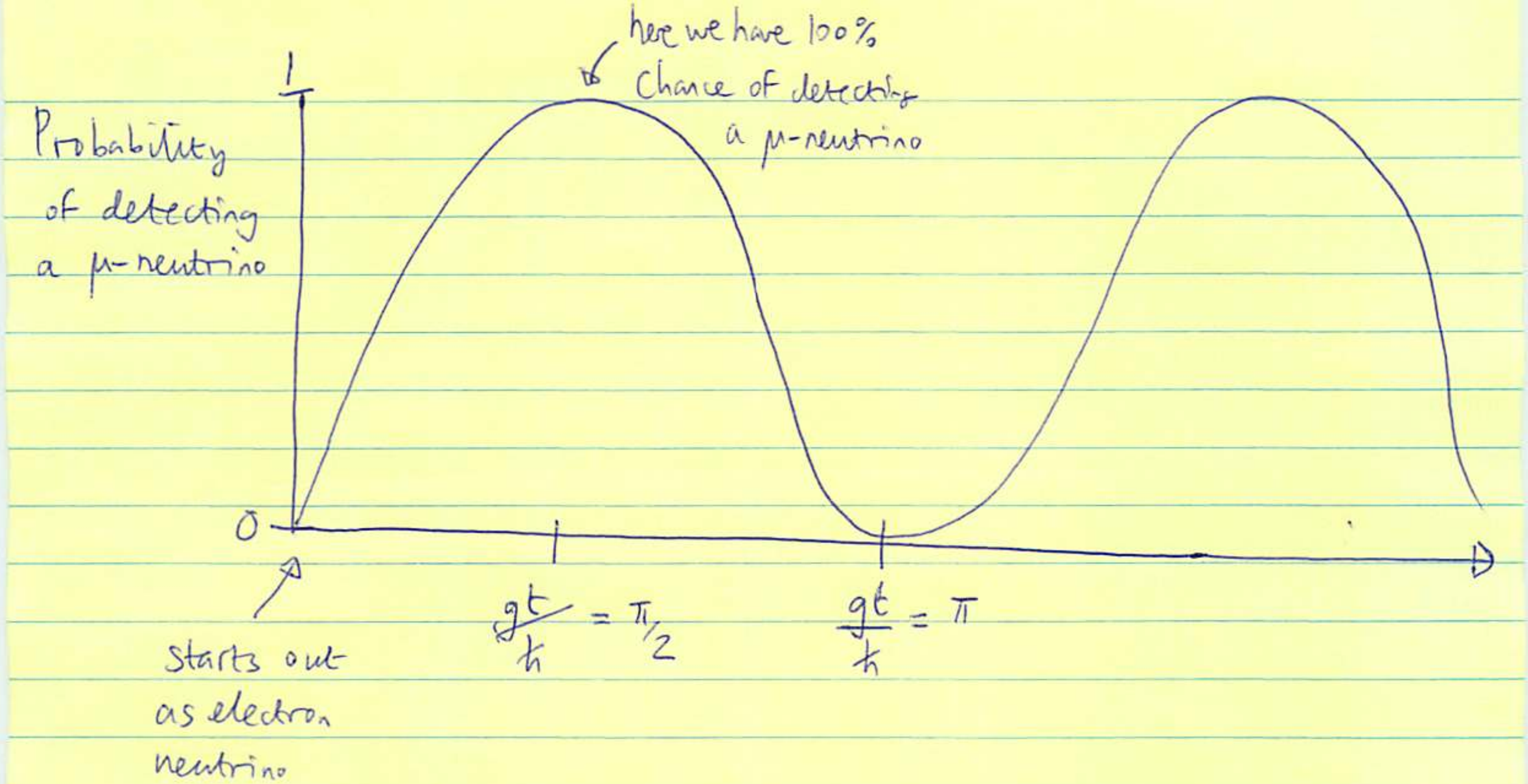
$$= \frac{1}{(\sqrt{2})^2} e^{-iht/\hbar}\begin{pmatrix} 2\cos gt/\hbar \\ -2i\sin gt/\hbar\end{pmatrix}$$

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

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

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

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



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.

Summary of Formalism

Let's try to summarize what we've been doing by considering a specific case of a particle in the ground state of a harmonic potential $V(x) \propto x^2$.

We write the state of the particle as $|\psi\rangle$. This contains all the information we know about the particle. For example the expectation value of any observable O is

$\langle\psi|\hat{O}|\psi\rangle$ where $\hat{O}$ is the operator corresponding to observable O.

The probability of measuring a specific value of O is

$|\langle O_1|\psi\rangle|^2$ where $|O\rangle$ is the eigenstate of $\hat{O}$ corresponding to the value $O = O_1$

eg. prob. the particle position is measured to be x

$|\langle x|\psi\rangle|^2$

momentum is measured to be p

$|\langle p|\psi\rangle|^2$

energy measured to be E_n

$|\langle\psi_n|\psi\rangle|^2$ where $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$
$|\psi_n\rangle$ is the nth eigenstate of $\hat{H}$.

If we want to write out the state $|\psi\rangle$ we can give, for example, the probability that the particle will be found at any position x, ie. we specify $\langle x|\psi\rangle = \psi(x)$ the wavefunction

(actually we're not specifying the probability $|\langle x|\psi\rangle|^2$ but the quantity $\langle x|\psi\rangle$. This is important because $\langle x|\psi\rangle$ has phase information (a piece $\propto e^{i\phi}$) that is lost when we take $|\langle x|\psi\rangle|^2 = \langle x|\psi\rangle^*\langle x|\psi\rangle$.)

or we could give $\langle p|\psi\rangle = A(p)$ momentum representation of the wavefunction.

or we could give $\langle \psi_n|\psi\rangle = c_n$ for all n.

We can think of all of these as coefficients in an expansion

$$
\begin{aligned}
|\psi\rangle &= \sum c_n |\psi_n\rangle \\
&= \int \psi(x)\,|x\rangle\,dx \\
&= \int A(p)\,|p\rangle\,dp
\end{aligned}
$$

They are also the coefficients of the vector $|\psi\rangle$ in Hilbert space. For example our particle in the ground state has $c_0 = 1$

$c_{n>0} = 0$

we can write its state as

$$|\psi\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$$

in the $|\psi_n\rangle$ basis.

A general operator $\hat{A}$ acts on $|\psi\rangle$ to give another vector $\hat{A}|\psi\rangle$, and we can think of this as a matrix operation

$$\begin{pmatrix} \quad \end{pmatrix} = \begin{pmatrix} & \hat{A} & \end{pmatrix}\begin{pmatrix} \psi \end{pmatrix}.$$

where the <u>matrix elements</u> of $\hat{A}$ are $\langle \psi_n | \hat{A} | \psi_m \rangle$ ← basis vectors

Consider the Hamiltonian operator acting on a general state

$$|\psi\rangle = \sum c_n |\psi_n\rangle = \begin{pmatrix} c_0 \\ c_1 \\ c_2 \\ \vdots \end{pmatrix}$$

$$\hat{H}|\psi\rangle = \sum c_n E_n |\psi_n\rangle$$

The matrix must be diagonal

$$\begin{pmatrix} E_0 & & & & & \\ & E_1 & & & 0 & \\ & & E_2 & & & \\ & & & E_3 & & \\ & 0 & & & E_4 & \\ & & & & & E_5 \ddots \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \\ c_2 \\ c_3 \\ \vdots \\ \cdot \end{pmatrix} = \begin{pmatrix} E_0 c_0 \\ E_1 c_1 \\ E_2 c_2 \\ \vdots \\ \vdots \end{pmatrix}$$

This is generally true — that the operator whose eigenstates are acting as the basis must be diagonal in that basis.

But other operators are not diagonal. We saw the example last time of the ladder operators.

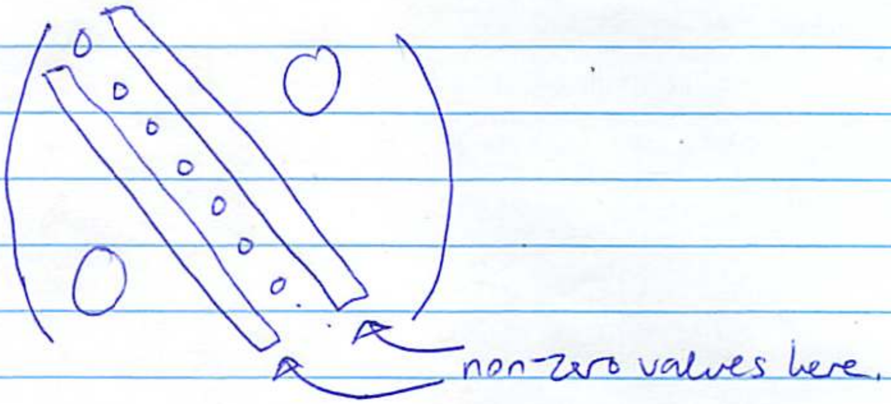
e.g. $\hat{a}^{\dagger} |\psi_n\rangle = \sqrt{n+1}\,\sqrt{\hbar}\,|\psi_{n+1}\rangle$

so that for our example $\hat{a}^{\dagger} |\psi_0\rangle = \sqrt{\hbar}\,|\psi_1\rangle$

$$\sqrt{\hbar}\begin{pmatrix} 0 & 0 & & & & & \\ \sqrt{1} & 0 & 0 & & 0 & & \\ & \sqrt{2} & 0 & 0 & & & \\ & & \sqrt{3} & 0 & 0 & & \\ & 0 & & \sqrt{4} & 0 & 0 & \\ & & & & \sqrt{5} & 0 & 0 \ddots \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \\ \sqrt{\hbar} \\ 0 \\ 0 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$$

Another example would be momentum. When we act $\hat{p}$ on the state $|\psi\rangle$ we get a different state back. You will show in HW 4 that $\hat{p}$ can be written as a combination of $\hat{a}$ and $\hat{a}^{\dagger}$ for the harmonic oscillator, so that $\hat{p}$ has matrix elements on both sides of the diagonal.

$\hat{p} =$



e.g. $\hat{p}|\psi_0\rangle \propto \frac{d}{dx}\psi_0(x) \propto \frac{d}{dx} e^{-x^2} \propto x e^{-x^2}$

$\propto |\psi_1\rangle$

So $\langle\psi_1|\hat{p}|\psi_0\rangle$ is non-vanishing
but $\langle\psi_0|\hat{p}|\psi_0\rangle = 0$.
(and in fact all $\langle\psi_m|\hat{p}|\psi_0\rangle$ for $m \neq 1$).

Similarly $\frac{d}{dx}\left(x e^{-x^2}\right)$ has two terms $\propto e^{-x^2}$
and $\propto e^{-x^2} x^2$

$\Rightarrow$ $\hat{p}|\psi_1\rangle$ has two terms $\propto |\psi_0\rangle$
and $\propto |\psi_2\rangle$

In the HW you will calculate this using only the ladder operators, without using the spatial representation of the wavefunction.

The last thing is to consider a case where we don't use the eigenstates of the Hamiltonian as the basis, but instead use some other basis. The Hamiltonian matrix will no longer be diagonal in this new basis, and the eigenstates of the Hamiltonian will no longer be simple vectors like $\begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$ or $\begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}$ but mixtures of the different basis vectors.

We can find the Hamiltonian eigenstates by diagonalising the matrix. Then any state can be decomposed into a sum of Hamiltonian eigenstates, each of which evolves in time as $e^{-iE_n t/\hbar}$. The solar neutrino problem gives an example of this approach.

Quantum Mechanics in 3D: Angular momentum, Hydrogen atom, and spin

We can straightforwardly extend what we've done to 3D. The wavefunction is now a function of $\underline{r} = (x, y, z)$

$$\psi(\underline{r}) = \psi(x, y, z)$$

and the probability density $|\psi|^2$ is now per unit volume, so that

$$|\psi(\underline{r})|^2 \, \underset{\uparrow \text{volume element}}{d^3\underline{r}}$$

is the probability of finding the particle in a small volume element $d^3\underline{r}$ located at $\underline{r}$.

Normalization is $$\int_{\text{all space}} |\psi|^2 \, d^3\underline{r} = 1$$

The momentum operator in each direction is

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

$$\hat{p}_y = \frac{\hbar}{i}\frac{\partial}{\partial y}$$

$$\hat{p}_z = \frac{\hbar}{i}\frac{\partial}{\partial z}$$

or as a vector $$\underline{\hat{p}} = \frac{\hbar}{i}\underline{\nabla}$$

The plane wave solution for a free particle is then (momentum eigenstate)

$$\psi \propto \exp(i\underline{k}.\underline{r} - i\omega t)$$

with $\underline{p} = \hbar \underline{k}$ and $E = \hbar\omega$

The Schrödinger equation is

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\,\Psi$$

With Hamiltonian

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

Laplacian

eg. $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ in Cartesian coordinates.

Previously we had $[\hat{p}, \hat{x}] = -i\hbar$
the same applies here but only when the position and momentum are in the same direction

$$[\hat{x}_i, \hat{p}_j] = i\hbar\,\delta_{ij}$$ where i and j represent $x, y,$ or z.

$$[\hat{x}_i, \hat{x}_j] = 0$$
$$[\hat{p}_i, \hat{p}_j] = 0$$

Momentum-position uncertainty relations apply but only in the same direction. It's okay to know the x-position precisely and the y-momentum precisely for example.

Rotations and angular momentum

We saw in HW3 that there is a link between translations and linear momentum. Similarly working in 3D opens up the possibility of rotations – these are linked to angular momentum.

Consider the rotation operator $\hat{R}(d\phi, \hat{\underline{k}})$ that rotates the wavefunction by an infinitesimal angle $d\phi$ around the vector $\hat{\underline{k}}$ which we'll take to be the unit vector in the z-direction.

Then $$\hat{R}(d\phi, \hat{\underline{k}})\,\psi(x,y,z) = \psi(x + y\,d\phi,\; y - x\,d\phi,\; z).$$

Now Taylor expand

$$\psi(x - y\,d\phi,\; y + x\,d\phi,\; z) = \psi(x,y,z) + (+y\,d\phi)\frac{\partial\psi}{\partial x} + (-x\,d\phi)\frac{\partial\psi}{\partial y} + \dots$$

$$= \psi(x,y,z) + (+y\,d\phi)\frac{i}{\hbar}\hat{p}_x\psi + (-x\,d\phi)\frac{i}{\hbar}\hat{p}_y\psi$$

$$= \left[1 + \frac{i\,d\phi}{\hbar}\underbrace{(-\hat{x}\hat{p}_y + \hat{y}\hat{p}_x)}\right]\psi$$

this is the z-component of angular momentum $\underline{L} = \underline{r} \times \underline{p}$

$$L_z = x p_y - y p_x$$

$\Rightarrow$ angular momentum operator $\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$

and $$\hat{R}(d\phi, \underline{\hat{k}}) = 1 - \frac{i}{\hbar}\hat{L}_z \, d\phi$$

If the Hamiltonian is invariant under rotation about $\underline{\hat{k}}$, then $\hat{R}$ and $\hat{H}$ commute $\Rightarrow$ $\hat{L}_z$ and $\hat{H}$ commute $\Rightarrow$ states of definite energy are also states of definite z-angular momentum.

Commutation relations

One important difference from linear momentum is that the different components of angular momentum $\hat{L}_x, \hat{L}_y, \hat{L}_z$ do not commute.

This is because rotations <u>do not</u> commute! [Try it!] (whereas translations and therefore linear momentum in different directions <u>do</u> commute!)

It is straightforward to show that

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

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

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

The total angular momentum operator $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ <u>does</u> commute with $\hat{L}_z$ however:

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

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

Now use the identity from the homework:

$$[\hat{L}_x^2, \hat{L}_z] = \hat{L}_x[\hat{L}_x, \hat{L}_z] + [\hat{L}_x, \hat{L}_z]\hat{L}_x$$

$$= \hat{L}_x(-i\hbar)\hat{L}_y + (-i\hbar)\hat{L}_y\hat{L}_x$$

$$[\hat{L}_y^2, \hat{L}_z] = \hat{L}_y[\hat{L}_y, \hat{L}_z] + [\hat{L}_y, \hat{L}_z]\hat{L}_y$$

$$= \hat{L}_y \, i\hbar \, \hat{L}_x + i\hbar\hat{L}_x\hat{L}_y$$

these terms cancel when summed

$$\Rightarrow \quad \underline{[\hat{L}^2, \hat{L}_z] = 0}$$

Therefore an eigenstate of $\hat{L}_z$: $\hat{L}_z|\psi\rangle = m\hbar|\psi\rangle$
is also an eigenstate of $\hat{L}^2$: $\hat{L}^2|\psi\rangle = \lambda\hbar^2|\psi\rangle$

(the $\hbar$'s are there to get the units right, $\hbar$ has units of angular momentum)

Ladder operators for angular momentum

The operators $\hat{L}_+ = \hat{L}_x + i\hat{L}_y$

and $\hat{L}_- = \hat{L}_x - i\hat{L}_y$

are ladder operators. They have the following commutation relations with $\hat{L}_z$:

$$[\hat{L}_z, \hat{L}_+] = \hbar\hat{L}_+$$

$$[\hat{L}_z, \hat{L}_-] = -\hbar\hat{L}_-$$

Therefore $$\hat{L}_z \hat{L}_+ |\psi\rangle = \hat{L}_+ \underbrace{\hat{L}_z |\psi\rangle}_{m\hbar|\psi\rangle} + \hbar \hat{L}_+|\psi\rangle$$

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

$\Rightarrow$ if $|\psi\rangle$ is an eigenstate of $\hat{L}_z$ with eigenvalue $\hbar m$,

then $\hat{L}_+|\psi\rangle$ is an eigenstate with eigenvalue $(m+1)\hbar$.

Similarly $$\hat{L}_z \hat{L}_- |\psi\rangle = \hat{L}_- \hat{L}_z|\psi\rangle - \hbar \hat{L}_-|\psi\rangle$$

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

$\Rightarrow$ $\hat{L}_-|\psi\rangle$ is an eigenstate with eigenvalue $m-1$.

The spectrum of values of m

We've seen that eigenstates of $\hat{L}_z$ are also eigenstates of $\hat{L}^2$, so we can know the magnitude of the total angular momentum, and the size of one of the components (eg. z-component given by $\hat{L}_z$) simultaneously.

What is the largest allowed value of m?

$\langle\psi| \hat{L}^2 - \hat{L}_z^2 |\psi\rangle$ must be > 0 (Lz cannot exceed $|\underline{L}|$)

$\Rightarrow \lambda - m^2 > 0$

or $m^2 < \lambda$.

If the maximum value of m is $m = \ell$
then

$$\hat{L}_+ |\ell\rangle = 0 \qquad -(1)$$

because we can't create the state $|\ell+1\rangle$ because $m = \ell+1$ is not allowed.

Now consider

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

Act this on the state $|\ell\rangle$:

$$\hat{L}_-\hat{L}_+|\ell\rangle = (\lambda - \ell^2 - \ell)\hbar^2|\ell\rangle$$

but from (1) we know that this should also $= 0$

$$\Rightarrow \quad \underline{\lambda = \ell(\ell+1)} \qquad -(3)$$

Similarly if the minimum value of m is $m = \ell'$
then

$$\hat{L}_- |\ell'\rangle = 0$$

because we can't lower any further

Try

$$\begin{aligned} \hat{L}_+\hat{L}_- |\ell'\rangle &= 0 \\ &= (\hat{L}^2 - \hat{L}_z^2 + \hbar\hat{L}_z)|\ell'\rangle \\ &= (\lambda - \ell'^2 + \ell')\hbar^2 |\ell'\rangle \end{aligned}$$

$$\Rightarrow \quad \underline{\lambda = \ell'(\ell'-1)} \quad — (4)$$

Now setting (3) = (4) $\Rightarrow$ $\quad \ell(\ell+1) = \ell'(\ell'-1)$

$\Rightarrow$ either $\ell' = -\ell$

$\ell' = \ell + 1$

but this doesn't work because ℓ is the maximum value of m so we need $\ell' < \ell$!

$\Rightarrow$

$$\boxed{\begin{array}{ll} \text{the minimum value of } m \text{ is} & -\ell \\ \text{the maximum value of } m \text{ is} & \ell \\ \text{the eigenvalue of } \hat{L}^2 \text{ is} & \ell(\ell+1) \end{array}}$$

So we label the states with the quantum numbers ℓ, m

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

$$\hat{L}_z \, | \ell, m \rangle = m \hbar \, | \ell, m \rangle$$

m has allowed values $m = \underbrace{-\ell, -\ell+1, -\ell+2 \cdots \ell-2, \ell-1, \ell}_{2\ell+1 \text{ states}}$

eg. $\ell = 0$ $\quad m = 0$ $\quad$ 1 state

$\ell = 1$ $\quad m = -1, 0, 1$ $\quad$ 3 states

$\ell = 2$ $\quad m = -2, -1, 0, 1, 2$ $\quad$ 5 states

and so on.

The angular momentum eigenfunctions in spherical coordinates

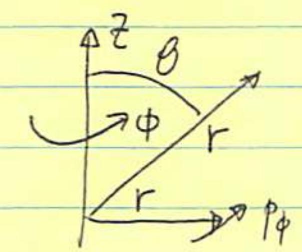
We will be interested in solving the Schrödinger equation in spherical coordinates, eg. for an electron in an atom. What are the eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ in spherical coordinates?

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

where in spherical coordinates

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

First consider the z-component of angular momentum.



$$\hat{L}_z = \underbrace{(r\sin\theta)}_{\substack{\text{distance from}\\ z\text{-axis}}}\underbrace{\left(\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\frac{\hbar}{i}}_{p_\phi}$$

or

$$\boxed{\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}}$$

The operator $\hat{L}^2$ is more complicated to calculate since we also need $\hat{L}_x^2$ and $\hat{L}_y^2$. See Griffiths p 168 for details of the algebra. The result is

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

What do the eigenfunctions $\psi_\ell^m(r,\theta,\phi)$ look like?

The simplest thing to consider is $\hat{L}_z$

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

$$\Rightarrow \quad \underline{\psi_\ell^m \propto e^{im\phi}}$$

The ϕ dependence of the eigenfunction is simple.

For the θ-dependence, we must solve

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

or

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

or since we know the ϕ dependence,

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\psi}{\partial\theta}\right) + \ell(\ell+1)\psi - \frac{m^2}{\sin^2\theta}\psi = 0$$

In terms of $\mu = \cos\theta$, this is

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

The <u>associated Legendre polynomials</u> $P_\ell^m(\mu)$ satisfy this equation.

The first few P_ℓ^m's are given in Table 4.2 of Griffiths (p 138)

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).

$P_0^0 = 1$

$P_1^1 = \sin\theta$

$P_1^0 = \cos\theta$

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

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

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

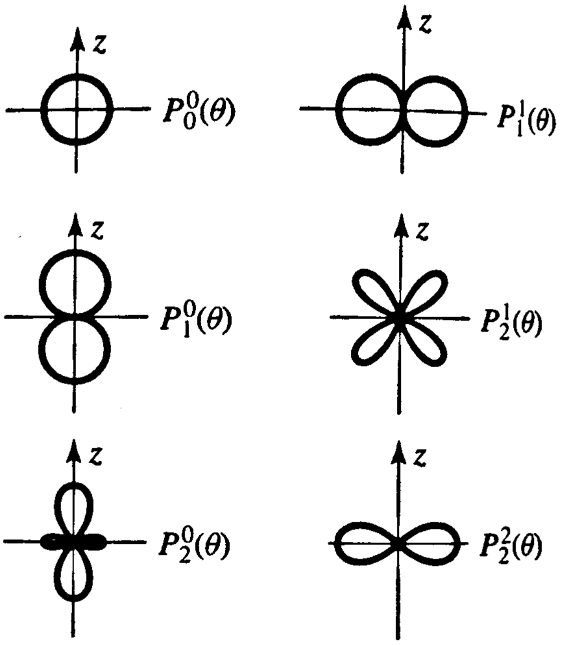
$P_3^3 = 15\sin\theta(1 - \cos^2\theta)$

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

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

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

(a)



(b)

We therefore see that we can write the eigenfunctions as

$$\boxed{\psi_\ell^m(r,\theta,\phi) = \underset{\substack{\uparrow \\ \text{normalization} \\ \text{constant}}}{A}\, \underset{\substack{\uparrow \\ \text{arbitrary radial function}}}{f(r)}\, P_\ell^m(\cos\theta)\, e^{im\phi}}$$

(a seperable solution)

The combination $P_\ell^m(\cos\theta)\, e^{im\phi}$ is a <u>spherical harmonic</u> $Y_\ell^m(\theta,\phi)$

so we can also write

$$\boxed{\psi_\ell^m(r,\theta,\phi) = \underset{\substack{\uparrow \\ \text{a different} \\ \text{normalization constant}}}{A'}\, f(r)\, Y_\ell^m(\theta,\phi)}$$

The $Y_\ell^m(\theta,\phi)$ functions are normalized such that

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

Table 4.3 of Griffiths gives the first few Y_ℓ^m's. (See p 139).

I've also included a Figure showing the shapes of the Y_ℓ^m's.

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

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

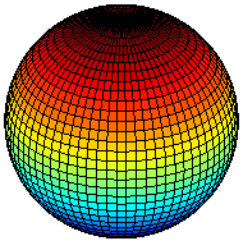
The normalized angular wave functions[8] are called **spherical harmonics:**

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

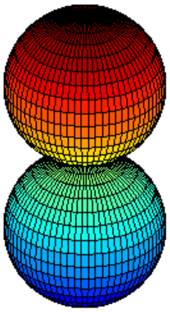
where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. As we shall prove later on, they are automatically orthogonal, so

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

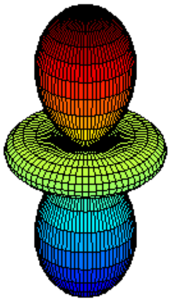
$Y_0^0 = 1$



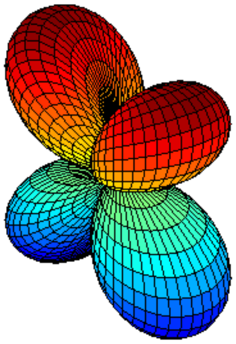
$Y_1^0 = \cos\theta$



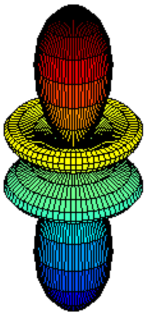
$Y_2^0 = 3\cos^2\theta\text{-}1$



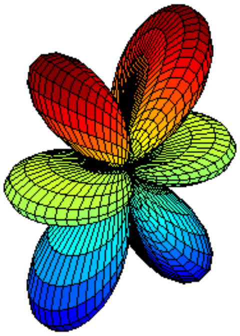
${}^{s}Y_2^1 = \cos\theta \sin\theta \sin\phi$



$Y_3^0 = 5\cos^3\theta\text{-}3\cos\theta$



${}^{c}Y_3^1 = (5\cos^2\theta\text{-}1)\sin\theta \cos\phi$



The Schrödinger equation in spherical coordinates

Let's go back to the Schrödinger equation in 3D

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

where we assume that the potential depends only on the distance to the origin r, and not on θ or ϕ. In other words the potential is spherically symmetric.

The Laplacian is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right).$$

If you look at the angular terms you should see something familiar! The angular terms are the same as the expression for $\hat{L}^2$!

So we can write

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) - \frac{\hat{L}^2\psi}{r^2\hbar^2}$$

This tells us that the solution must be of the form

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

where $$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{df}{dr}\right) - \frac{\hbar^2\ell(\ell+1)f}{r^2\hbar^2}\right) + V(r)f = Ef$$

or $$\boxed{-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{df}{dr}\right)+\left[V(r)+\frac{l(l+1)\hbar^2}{2mr^2}\right]f=Ef}$$

We see that

1) the eigenfunctions of the Hamiltonian are also eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$. Therefore the solutions will be labelled by l and m (as well as a radial quantum number that will come from solving the equation for $f(r)$).

2) the equation for $f(r)$ is independent of m – therefore the energies of the eigenstates with different m but the same n and l will be the same – (degenerate states).

We can simplify further if we define a new function $g(r) = rf(r)$

$$\cancel{-\frac{\hbar^2}{2m}\frac{d^2f}{dr^2}} + \quad r\frac{dg}{dr} = rf + r^2\frac{df}{dr} = g + r^2\frac{df}{dr}$$

then $$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{df}{dr}\right) = \frac{1}{r^2}\frac{d}{dr}\left(r\frac{dg}{dr}-g\right)$$
$$= \frac{1}{r}\frac{d^2g}{dr^2}$$

$$\Rightarrow \quad -\frac{\hbar^2}{2m}\frac{d^2g(r)}{dr^2}+\left[V(r)+\frac{\hbar^2 l(l+1)}{2mr^2}\right]g(r) = E\,g(r)$$

This is the same form as the 1D time-independent Schrödinger equation, with an effective potential

$$V_{\text{eff}}(r) = V(r) + \underbrace{\frac{\hbar^2}{2mr^2}\,\ell(\ell+1)}_{\text{"centrifugal term"}}$$

So for a given potential $V(r)$ we can solve for $g(r)$ just as we have been doing for 1D. Then the solution is

$$\psi(r,\theta,\phi) = \frac{g(r)}{r}\,Y_\ell^m(\theta,\phi) \qquad \text{with energy } E_{n,\ell}$$

Boundary conditions

For the integration of $g(r)$, we need boundary conditions. At large distances $r \to \infty$ we need ~~g~~ $\psi \to 0$ for bound states. If the integral

$$\int d^3\underline{r}\,|\psi|^2 \;\propto\; \int r^2 dr\,|\psi|^2$$

is to converge, ψ must go to zero faster than $\frac{1}{r}$

and so we need $\underline{g(r) \to 0 \quad \text{as} \quad r \to \infty}$.

What about at the origin? As $r \to 0$ the centrifugal term dominates $\left(\propto 1/r^2\right)$ so that

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

try a powerlaw solution $g \propto r^n \Rightarrow n(n-1) = \ell(\ell+1)$

$\Rightarrow$ either $g \propto r^{-\ell}$ or $\boxed{g \propto r^{\ell+1}}$

↑ this one diverges as $r \to 0$

↖ this is the one we want

The Hydrogen atom

The electron in a hydrogen atom experiences a potential

$$V(r) = \frac{-e^2}{4\pi\varepsilon_0 r}$$

so that

$$-\frac{\hbar^2}{2m}\frac{d^2 g}{dr^2} + \left(\frac{-e^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2}{2mr^2}\ell(\ell+1)\right) g = E g$$

(We write m here for the electron mass – it should actually be the reduced mass $\mu = \frac{m_e m_p}{m_p + m_e}$ but since $m_p \simeq 1800\, m_e \gg m_e$ it's a good approximation to assume the proton remains at rest at the origin).

We'll look for a numerical solution to this equation. First, let's try to make it dimensionless – this will reveal the natural size and energy scales of the atom.

A useful quantity is the fine structure constant

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} = \frac{1}{137}$$

define $\tilde{E} = \frac{E}{\frac{1}{2}\alpha^2 mc^2}$

where $\frac{1}{2}\alpha^2 mc^2 = \frac{511\text{ keV}}{2\times(137)^2} = 13.6\text{ eV}$

Then

$$\frac{-\frac{\hbar^2}{2m} g''}{\frac{1}{2}\alpha^2 mc^2} + \left(\frac{-\frac{\alpha\hbar c}{r} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}}{\frac{1}{2}\alpha^2 mc^2} \right) g = \tilde{E} g$$

$$-\frac{\hbar^2}{m^2c^2\alpha^2} g'' + g\left(\frac{-2\hbar}{\alpha mcr} + \frac{\ell(\ell+1)\hbar^2}{\alpha^2 m^2 c^2 r^2} \right) = \tilde{E} g$$

Now introduce a lengthscale

$$\tilde{r} = r\left(\frac{mc\alpha}{\hbar}\right)$$

where $\frac{\hbar}{mc\alpha} = 5.3 \times 10^{-11}\,\text{m} = 0.53\,\text{Å} = a_0$ Bohr radius

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

This is the equation we will solve numerically, but notice that we see already the natural energy scale

$$\frac{1}{2}\alpha^2 mc^2 = 13.6\,\text{eV}$$

and lengthscale $a_0 = \frac{\hbar}{mc\alpha} = 0.53\,\text{Å}$.

Numerical solution for H radial wavefunctions

define $\tilde{f} = \frac{dg}{d\tilde{r}}$

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

we integrate outwards starting from $\tilde{r} = \Delta\tilde{r} \ll 1$

at $r = 0$ we need $g \propto r^{\ell+1}$

or $\frac{dg}{dr} = (\ell+1)\frac{g}{r}$

or $\tilde{f} = \frac{(\ell+1)g}{\tilde{r}}$ at $\tilde{r} = \Delta\tilde{r}$

So we start the integration at $\tilde{r} = \Delta\tilde{r}$

with $g = 1$

$\tilde{f} = \frac{(\ell+1)}{\Delta\tilde{r}}$

We then look for values of $\tilde{E}$ that give $g \to 0$ as $\tilde{r} \to \infty$.

We'll run the MATLAB code in class.

Properties of the H atom wavefunctions

The radial wavefunction depends on n and ℓ, so we can write it as $f_{n\ell}(r)$ where the total wavefunction is

$$\psi_{n\ell m}(r,\theta,\phi) = f_{n\ell}(r)\, Y_\ell^m(\theta,\phi)$$

Some points to note are:

1) the energy levels depend only on n, not on ℓ or m.

$$E_n = -\frac{13.6\,\mathrm{eV}}{n^2}$$

It is not obvious in advance that the energies would be independent of ℓ, since ℓ enters into the centrifugal term in the Schrödinger equation. It is a special property of the $1/r$ potential. (Similarly you may recall that in classical mechanics the $1/r$ potential is special because the orbits close on themselves, this is not the case for other potentials. There is a similar degeneracy in the sense that orbits with the same semi-major axis a have the same energy, no matter what their angular momentum or eccentricity.

$$E = -GMm/2a \qquad L = m\sqrt{GMa(1-e^2)} \qquad).$$

2) The allowed values of ℓ are $\ell = 0, 1, \ldots n-1$

Therefore $\ell = 0$ is the only possible value for $n=1$ (s-orbital)
$\ell = 0, 1$ $n=2$ (s and p)
$\ell = 0, 1, 2$ $n=3$ (s, p, d)

3) The total degeneracy of level n is $\displaystyle\sum_{\ell=0}^{n-1} (2\ell+1) = n^2$

$\nearrow$ sum over allowed values of ℓ

$\uparrow$ there are $2\ell+1$ values of m for each ℓ

4) The radial wavefunctions have $n-\ell-1$ nodes (see Figure on next page).

The first few are:

$$f_{10}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0}$$

$$f_{20}(r) = \frac{2}{(2a_0)^{3/2}} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$

$$f_{21}(r) = \frac{1}{\sqrt{3}} \frac{1}{(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$$

(notice that $f \propto r^\ell$ at $r=0$ as expected – see p18).

(general form is polynomial × exponential)

5) The angular part of the wavefunction is normalized such that

$$\int |Y_m^\ell|^2 \sin\theta \, d\theta \, d\phi = 1 \qquad \text{(see p11)}$$

$\Rightarrow$ the probability of finding an electron between r and r+dr is

$$\int |\psi|^2 r^2 \sin\theta \, d\theta \, d\phi \, dr$$

$$= \underline{r^2 |f_{n\ell}(r)|^2 dr} \, .$$

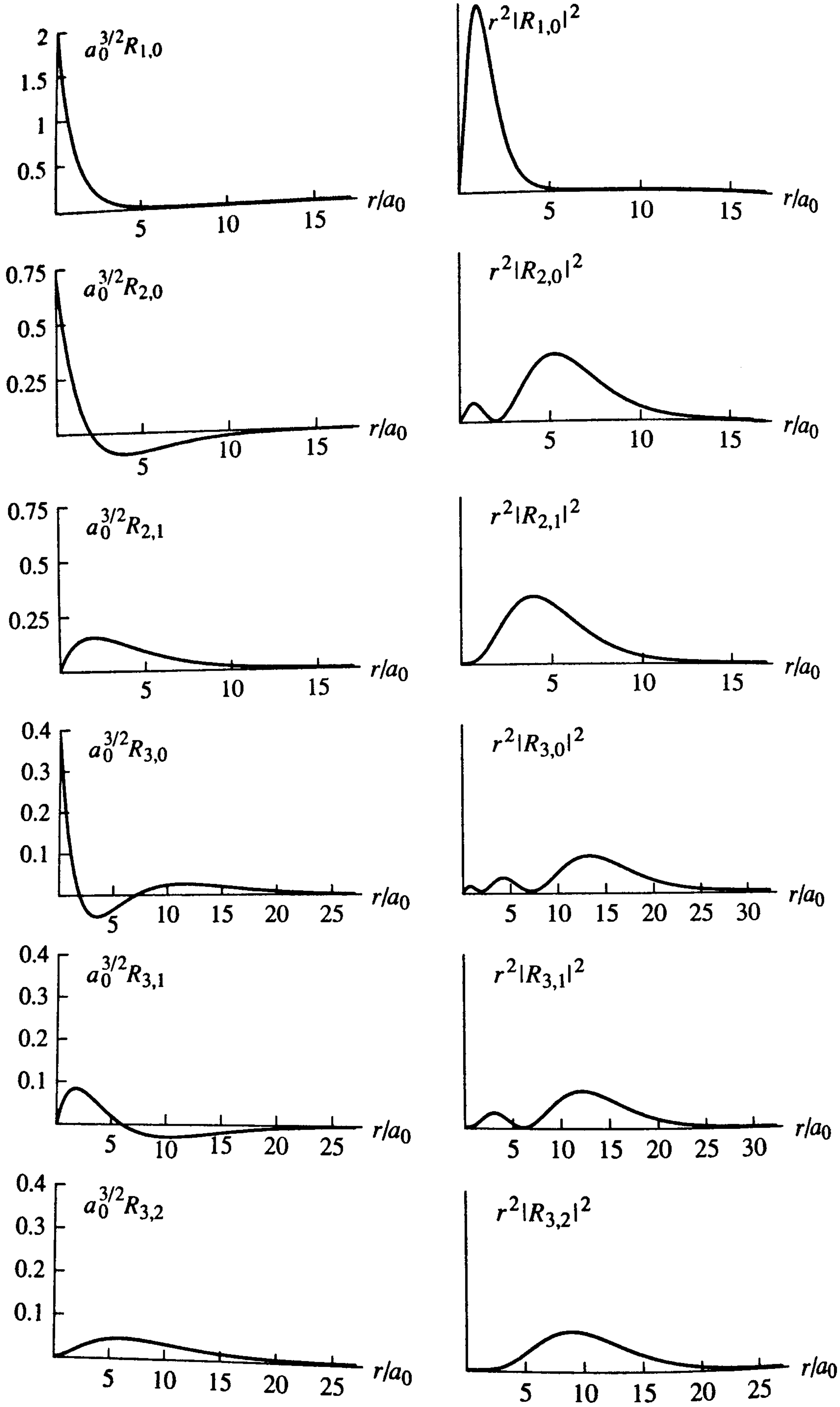
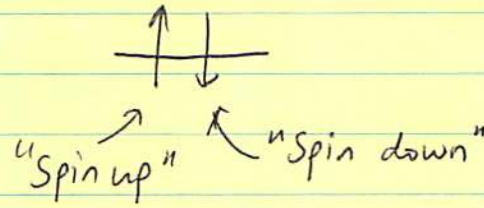


FIGURE 10.5

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).

Spin

You may already know that each level of the atom (ie. each state $|n\,l\,m\rangle$) can be occupied by two electrons



Spin is a fundamental property of a particle that obeys the rules of angular momentum in quantum mechanics. A particle with spin s has states $|s\,m\rangle$

$$\text{where} \quad m = -s \ldots +s$$

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

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

The number of states is $2s+1 \Rightarrow$ an electron has $s = \frac{1}{2}$

it is a "spin-$\frac{1}{2}$" particle

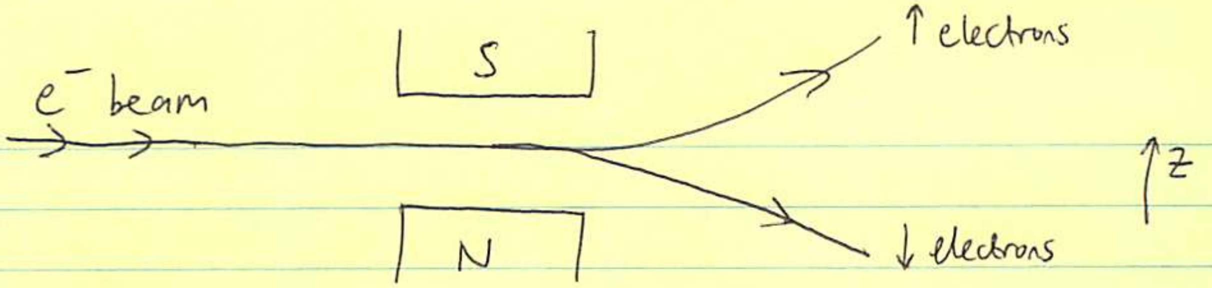
the two states are $|\uparrow\rangle = |\tfrac{1}{2}\ \tfrac{1}{2}\rangle \quad s=\tfrac{1}{2}\ \ m=\tfrac{1}{2}$

$|\downarrow\rangle = |\tfrac{1}{2}\ -\tfrac{1}{2}\rangle \quad s=\tfrac{1}{2}\ \ m=-\tfrac{1}{2}$

$$\hat{S}^2|\uparrow\rangle = \frac{3}{4}\hbar^2|\uparrow\rangle$$

and the same for $\hat{S}^2|\downarrow\rangle$.

The quantized nature of spin is also revealed by the classic Stern-Gerlach experiment. An electron beam passing through an inhomogeneous magnetic field splits into two beams with equal and opposite deflections.



The force on an electron is $F_z = \mu_z \frac{\partial B}{\partial z}$

and the magnetic moment μ_z is related to the spin

$$\boxed{\mu_z = \gamma S_z}$$

The beam is split in two, showing that μ_z and therefore S_z takes only two discrete values (either $+\hbar/2$ or $-\hbar/2$).

[From classical electromagnetism it should make sense that rotational motion of a charge gives rise to a magnetic dipole moment. E.g. a charge moving in a circle

$$I = q\frac{\omega}{2\pi} \qquad \mu = I\pi a^2 = \frac{qa^2\omega}{2}$$

$$\Rightarrow \quad \underline{\mu = \left(\frac{q}{2m}\right)L}$$

The same kind of relation carries over to particle spin — although it doesn't make sense to think of the rotation of a point particle.]

Spin $\frac{1}{2}$ and Pauli matrices

If we use the states $|\uparrow\rangle$ and $|\downarrow\rangle$ as a basis, then

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

$$\hat{S}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \frac{\hbar}{2}$$

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

[To show this, compute the matrix elements, eg. $\langle\uparrow|\hat{S}^2|\uparrow\rangle$

$$= \frac{3}{4}\hbar^2 \langle\uparrow|\uparrow\rangle$$

$$= \tfrac{3}{4}\hbar^2$$]

Just as for orbital angular momentum, we can define ladder operators

$$\hat{S}_+ |s\ m\rangle = \sqrt{s(s+1)-m(m+1)}\ \hbar\ |s, m+1\rangle$$

$$\hat{S}_- |s\ m\rangle = \sqrt{s(s+1)-m(m-1)}\ \hbar\ |s, m-1\rangle$$

$$\Rightarrow \quad \hat{S}_+|\downarrow\rangle = \hbar\,|\uparrow\rangle$$

$$\hat{S}_-|\uparrow\rangle = \hbar\,|\downarrow\rangle$$

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

[eg. $\hat{S}_+|\downarrow\rangle$ can be written $\hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \hbar \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

$$= \hbar\,|\uparrow\rangle$$

✓]

Using the ladder operators, we can write the $\hat{S}_x$ and $\hat{S}_y$ operators

$$\hat{S}_x = \frac{1}{2}(\hat{S}_+ + \hat{S}_-) \qquad \hat{S}_y = -\frac{i}{2}(\hat{S}_+ - \hat{S}_-)$$

(since $\hat{S}_+ = \hat{S}_x + i\hat{S}_y$
$\hat{S}_- = \hat{S}_x - i\hat{S}_y$)

or in the basis of eigenstates of $\hat{S}_z$ which we are using

$$\hat{S}_x = \frac{1}{2}\hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} + \frac{1}{2}\hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

$$= \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

Similarly $\hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$

These matrices without the $\hbar/2$ factor are known as the <u>Pauli spin matrices</u>

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

eg. check commutation relation: $[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z$

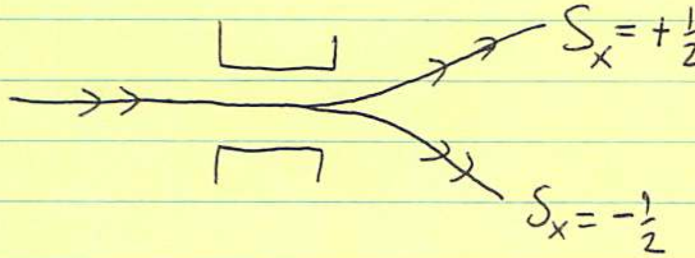
$$\sigma_x\sigma_y - \sigma_y\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ +i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$$

$$= 2i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = 2i\,\sigma_z \quad ✓$$

Measurement of spin in an orthogonal direction

Imagine a Stern Gerlach experiment that first splits the beam in the x-direction



$\longleftarrow$ now take this beam and split in z-direction – what do we get?

To answer this question, we need to write the state $|S_x = +\frac{1}{2}\rangle$ in terms of $|\uparrow\rangle$ and $|\downarrow\rangle$ (the $\hat{S}_z$ eigenstates).

To find the eigenstates of $\hat{S}_x$ in the $\hat{S}_z$ basis, we diagonalize the matrix.

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\det\begin{pmatrix} -\lambda & \hbar/2 \\ \hbar/2 & -\lambda \end{pmatrix} = 0 \quad \Rightarrow \quad \lambda^2 = \hbar^2/4$$

$$\Rightarrow \text{ eigenvalues } \pm \hbar/2$$

as expected

To find the eigenstates:

$$\lambda = +\frac{\hbar}{2}: \quad \begin{pmatrix} -\hbar/2 & \hbar/2 \\ \hbar/2 & -\hbar/2 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = 0 \quad \Rightarrow \quad \begin{matrix} -a+b=0 \\ a-b=0 \end{matrix} \quad \Rightarrow \quad a = b$$

$$\Rightarrow \quad \underline{|S_x = +1/2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}} = \frac{1}{\sqrt{2}}\left(|\uparrow\rangle + |\downarrow\rangle\right)$$

Similarly $\lambda = -\hbar/2 \Rightarrow$ $|S_x = -\tfrac{1}{2}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}}\left(|\uparrow\rangle - |\downarrow\rangle\right)$

This answers our question. If we take the state $|S_x = +\tfrac{1}{2}\rangle$ and measure S_z, then

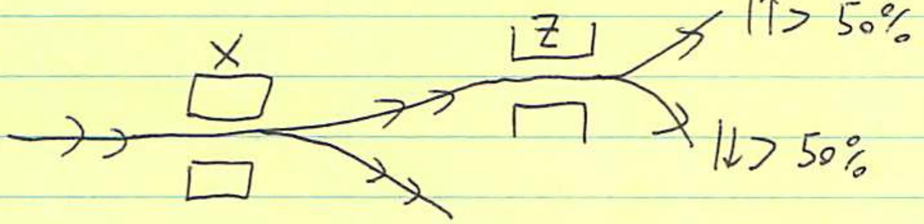
Probability of measuring $S_z = +\hbar/2$ $= \left|\langle\uparrow|S_x = +\tfrac{1}{2}\rangle\right|^2$

$= \frac{1}{2}$

Probability of measuring $S_z = -\hbar/2$ $= \left|\langle\downarrow|S_x = +\tfrac{1}{2}\rangle\right|^2$

$= \frac{1}{2}$

So the beam is split 50/50



Addition of angular momentum : two electrons

Consider two electrons. We write the possible spin states as

$$|\uparrow\uparrow\rangle = |\uparrow\rangle|\uparrow\rangle$$
$$|\uparrow\downarrow\rangle = |\uparrow\rangle|\downarrow\rangle$$
$$|\downarrow\uparrow\rangle = |\downarrow\rangle|\uparrow\rangle$$
$$|\downarrow\downarrow\rangle = |\downarrow\rangle|\downarrow\rangle$$

spin of electron 2

spin of electron 1

These are all eigenstates of the total S_z operator

$$\hat{S}_z = \hat{S}_{z,1} + \hat{S}_{z,2}$$

e.g.
$$\begin{aligned}\hat{S}_z|\uparrow\uparrow\rangle &= (\hat{S}_{z,1} + \hat{S}_{z,2})|\uparrow\rangle|\uparrow\rangle \\ &= \frac{\hbar}{2}|\uparrow\rangle|\uparrow\rangle + \frac{\hbar}{2}|\uparrow\rangle|\uparrow\rangle \\ &= \hbar|\uparrow\rangle|\uparrow\rangle \\ &= \hbar|\uparrow\uparrow\rangle\end{aligned}$$

$\Rightarrow$

state	$\langle S_z\rangle/\hbar$
$\lvert\uparrow\uparrow\rangle$	1
$\lvert\uparrow\downarrow\rangle$	0
$\lvert\downarrow\uparrow\rangle$	0
$\lvert\downarrow\downarrow\rangle$	-1

Now, what about the total angular momentum of the two electrons? The fact that there are $m=-1$, 0 and +1 states suggest that we have definitely a spin 1 system:

Where for $s = 1$ we are allowed to have

$m = +1 \longrightarrow$ eigenstate here must be $|\uparrow\uparrow\rangle$

$m = -1 \longrightarrow$ eigenstate here must be $|\downarrow\downarrow\rangle$

$m = 0 \rightarrow$ what is the eigenstate here? Any linear combination of $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ would work.

Two ways to approach this:

1) <u>look for eigenstates of $\hat{S}^2$</u>

$$\hat{S}^2 = \left(\hat{\underline{S}}_1 + \hat{\underline{S}}_2\right)^2 = S_1^2 + S_2^2 + 2\hat{\underline{S}}_1 . \hat{S}_2$$

$$\underline{S}_1 . \underline{S}_2 = S_{1x} S_{2x} + S_{1y} S_{2y} + S_{1z} S_{2z}$$

$$= \frac{1}{4}\left(S_{1+} + S_{1-}\right)\left(S_{2+} + S_{2-}\right)$$

(using S_x and S_y written in terms of ladder operators)

$$- \frac{1}{4}\left(S_{1+} - S_{1-}\right)\left(S_{2+} - S_{2-}\right)$$

$$+ S_{1z} S_{2z}$$

$$= \frac{1}{2}\left(S_{1+} S_{2-} + S_{1-} S_{2+}\right) + S_{1z} S_{2z}$$

$$\Rightarrow \boxed{S^2 = S_1^2 + S_2^2 + S_{1+} S_{2-} + S_{1-} S_{2+} + 2 S_{1z} S_{2z}}$$

Now check each eigenstate

$$\hat{S}^2 |\uparrow\uparrow\rangle = \hbar^2\left(\frac{3}{4} + \frac{3}{4} + (0) + (0) + 2\,\frac{1}{2}\,\frac{1}{2}\right)|\uparrow\uparrow\rangle$$

$$= 2\hbar^2 |\uparrow\uparrow\rangle$$

$$\Rightarrow s(s+1) = 2 \Rightarrow \underline{s = 1}$$

$$\hat{S}^2 |\downarrow\downarrow\rangle = \hbar^2\left(\frac{3}{4}+\frac{3}{4}\right)|\downarrow\downarrow\rangle + (0) + (0) + 2\left(-\frac{1}{2}\cdot-\frac{1}{2}\right)|\downarrow\downarrow\rangle$$

$$= 2\hbar^2 |\downarrow\downarrow\rangle$$

So $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ are eigenstates of $\hat{S}^2$ with $s=1$.

Next, try $\hat{S}^2|\uparrow\downarrow\rangle = \left(\frac{3}{4}+\frac{3}{4}\right)\hbar^2|\uparrow\downarrow\rangle + (0)$

$$+\hbar^2|\downarrow\uparrow\rangle + 2\left(\frac{1}{2}\cdot\frac{-1}{2}\right)|\uparrow\downarrow\rangle$$

$$= \hbar^2|\uparrow\downarrow\rangle + \hbar^2|\downarrow\uparrow\rangle \qquad -(1)$$

So this is not an eigenstate of $\hat{S}^2$!

Similarly

$$\hat{S}^2|\downarrow\uparrow\rangle = \hbar^2|\downarrow\uparrow\rangle + \hbar^2|\uparrow\downarrow\rangle \qquad -(2)$$

not an eigenstate either!

But if we add (1) and (2):

$$\hat{S}^2\underbrace{\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)}_{\text{this is an eigenstate with } s=1} = 2\hbar^2\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)$$

Subtract (1) and (2):

$$\hat{S}^2\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) = 0 \qquad \Rightarrow \quad s=0$$

So we see that the joint eigenstates of $\hat{S}^2$ and $\hat{S}_z$ for the two particles are

$$\left.\begin{array}{lll} |\uparrow\uparrow\rangle & s=1 & m=1 \\ \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle+|\downarrow\uparrow\rangle\right) & s=1 & m=0 \\ |\downarrow\downarrow\rangle & s=1 & m=-1 \end{array}\right\} \text{spin } \underline{\text{triplet}}$$

$$\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle\right) \quad s=0 \quad m=0 \qquad \text{spin } \underline{\text{singlet}}$$

2) We can also recover these states with the ladder operators:

apply $\hat{S}_- = \hat{S}_{-,1} + \hat{S}_{-,2}$ to $|\uparrow\uparrow\rangle$:

$$\hat{S}_-|\uparrow\uparrow\rangle = \left(\hat{S}_{-,1}+\hat{S}_{-,2}\right)|\uparrow\rangle_1|\uparrow\rangle_2$$

$$= |\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle$$

$$\Rightarrow \text{ if } |\uparrow\uparrow\rangle = |1\ 1\rangle \left(= |s\ m\rangle\right)$$

$$\text{then } |1\ 0\rangle = \underset{\uparrow \text{(normalization factor)}}{\frac{1}{\sqrt{2}}}\left(|\downarrow\uparrow\rangle+|\uparrow\downarrow\rangle\right)$$

You can check that

$\hat{S}_-|1\ 0\rangle$ then gives $|1\ -1\rangle = |\downarrow\downarrow\rangle$ as needed.

So this gives us the triplet of $s=1$ states. To find the remaining state, we look for the linear combination of $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ that is orthogonal to the $|1\ 0\rangle$ state — this gives the

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

Addition of angular momenta: general case

In general, if we add two spins s_1 and s_2 the possible total spins are

$$s_1+s_2,\ s_1+s_2-1,\ \ldots\ |s_2-s_1|$$

The same applies to addition of spin and angular momentum, eg. if we ignore the nucleus the possible spins of a single electron atom range from

$$l+s \quad \text{to} \quad |l-s|$$

In general, when adding two spins the states can be written as a sum of the single particle states

$$|s\ m\rangle = \sum_{m=m_1+m_2} C^{s_1,s_2,s}_{m_1,m_2,m}\ |s_1\ m_1\rangle|s_2\ m_2\rangle$$

(eg. we had $|1\ 0\rangle = \frac{1}{\sqrt{2}}|\uparrow\rangle|\downarrow\rangle + \frac{1}{\sqrt{2}}|\downarrow\rangle|\uparrow\rangle$

$= \frac{1}{\sqrt{2}}|\tfrac{1}{2}\ \tfrac{1}{2}\rangle|\tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle + \frac{1}{\sqrt{2}}|\tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle|\tfrac{1}{2}\ \tfrac{1}{2}\rangle$)

so that $C^{\frac{1}{2}\ \frac{1}{2}\ 1}_{\frac{1}{2}\ -\frac{1}{2}\ 0} = \frac{1}{\sqrt{2}}$

The coefficients $C^{s_1,s_2,s}_{m_1,m_2,m}$ is a Clebsch-Gordan coefficient which you can look up in tables.

Identical particles

In classical mechanics, two electrons are distinguishable in the sense that we can follow the trajectories of each one. In quantum mechanics, all we can do is write a two particle wavefunction

$$\psi(\underline{r}_1, \underline{r}_2)$$

and evaluate the probability of finding an electron at $\underline{r} = \underline{r}_1$ and another electron at $\underline{r} = \underline{r}_2$:

$$|\psi|^2 \, d^3\underline{r}_1 \, d^3\underline{r}_2$$

There is no concept of which electron is which – two identical particles are indistinguishable.

This has important implications for how we construct two particle wavefunctions from single particle states. If we swap the labels 1 and 2 then $|\psi|^2$ should stay the same.

The singlet and triplet spin states have this property, eg. consider

$$|1\ 0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\rangle_1 |\downarrow\rangle_2 + |\downarrow\rangle_1 |\uparrow\rangle_2 \right)$$

Define the exchange operator $\hat{X}$ that exchanges the labels 1 and 2

$$\begin{aligned} \hat{X}|1\ 0\rangle &= \frac{1}{\sqrt{2}}\left(|\uparrow\rangle_2 |\downarrow\rangle_1 + |\downarrow\rangle_2 |\uparrow\rangle_1 \right) \\ &= \frac{1}{\sqrt{2}}\left(|\downarrow\rangle_2 |\uparrow\rangle_1 + |\uparrow\rangle_2 |\downarrow\rangle_1 \right) \\ &= \frac{1}{\sqrt{2}}\left(|\uparrow\rangle_1 |\downarrow\rangle_2 + |\downarrow\rangle_1 |\uparrow\rangle_2 \right) = |1\ 0\rangle \end{aligned}$$

Similarly,
$$\begin{aligned}\hat{X}|00\rangle &= \hat{X}\frac{1}{\sqrt{2}}\left(|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2\right)\\ &= \frac{1}{\sqrt{2}}\left(|\uparrow\rangle_2|\downarrow\rangle_1 - |\downarrow\rangle_2|\uparrow\rangle_1\right)\\ &= \frac{1}{\sqrt{2}}\left(|\downarrow\rangle_1|\uparrow\rangle_2 - |\uparrow\rangle_1|\downarrow\rangle_2\right)\\ &= -\frac{1}{\sqrt{2}}\left(|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2\right)\\ &= -|00\rangle\end{aligned}$$

The triplet states are <u>symmetric</u> under interchange $\hat{X}\psi = \psi$
The singlet state is <u>antisymmetric</u> under interchange $\hat{X}\psi = -\psi$

Note that both of these mean that $\hat{X}^2\psi = \psi$
(if I swap the labels twice, I get to where I started)
and also probabilities computed using ψ are the same as those computed with $\hat{X}\psi$ since probability is the square of the amplitude.

Spin-statistics theorem

The symmetry of multi-particle wavefunctions under interchange of two particles is related to the particle spin.

ψ symmetric under interchange	$\longleftrightarrow$	integer spin	BOSONS
ψ antisymmetric under interchange	$\longleftrightarrow$	half-integer spin	FERMIONS

For fermions this gives rise to the $\boxed{\text{PAULI EXCLUSION PRINCIPLE.}}$
Fermions must have an antisymmetric wavefunction

eg. two particles $\Psi(\underline{r}_1,\underline{r}_2) = \psi_n(\underline{r}_1)\,\psi_m(\underline{r}_2) - \psi_m(\underline{r}_1)\,\psi_n(\underline{r}_2)$

Here we've constructed Ψ from two single particle states ψ_m and ψ_n.
<u>If $n=m$, the wavefunction vanishes!</u>

$\Rightarrow$ two fermions cannot occupy the same state

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

$$|\psi\rangle = \underbrace{|n\;\ell\;m\rangle}_{\text{this is } \psi_{n\ell m}(\theta,\phi)}\;\underbrace{|\tfrac{1}{2}\;m_s\rangle}_{\text{this is the spin state}}$$

$= R_{n\ell}(r)\,Y_\ell^m(\theta,\phi)$

$m_s = +\frac{1}{2}$ or $-\frac{1}{2}$
(up or down)

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

singlet spin state: ↓

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

$$\times\; |n\;\ell\;m\rangle_1\,|n\;\ell\;m\rangle_2 \qquad -(*)$$

Same spatial wavefunction for each electron →

This is what we mean when we draw the energy levels of an atom in chemistry with up and down electrons $\uparrow\downarrow$

Bosons on the other hand can occupy the same state.
eg. we can write

$$\psi(\underline{r}_1, \underline{r}_2, \cdots \underline{r}_n) = \prod_{i=1}^{n} \psi_\alpha(\underline{r}_i)$$

where we put n particles in the state ψ_α.
ψ is symmetric under interchange of any two particles as it must be.
This leads to the phenomenon of BOSE-EINSTEIN CONDENSATION where a macroscopic number of particles can occupy the ground state. The idea underlies superfluidity and superconductivity.

Note that when we construct a multi-particle wavefunction from a combination of single particle wavefunctions, eg. the two-electron atomic wavefunction in (*), we are ignoring interactions between the two particles. I.e. we are assuming we can write

$$\underbrace{\hat{H} = \underset{\substack{\uparrow \\ \text{particle 1}}}{\hat{H}_1} + \underset{\substack{\nwarrow \\ \text{particle 2}}}{\hat{H}_2}}_{\text{for identical particles these are the same, ie. } [\hat{X}, \hat{H}] = 0}$$

then the stationary states are products of the one particle stationary states.

Often the interaction terms in the Hamiltonian are small, and so this is a good approximation.

Infinite square well with fermions and bosons (see Griffiths example 5.1)

Let's do a concrete example and put two particles into an infinite square well. The one particle wavefunctions are

$$\psi_n(x) = \sqrt{\frac{2}{a}}\,\sin\left(\frac{n\pi x}{a}\right)$$

with energies $E_n = E_0 n^2$ where $E_0 = \frac{\hbar^2\pi^2}{2ma^2}$

is the ground state energy.

For two particles, we write the Hamiltonian

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2} + V(x_1) + V(x_2)$$

eg. consider $\psi(x_1, x_2) = \psi_n(x_1)\,\psi_m(x_2)$

$$\hat{H}\psi = \psi_m\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2\psi_n}{\partial x_1^2} + \psi_n\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2\psi_m}{\partial x_2^2}$$

$$+\underbrace{\left[V(x_1) + V(x_2)\right]}_{V=0 \text{ for inside the well}}\psi_n(x_1)\,\psi_m(x_2)$$

$$= \psi_m\psi_n\left(-\frac{\hbar^2}{2m}\right)\left(-\frac{n^2\pi^2}{a^2}\right) + \psi_n\psi_m\left(-\frac{\hbar^2}{2m}\right)\left(-\frac{m^2\pi^2}{a^2}\right)$$

$$= \frac{\hbar^2\pi^2}{2ma^2}\left(n^2+m^2\right)\psi_m\psi_n$$

$$= E\psi \quad \Rightarrow \quad \text{energy is } \underline{E = E_0\left(n^2+m^2\right)}.$$

This would be okay for distinguishable particles, but for identical particles we need a symmetric (bosons) or antisymmetric (fermions) state:

$$\psi_\pm(x_1, x_2) = \frac{1}{\sqrt{2}}\Big(\psi_n(x_1)\psi_m(x_2) \pm \psi_m(x_1)\psi_n(x_2)\Big)$$

Substituting into the Schrödinger equation, you should find that the energy is still $E_0(n^2+m^2)$.
But for fermions, $\psi = 0$ if $n=m$ so we must have $n \neq m$.

This implies that the ground state energy for bosons is $2E_0$
$(n=m=1)$

but for fermions the ground state is $n=1$ $m=2$
(or vice versa)
with energy $E = 5E_0$.

The Postulates of Quantum Mechanics

The basic ideas underlying quantum mechanics are often summarized as a set of "postulates"

1. All the information we know (and can know) about a system is contained in its state $|\psi\rangle$.

   $|\psi\rangle$ is a normalized vector in Hilbert space, $\langle\psi|\psi\rangle = 1$.

2. For every observable A there is a corresponding Hermitian operator $\hat{A}$
   (Hermitian because the eigenvalues must be real)

3. A measurement of observable A returns one of the eigenvalues a and puts the system into the corresponding eigenstate $|\psi_a\rangle$.

   $$\hat{A}|\psi_a\rangle = a|\psi_a\rangle$$

4. The probability of measuring eigenvalue a is $|\langle\psi_a|\psi\rangle|^2$.

   The eigenstates $|\psi_a\rangle$ form a complete basis in which we can write $|\psi\rangle$ as a linear sum $|\psi\rangle = \sum \underbrace{\langle\psi_a|\psi\rangle}\, |\psi_a\rangle$

   these numbers are a way of specifying $|\psi\rangle$, ie. a representation

   eg. $\psi(x) = \langle x|\psi\rangle$
   $A(p) = \langle p|\psi\rangle$
   $c_n = \langle\psi_n|\psi\rangle$

5. The expectation value of A is $\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle$.
   (the mean value of many measurements of an ensemble of systems).

5. The state $|\psi\rangle$ evolves in time according to

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = \hat{H}|\psi\rangle$$

Stationary states or in other words eigenfunctions of the Hamiltonian $\hat{H}$ have a simple time dependence $e^{-iEt/\hbar}$.

We could also add a number 6 for multiparticle states that $|\psi\rangle$ must be symmetric (antisymmetric) under exchange of two particle labels for bosons (fermions).

That ends this course! You now have all the basic ideas of quantum mechanics that will allow you to study a range of fascinating examples from electrons in metals, to the response of atoms to applied electric or magnetic fields, molecular bonding, scattering of particles, quantum entanglement and information. These are all touched on in the second half of Griffith's book, and many of these and more will be talked about in PHYS 436 next term.