Part IB — Quantum Mechanics

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0 Introduction

Quantum Mechanics (QM) is a radical generalization of classical physics involving a new fundamental constant, *Planck's constant*:

$$\hbar = h/2\pi \approx 1.05 \times 10^{-34}\text{Js},$$

with dimensions

$$\begin{aligned}[\hbar] = ML^2T^{-1} &= [\text{position}] \times [\text{momentum}] \\ &= [\text{energy}] \times [\text{time}]\end{aligned}$$

Profound new features of QM include:

- *Quantisation.* Physical quantities such as energy may be restricted to discrete sets of values, or may appear only in specific amounts, called *quanta.*
- *Wave-particle duality.* Classical concepts of a particle and a wave are merged; they become different aspects of a single entity that shows either particle-like or wave-like behaviour, depending on the circumstance.
- *Probability and uncertainty.* Predictions in QM involve probability in a fundamental way and there are limits to what can be asked about a physical system, even in principle[1]. A famous example is the *Heisenberg uncertainty principle relation* for position and momentum.

Despite these radical changes, classical physics must be recovered in the limit $\hbar \to 0$ (which may require careful interpretation).

The following sections provide some physical background and summarise key experimental evidence for these novel features of QM.

0.1 Light Quanta

An electromagnetic (EM) wave, eg. light, consists of quanta called *photons.* Photons can be regarded as particles with energy, E, and momentum, p, related to frequency ν or ω, and[2] wavelength λ, or wavenumber k, according to

$$E = hv = \hbar\omega$$
$$p = h/\lambda = \hbar k$$

From the wave equation (satisfied by each EM field component)

$$c = \omega/k = vk \quad \text{or} \quad E = cp \text{ massless particle}$$

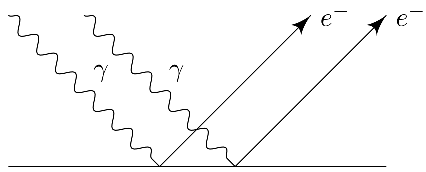
so the relations are consistent with photons being particles of rest mass zero, moving with the speed of light, c.

Compelling evidence for the existence of photons is provided by the *photoelectric effect.* Consider (Fig. 1) light of EM radiation (γ) of frequency ω

[1] If we were able to keep track of every single particle we would know exactly what the system is doing. But in QM, we *still* can't know what the system is doing precisely.

[2] v, ω both called frequency, and differ by a factor of 2π.

incident on a metal surface. For certain metals and suitable frequencies this results in the emission of electrons (e^-) and their maximum kinetic energy K can be measured.



Experiments find that:

(i) the rate at which electrons are emitted is proportional to the intensity of the radiation (the 'brightness' of the source);

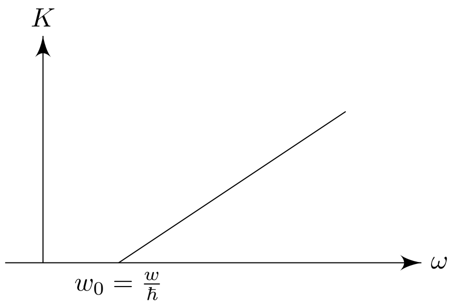
(ii) K depends linearly on ω but *not* on the intensity;

(iii) for $\omega < \omega_0$, some critical value, *no* electrons are emitted, irrespective of the intensity.

The results are extremely hard to understand in terms of classical EM waves. However, they follow naturally from the assumption that the wave consists of photons, each with energy $E = \hbar\omega$, and with the intensity of the radiation proportional to the number of photons incident per unit time. Suppose that an electron is emitted as a result of absorbing a single photon with sufficiently high energy. If W is the minimum energy needed to liberate an electron from the metal then

$$K = \hbar\omega - W$$

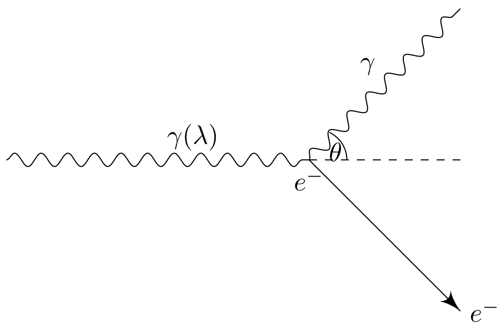
is the maximum kinetic energy of an emitted electron if $\omega > \omega_0$, where $\omega_0 = W/\hbar$, and no emission is possible if $\omega < \omega_0$ (Fig 2). Furthermore, the rate at which electrons are emitted will be proportional to the rate at which incident photons arrive, and hence the intensity.



The energy-frequency relation for photons was introduced by Planck and used to derive the *black body spectrum.* This is the distribution of energy with frequency for EM radiation in thermal equilibrium, a fundamental result in thermodynamics of far-reaching importance (understanding the *cosmic microwave background*, for example). Einstein then applied the energy-frequency relation to explain the photoelectric effect. Further conclusive evidence for photons as particles, including the momentum-wavelength relation, came from subsequent experiments involving *Compton scattering.*

Consider a photon of wavelength λ colliding with an electron that is stationary in the laboratory frame. Let λ' be the wavelength of the photon after the collision and θ the angle through which it is deflected. Treating the photon as a massless relativistic particle, conservation of four-momentum implies

$$\lambda' - \lambda = \frac{h}{m_e c}(1 - cos\theta)$$



This dependence of the change in wavelength (or decrease in energy) can be verified experimentally (for X-rays, or γ-rays, for instance).

0.2 Bohr Model of the Atom

The *Rutherford model* of the atom was proposed to explain the results of scattering experiments (eg. alpha particles scattered by gold foil). The key assumption is that most of the mass of the atom is concentrated in a compact, positively-charged *nucleus* (subsequently understood to consist of protons and neutrons), with light, negatively charged electrons orbiting around it. The simplest case is the Hydrogen atom, in which a single electron with charge $-e$ and mass m_e orbits a nucleus consisting of a single proton with charge $+e$ and mass m_p. Since $m_p >> m_e$ it is a good approximation to assume the proton is stationary, at the origin, say. The electron and proton interact via Coulomb's Law: the potential energy of the electron and the force it experiences are:

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} \qquad \mathbf{F}(\mathbf{r}) = -\nabla V = -\frac{e^2}{4\pi\varepsilon_0}\hat{\mathbf{r}}$$

The classic equations of motion for the electron imply that its angular momentum, $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, and its total energy,

$$E = \frac{1}{2}m_e v^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

are constant. The orbits are therefore planar and they can be determined exactly. For any value of $E < 0$ there is a closed orbit and the electron is *bound* to the proton to form a Hydrogen atom. For orbits with $E > 0$ the electron eventually escapes to infinity: it is not bound to the proton.

Despite its success in accounting for Rutherford scattering, this model has a number of problems. The treatment is identical, mathematically, to planetary orbits governed by gravity (see Part IA Dynamics and Relativity, for example) but an important additional feature of electromagnetism has been left out. An accelerating charge radiates energy (carried away via EM fields) and this means that the electron would actually spiral inwards towards the proton: this is not a good model of a stable atom!

There is also experimental evidence for complex discrete structure within atoms. This comes from *line spectra*: bright emission lines (from a hot sample) or dark absorption lines (if radiation is passed through a cooler sample), both occurring at certain characteristic wavelengths or frequencies. This suggests that an atom can emit or absorb radiation only at these particular frequencies or wavelengths, which corresponds to photon with particular energies.

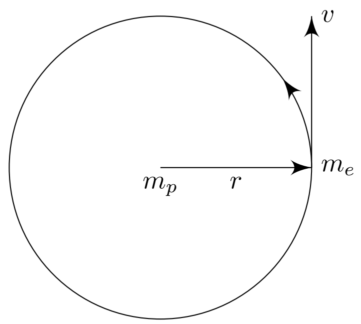
The *Bohr model* restricts the classical orbits of the Rutherford model by postulating that the angular momentum of the electron obeys the *Bohr quantisation condition*

$$L = n\hbar, \qquad n = 1, 2, \cdots,$$

with only these discrete values are allowed. This might seem to be an unsatisfactory way to address the issue of stability, but it proves to be remarkably successful in reproducing the complex experimental data relating to line spectra.

Specializing to circular orbits (Fig. 4) for simplicity, we have

$$F = m_e v^2/r \qquad \text{and} \qquad L = m_e r v$$



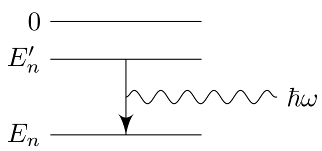
It is then straightforward to check that the quantisation condition leads to the following set of *Bohr orbits*

$$r_n = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} n^2, \quad v_n = \frac{e^2}{4\pi\varepsilon_0\hbar}\frac{1}{n}, \quad E_n = -\frac{1}{2} m_e \left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2 \frac{1}{n^2}, \quad n = 1, 2, \cdots$$

Note that the allowed energy levels are now discrete.

Suppose that an electron makes a transition between levels n and n' (with $n' > n$, say) accompanied by emission or absorption of a photon of frequency ω (Fig 5). Then

$$\hbar\omega = E_{n'} - E_n = \frac{1}{2} m \left(\frac{e^2}{4\pi\varepsilon_0\hbar}^2\right)^2 \left(\frac{1}{n^2} - \frac{1}{n'^2}\right)$$



This formula accounts for a vast amount of experimental data on spectral lines for Hydrogen. The Bohr model also provides an estimate for the *size* of the Hydrogen atom $r_1 \approx 5.29 \times 10^{-11}$m, the *Bohr radius.* Despite these considerable successes, the origin of the Bohr quantisation condition seems obscure. A better explanation is needed.

0.3 Matter Waves

The relations used to associate particle properties (E and p) to waves can also be used to associate wave properties (v or $omega$ and λ or k) to particles. This applies not just to relativistic photons but also to non-relativistic particles, electrons for example, and λ is called the *de Broglie wavelength* of the particle. A strong hint that this might be important for a better understanding of the Bohr quantisation condition comes from observing that for a circular orbit

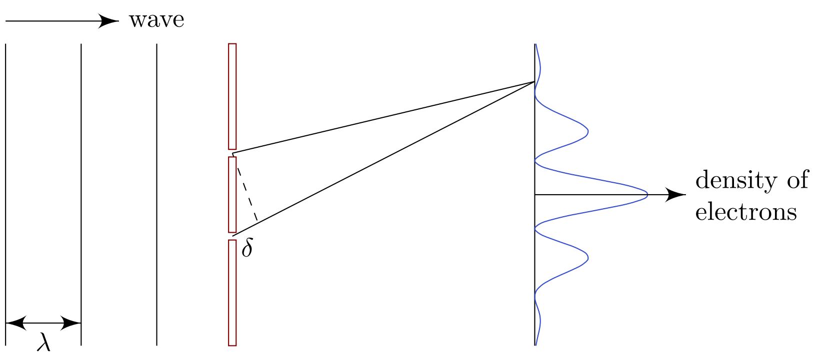
$$L = pr = n\hbar \qquad \Longleftrightarrow \qquad n\lambda = 2\pi r$$

The Bohr condition therefore says that the circumference of each orbit is exactly an integral number of de Broglie wavelengths.

[Fig 6]

It can also be verified experimentally that electrons do indeed exhibit wave-like behaviour, and a helpful idealisation is the *double slit experiment.* Consider a source which emits a beam of electrons, a barrier with two slits that can be open or closed, and a screen on which the electrons are detected.

Suppose that first one slit is open and the other is closed. We cannot say with certainty where any particular electron will be detected, but after many electrons have been emitted, the number detected varies with tranverse position. If *both* slits are open, however, then the electrons produce (perhaps unexpectedly) an interference pattern.



This matches the interference pattern obtained for waves of length λ incident on a barrier. Consider a point P at some fixed perpendicular distance from the barrier, and let δ be the difference of the distances to P from each of the slits.

Constructive interference occurs for $\delta = n\lambda$ while destructive interference occurs for $\delta = (n + 1/2)\lambda$. The result is that the $(\text{amplitude})^2$ of the superposed waves varies as P varies.

In diffraction experiments with electrons, we cannot predict what will happen to any *single* particle; the most that can be said is that it will be detected at a given position with a certain *probability*. The diffraction pattern is conclusive evidence of interference and so confirms the existence of matter waves, and diffraction experiments allow an experimental determination of the de Broglie wavelength. The results also suggest that the probability distribution for particles can be expressed as the $(\text{amplitude})^2$ of a wave.

1 Wave functions and Operators

In first few chapters we consider a quantum particle in one dimension, introduce some key ideas and three postulates for how to extract physical information from mathematical framework. Later (Chapter 6) we will state general axioms from which these follow.

1.1 Wave functions and States

A classical point particle in one-dimension has a position x at each time. In QM a particle has a *state* at each time given by a complex-valued, [3] wavefunction

$$\psi(x)$$

Postulate(P1): A measurement of position gives a result with probability density $|\psi(x)|^2$. ie. $|\psi(x)|^2\delta x$ prob particle is found between x and $x+\delta x$, or

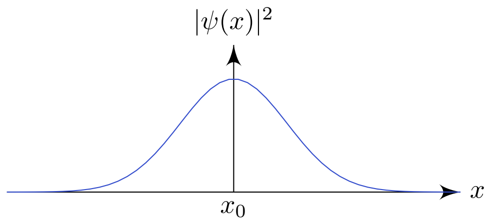
$$\int_a^b |\psi(x)|^2 \,\mathrm{d}x$$

is the probability the particle is found in the interval $a \leq x \leq b$. This requires $\psi(x)$ is *normalised.*

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \,\mathrm{d}x = 1 \qquad \text{single particle - total probability 1}$$

Example. (Gaussian wavefunction)

$$\psi(x) = Ce^{-(x-x_0)^2/2\alpha} \qquad \text{real } \alpha > 0$$



$$\begin{aligned}\int_{-\infty}^{\infty} |\psi(x)|^2 \,\mathrm{d}x &= |C|^2 \int_{-\infty}^{\infty} e^{-(x-x_0)^2/\alpha} \,\mathrm{d}x \\ &= |C|^2(\alpha\pi)^{\frac{1}{2}} = 1\end{aligned}$$

So [4] ψ normalised if $C = \left(\frac{1}{\alpha\pi}\right)^{\frac{1}{4}}$. α small $\Rightarrow$ sharp peak around $x = x_0$, $\Rightarrow$ "particle-like". α large $\Rightarrow$ more spread out (diffuse)

[3] non-zero

[4] Recall $\int_{-\infty}^{\infty} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \,\mathrm{d}x = \sqrt{2\pi\sigma^2}$

It is convenient to deal more generally with *normalisable* wavefunctios

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \, \mathrm{d}x < \infty \qquad \text{finite/convergent}$$

Then $\psi(x)$ and $\phi(x) = \lambda\psi(x)$ are physically equivalent and represent same state for any $\lambda \neq 0$. Provided ψ normalisable, we can choose λ so that ϕ normalised. But if ψ normalised already, then $\phi(x) = e^{i\alpha}\psi(x)$ (for any real α) gives some probability distribution.

$$|\phi(x)|^2 = |\psi(x)|^2$$

So quantum state is strictly an equivalence class of non-zero wave functions but in practice we often refer to $\psi(x)$ as "the state".

Any non-zero normalisable wave function $\phi(x)$ represents a physical state. For our purposes we can assume, *unless* we say otherwise, $\psi(x)$ is smooth (can be differentiated any number of times), and $\psi(x) \to 0$ as $|x| \to \infty$

If $\psi_1(x)$ and $\psi_2(x)$ are normalisable then so is

$$\psi = \lambda_1\psi_1 + \lambda_2\psi_2$$

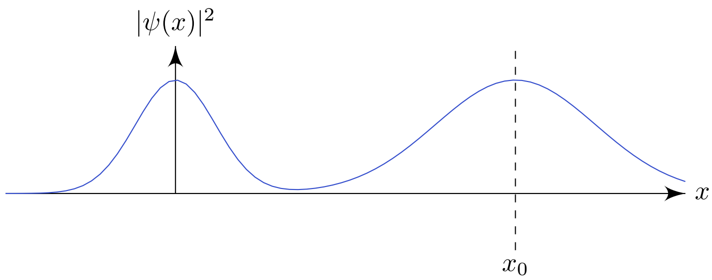
for any complex λ_1, λ_2.

Physically: principle of super position Mathematically: structure of complex vector space.

Example. (Superposition of Gaussians)

$$\psi(x) = B(e^{\frac{-x^2}{2\alpha}} + e^{-(x-x_0)^2/2\beta})$$

Can choose B so that ψ is normalised



1.2 Operators and Observables

A quantum state contains information about other physical quantities or *observables* (momentum, energy) not just position. In QM each observable is represented by an *operator* (denoted by a hat when necessary) acting on wave functions

position	$\hat{x} = x$	$\hat{x}\psi = x\psi(x)$
momentum	$\hat{p} = -i\hbar\frac{\partial}{\partial x}$	$\hat{p}\psi = -i\hbar\psi'(x)$
energy	$H = \frac{\hat{p}^2}{2m} + V(\hat{x})$	$H\psi = -\hbar^2\frac{\partial^2}{\partial x^2}\psi + V(x)\psi(x)$

for a particle of mass m in a potential $V(x)$.

If we measure one of these quantities, what answers can we get and what are the probabilities? Partial answers provided by (P2) and (P3)

1.2.1 Expectation Values

For any (normalisable) $\psi(x)$ and $\phi(x)$, define

$$(\psi, \phi) := \int_{-\infty}^{\infty} \psi(x)^* \phi(x) \, \mathrm{d}x$$

Note that this is the complex inner product on vector space,

For $\psi(x)$ normalised, define the *expectation value* of an observable Q in this state, to be

$$\begin{aligned} < Q >_\psi &:= (\psi, Q\psi) \\ &= \int_{-\infty}^{\infty} \psi^* (Q\psi) \, \mathrm{d}x \end{aligned}$$

Note

$$\begin{aligned} < \hat{x} > &= (\psi, \hat{x}\psi) \\ &= \int_{-\infty}^{\infty} x |\psi(x)|^2 \, \mathrm{d}x \end{aligned}$$

standard expression for mean, or expected value of x, given (P1)

Postulate (P2): For any observable, $< Q >_\psi$ is the mean result (expected value) if Q is measured many times (N times and then $N \to \infty$) with the particle in state ψ before each measurement.

Consider wave functions:

$$\phi(x) = \psi(x) e^{ikx} \qquad \text{with } k \text{ real constant}$$

Clearly

$$|\phi(x)|^2 = |\psi(x)|^2$$

and so

$$< \hat{x} >_\phi = < \hat{x} >_\psi$$

But

$$\begin{aligned} < \hat{p} >_\phi &= \int_{-\infty}^{\infty} \phi^* (-i\hbar\phi') \, \mathrm{d}x \\ &= \int_{-\infty}^{\infty} \psi^* (-i\hbar\psi') \, \mathrm{d}x + \hbar k \int_{-\infty}^{\infty} \psi^* \psi \, \mathrm{d}x \\ &= < \hat{p} >_\psi + \hbar k \end{aligned}$$

where $\hat{p} = -i\hbar \frac{\mathrm{d}}{\mathrm{d}x}$

Example.

$$\psi(x) = Ce^{-x^2/2\alpha}$$

as in 1.1 with $x_0 = 0$

$$\Rightarrow \langle \hat{p} \rangle_\psi = 0$$

and

$$\phi(x) = Ce^{-x^2/2\alpha} e^{ikx}$$

$$\Rightarrow < \hat{p} >_\psi = \hbar k$$

If we accept (P2) then this result accounts for the choice of momentum operator $\hat{p} = -i\hbar \frac{\mathrm{d}}{\mathrm{d}x}$

1.2.2 Eigenstates and Eigenvalues

A state ψ ($\neq 0$) is an *eigenstate* or *eigenfunction* of an operator or observable Q with eigenvalue q if

$$Q\psi = q\psi$$

Postulate (P3): If Q is measured when the particle is an eigenstate ψ, as above, then the result is the eigenvalue q with probability 1.

Example. (i) $Q = \hat{x}$ no (continuous) eigenfunctions since

$$\hat{x}\psi(x) = x\psi(x) = q\psi(x) \Rightarrow \psi(x) = 0 \text{ for } x \neq q$$

(ii) $Q = \hat{p} = -i\hbar \frac{\mathrm{d}}{\mathrm{d}x}$ eigenfunctions obey

$$-i\hbar\psi' = q\psi$$

$$\Rightarrow \psi(x) = Ce^{ikx} \quad \text{with } q = \hbar k$$

But not normalisable since $|\psi(x)|^2 = |C|^2$, so can't interpret this directly as wave function for a single particle on $-\infty < x < \infty$.

Could normalise on interval of length l by choosing $C = \frac{1}{\sqrt{l}}$, but then need to look carefully at boundary conditions on interval

(iii) $Q = H$ Hamiltonian (energy) with particular choice of potential $V(x) = \frac{1}{2}Kx^2$ with $K > 0$.

So

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

and

$$H\psi = -\frac{\hbar^2}{2m}\psi'' + \frac{1}{2}Kx^2\psi = E\psi$$

This is satisfied for

$$\psi(x) = Ce^{-x^2/2\alpha}$$

if we choose $\alpha^2 = \hbar^2/Km$ and then

$$E = \frac{\hbar}{2}\sqrt{\frac{K}{m}}$$

is energy eigenvalue.

Note classically for fixed E have $|x| \leq (2E/K)^{\frac{1}{2}}$ but wave function above gives non-zero probability density along entire x-axis

In general, the energy eigenvalue equation

$$H\psi = E\psi$$

or

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

for a particle of mass m in potential determines states of definite energy and allowed energy values.

This is the *time-independent Schrödinger Equation*

Solving this for H-atom is our eventual aim.

1.2.3 Comments

(i) Defined $\langle Q\rangle_\psi = (\psi, Q\psi)$ used in (P2) for ψ normalised: if ψ is not normalised,

$$\langle Q\rangle_\psi = \frac{(\psi, Q\psi)}{\psi, \psi}$$

(ii) Definition for $Q = \hat{x}$ reproduce standard defn of mean. For $\hat{p}$ and H can check explicitly (taking complex conjugates and integrating by parts) that $\langle\hat{p}\rangle_\psi$ and $\langle H\rangle_\psi$ are real

(iii) (P3) is consistent with (P2) - consider energy, for example.

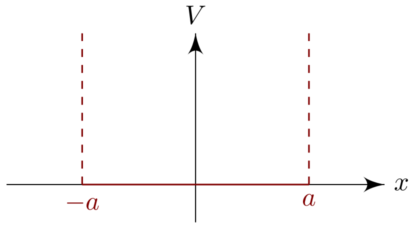
$$\begin{aligned} H\psi = E\psi \Rightarrow (\psi, H\psi) &= \langle H\rangle_\psi \\ &= (\psi, E\psi) = E \text{ if } \psi \text{ normalised} \end{aligned}$$

ie. measurement of energy gives result E with prob $= 1 \Rightarrow$ mean result is E.

(iv) From (ii) and (iii) we deduce that any eigenvalue of H is real.

1.3 Infinite Potential Well or Particle in a Box

Example.



$$V(x) = \begin{cases} 0 & \text{if } |x| \leq a \\ U & \text{if } |x| > a \end{cases}$$

in the limit $U \to \infty$.

Time indep SE:

$$\frac{-\hbar^2}{2m}\psi'' = E\psi \qquad |x| \leq a$$

$$\frac{-\hbar^2}{2m}\psi'' + U\psi = E\psi \qquad |x| > a$$

Taking the limit as $U \to \infty$, 2nd equation suggests we must take $\psi = 0$ for $|x| > a$.

This will be justified shortly. In this case the appropriate boundary conditions are $\psi = 0$ for $|x| > a$ and ψ continuous at $x = \pm a$. So we are left to solve

$$-\frac{\hbar^2}{2m}\psi'' = E\psi \quad \text{on } -a \leq x \leq a \text{ with } \psi(\pm a) = 0$$

For $E > 0$ set

$$E = \frac{\hbar^2 k^2}{2m} \quad \text{with } k > 0$$

and we get

$$\psi'' + k^2\psi = 0$$

$$\Rightarrow \psi = A\cos kx + B\sin kx$$

and boundary conditions imply $A\cos ka \pm B\sin ka = 0$ ie. $A\cos ka = B\sin ka = 0$. Since $\sin ka$ and $\cos ka$ cannot both be zero simultaneously, we have:

(i) $B = 0$ and $ka = n\pi/2$ for $n = 1, 3, \cdots$ or

(ii) $A = 0$ and $ka = n\pi/2$ for $n = 2, 4, \cdots$

Hence

$$E_n = \frac{\hbar^2\pi^2}{8ma^2}n^2 \quad \text{for } n = 1, 2, 3, 4, \cdots$$

discrete set of allowed energies, with normalised wave functions

$$\psi_n(x) = \left(\frac{1}{a}\right)^{\frac{1}{2}} \begin{cases} \cos\frac{n\pi x}{2a} & n \text{ odd} \\ \sin\frac{n\pi x}{2a} & n \text{ even} \end{cases}.$$

Comments

(i) Since $\psi_n(x) = 0$, $|x| \geq a$ normalisation condition is $\int_{-a}^{a} |\psi_n(x)|^2 \, \mathrm{d}x = 1$.

(ii) for $E < 0$ diff eqn has solutions of type cosh/sinh instead of cos/sin $\Rightarrow$ no eigenfunctions satisfying boundary conds.

(iii) Before taking $U \to \infty$, we have normalisable solutions $e^{\pm\kappa x}$ in $x > a, x < -a$ with $\kappa > 0$ st. $\frac{\hbar^2\kappa^2}{2m} = U - E$. but then we see that $\kappa \to \infty$ as $U \to \infty$, confirming $\psi(x) = 0$ for $|x| \geq a$

(iv) Superposition eg. $\psi_1 + \psi_2$ produces state that is *not* an energy eigenstate.

2 Schrödinger Equation

In chapter 1 we discussed wavefunctions or states at some fixed time. Now consider evolution in time for QM of a particle in 1d, described[5] by wavefunction $\Psi(x,t)$.

Classically, dynamics governed by potential $V(x)$ (produces force $F = -V'$). In QM, time evolution is governed by Hamiltonian

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

(again specified by $V(x)$). The wavefunction satisfies the *time-dependent Schrödinger Equation*

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi \qquad (*)$$

Note operators do not change in time (in this formulation) eg. momentum is now $\hat{p} = -i\hbar\frac{\partial}{\partial x}$

and t-dep SE becomes

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

Linear PDE but first oredr in t, so specifying $\Psi(x,0)$ determines $\Psi(x,t)$ for $t \geq 0$.

2.1 Stationary States

Consider a wavefunction of frequency ω:

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

This satisfies (*) iff

$$\psi\hbar\omega e^{-i\omega t} = (H\psi)e^{-i\omega t}$$
$$\iff H\psi = E\psi \qquad \text{with} \qquad E = \hbar\omega$$

OR have a separable $\Psi(x,t) = \psi(x)f(t)$ of SE iff

$$\frac{1}{\psi}H\psi = i\hbar\frac{1}{f}\dot{f} = E, \text{ separation const.}$$
$$\Rightarrow H\psi = E\psi \text{ and } f(t) = f(0)e^{-i\omega t}, \text{ but } f(0) = 1 \text{ wlog}$$

So t-dep SE produces desired energy-frequency relation. For a solution of this special type,

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} \qquad \text{with } H\psi = E\psi$$

both Ψ and ψ are called *stationary states*. In this case

(i) $\Psi(x,t)$ is an energy eigenstate at each time t

(ii) $|\Psi(x,t)|^2 = |\psi(x)|^2$ indep of time

[5] usually reserve capitals to emphasze t-dep

2.2 Conservation of Probability

The probability density

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

obeys a *conservation equation*

$$\frac{\partial P}{\partial t} = -\frac{\partial J}{\partial x}$$

where

$$J(x,t) = -\frac{i\hbar}{2m}(\Psi^*\Psi' - \Psi'^*\Psi)$$

is *probability current*

This follows for any $\Psi(x,t)$ satisfying $(*)$, by taking $(*)$ and its complex conjugate

$$-i\hbar\frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m}\Psi''^* + V\Psi^* \qquad \text{(V real)}$$

since

$$\begin{aligned}\frac{\partial P}{\partial t} &= \Psi^*\dot{\Psi} + \dot{\Psi}^*\Psi \\ &= \Psi^*\frac{i\hbar}{2m}\Psi'' - \frac{i\hbar}{2m}\Psi''^*\Psi \qquad \text{v terms cancel} \\ &= -\frac{\partial J}{\partial x} \text{ as claimed}\end{aligned}$$

The conservation eqn implies

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_a^b P(x,t)\,\mathrm{d}t &= \int_a^b \frac{\partial P}{\partial t}\,\mathrm{d}x = -\int_a^b \frac{\partial J}{\partial t}(x,t)\,\mathrm{d}x \\ \text{fixed a,b } &= -J(b,t) + J(a,t)\end{aligned}$$

with boundary conditions such that $\Psi, J \to 0$ as $x \to \pm\infty$ (fixed t) we find

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2\,\mathrm{d}x \text{ independent of } t$$

ie. $\Psi(x,0)$ normalised $\Rightarrow$ $\Psi(x,t)$ normalised for all $t \geq 0$

2.3 Wavepackets and Particles

A wavefunction localised in space, about some point, on some scale, will be called a *wavepacket* - may interpret this as a particle of scale is sufficiently small.

Consider Gaussian as in Section 1.1

$$\psi(x) = A\frac{1}{\alpha^{\frac{1}{2}}}e^{-x^2/2\alpha} \qquad \text{with } A = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}$$

wavepacket localised around $x = 0$ on scale $\sqrt{\alpha}$

For $V = 0$, *free* particle, this is not a stationary state; in fact, soln of t-dep SE with $\Psi(x, 0) = \psi(x)$ is

$$\Psi(x,t) = A\frac{1}{\gamma(t)^{1/2}}e^{-x^2/2\gamma(t)}$$

with

$$\gamma(t) = \alpha + \frac{i\hbar}{m}t \qquad \text{see eg sheet 1}$$

Probability density

$$P_\Psi(x,t) = |\Psi(x,t)|^2 = \frac{|A|^2}{|\gamma(t)|}e^{-\alpha x^2/|\gamma(t)|^2}$$

localised around $x = 0$ on scale

$$\frac{|\gamma(t)|}{\sqrt{\alpha}} \qquad \text{solution "diffuses"}$$

how quickly does solution "diffuse"?
Time scale $m\alpha/\hbar$
For $m = m_e$, and $\sqrt{\alpha} = 10^{-12}$ m $\Rightarrow$ time scale $\sim 10^{-20}$ s
For $m = 10^{-6}$ kg, $\sqrt{\alpha} = 10^{-6}$ m, $\Rightarrow$ time scale $\sim 10^{16}$ s.
Solution $\Psi(x, t)$ depends on time but

$$\langle \hat{x} \rangle_\Psi = 0 \text{ and } \langle \hat{p} \rangle_\Psi = 0$$

Now consider solution $\Phi(x, t)$ with

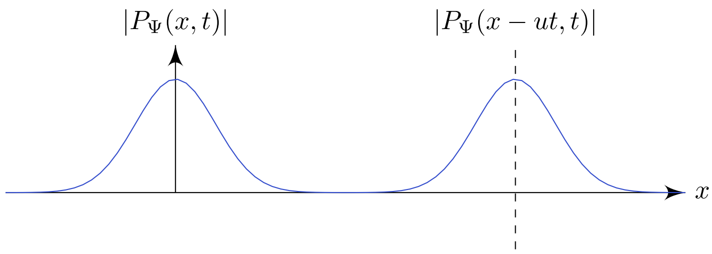
$$\Phi(x, 0) = \phi(x) = \psi(x)e^{ikx}$$

Can check that this is given by

$$\Phi(x,t) = \Psi(x - ut, t)e^{ikx}e^{-i\hbar k^2 t/2m}$$

provided $mu = \hbar k$
Probability density

$$P_\Phi(x,t) = |\Phi(x,t)|^2 = |\Psi(x - ut, t)|^2 = P_\Psi(x - ut, t)$$



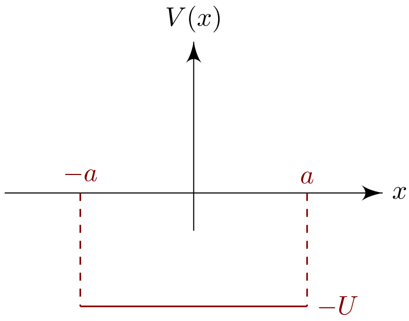
Also easy to check that

$$\langle \hat{x} \rangle_\Psi = ut \text{ and } \langle \hat{p} \rangle_\Psi = \hbar k$$

3 Bound States in One Dimension

Study in this chapter normalisable solutions of t-indep SE (energy eigenvalue problem) corresponding to particle "bound" in the potential (compare with electron bound to proton for $E < 0$)

3.1 Potential Well



$$V(x) = \begin{cases} -U & \text{if } |x| < a \quad (U > 0) \\ 0 & \text{if } |x| \geq a \end{cases}$$

in the limit $U \to \infty$.

Seek energy functions and eigenvalues given by

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

with energies in range $-U < E < 0$

SE becomes

$$-\frac{\hbar^2}{2m}\psi'' = (E+U)\psi \text{ and } -\frac{\hbar^2}{2m}\psi'' = E\psi$$

$$|x| < a \qquad \text{and} \qquad |x| > a$$

Set

$$U + E = \frac{\hbar^2 k^2}{2m} \text{ and } E = \frac{-\hbar^2\kappa^2}{2m}$$

$$k > 0 \qquad \text{and} \qquad \kappa > 0$$

then SE is

$$\psi'' + k^2\psi = 0 \text{ and } \psi'' - \kappa^2\psi = 0$$

$$|x| < a \qquad \text{and} \qquad |x| > a$$

At $x = \pm a$, ψ, ψ' continuous (ψ'' discontinuous, matching step in $V(x)$)

[Integrate SE from $a - \varepsilon$ to $a + \varepsilon$, then provided U, ψ bounded, find $[\psi']_{a-\varepsilon}^{a+\varepsilon} \to 0$ as $\varepsilon \to 0^+$]

Consider *even parity* solutions, ie. those with $\psi(-x) = \psi(x)$,

$$\psi = \begin{cases} A\cos kx & \text{if } |x| < a \\ Be^{-\kappa x} & \text{if } x > a \end{cases}$$

Note the solution for $x < -a$ fixed by parity. Matching at $x = a$,

$$\begin{aligned} \psi \text{ cts } &: A\cos ka = Be^{-\kappa a} \\ \psi' \text{ cts } &: -kA\sin ka = -B\kappa e^{-\kappa a} \end{aligned}$$

These equations give same solution for A or B iff:

$$k\tan ka = \kappa$$

To find when solutions exists it is convenient to set

$$\xi = ak, \quad \eta = a\kappa \quad \text{dimensionless and positive}$$

So

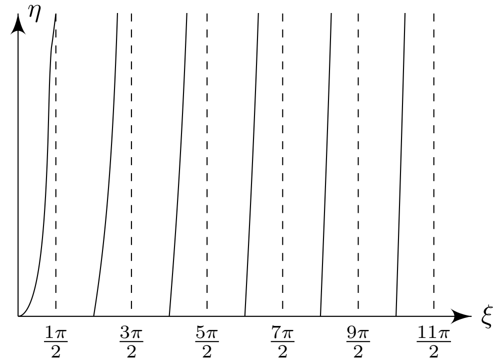
$$\eta = \xi\tan\xi$$

but also

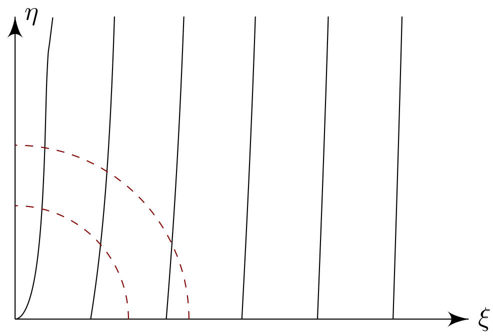
$$\xi^2 + \nu^2 = \frac{2ma^2U}{\hbar^2} \quad \text{from definitions of } k \text{ and } \kappa$$

Intersection of $\nu = \xi\tan\xi$ with circle of $(\text{radius})^2 = \frac{2ma^2U}{\hbar^2}$. Have energy eigenstate for each point of intersection (a, U fixed parameters, determining ξ, ν determines E)

We can look for solutions by plotting these two equations. We first plot the curve $\eta = \xi\tan\xi$:



The other equation is the equation of a circle. Depending on the size of the constant $2ma^2U/\hbar^2$, there will be a different number of points of intersections.



So 1 solution for

$$\frac{2ma^2U}{\hbar^2} < \pi^2$$

and then we have exactly n even parity solutions (for $n \geq 1$).

$$(n-1)^2\pi^2 < \frac{2ma^2U}{\hbar^2} < n^2\pi^2$$

We can do exactly the same thing for odd parity eigenstates. . . on example sheet 1.

3.2 General Properties

Consider t-indep SE for particle of mass m

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

with potential $V(x) \to 0$ (rapidly) as $x \to \pm\infty$

3.2.1 Bond State Energies

From assumption above

$$-\frac{\hbar^2}{2m}\psi'' \sim E\psi \qquad x \to \pm\infty$$

If $E = \frac{\hbar^2 k^2}{2m} > 0$ then $\psi \sim A \pm e^{ikx} + B \pm e^{-ikx}$ as $x \to \pm\infty$.

In this case, no normalisable solution - nevertheless these solutions are of physical interest - Chapter 5.

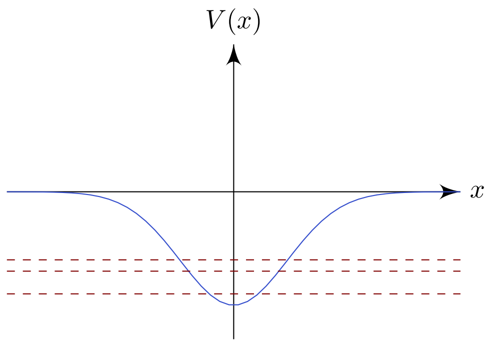
If $\underbrace{E = -\frac{\hbar\kappa^2}{2m}}_{\kappa>0} < 0$ then $\psi \sim A \pm e^{\kappa x} + B \pm e^{-\kappa x}$ as $x \to \pm\infty$.

2nd order ODE so 2 complex constants in general solution.

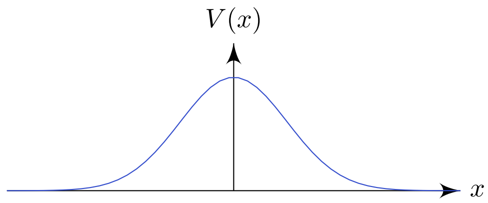
But eqn linear and changing $\psi \to \lambda\psi$ for any complex $\lambda \neq 0$ does not change physical content. Left with one complex degree of freedom

Also, for a normalisable solution we need to fix $A_+ = 0$ and $B_- = 0$, imposing two conditions. Overconstrained problem $\Rightarrow$ solutions exist only for *particular* values of E.

In general, expect bound state energy levels to be *quantised*. May have several solutions.



or none



Furthermore, if $V(x) \geq V_0$ (const) then for normalised ψ with

$$H\psi = E\psi$$

, we have

$$E = \langle H \rangle_\psi$$

$$\begin{aligned}
&= \int_{-\infty}^{\infty} \left(\frac{\hbar^2}{2m} \psi^* \psi'' + \psi^* V(x) \psi \right) \, \mathrm{d}x \\
&= \int_{-\infty}^{\infty} \left(\frac{\hbar^2}{2m} |\psi'|^2 + V(x) |\psi(x)|^2 \right) \, \mathrm{d}x \\
&\geq 0 + \int_{-\infty}^{\infty} V_0 |\psi(x)|^2 \, \mathrm{d}x \\
&= V_0
\end{aligned}$$

So in general have discrete eigenvalues with $0 > E > V_0$

Bound state is a normalisable energy eigenstate. State with lowest energy eigenvalue is called the *ground state*. States with higher energy eigenvalues are often referred to as *excited states*.

3.2.2 Parity

Consider SE with $V(-x) = V(x)$. By changing variables $x \to -x$ find

$$\begin{aligned}
&\psi(x) \text{ eigenstate of } H \text{ with energy } E \\
\iff\ &-\psi(x) \text{ eigenstate of } H \text{ with energy } E
\end{aligned}$$

Assume $\psi(\pm x)$ have same physical content, so that

$$\psi(-x) = \eta\psi(x) \text{ (say)}$$

Then

$$\psi(x) = \eta\psi(-x) = \eta^2\psi(x)$$
$$\Rightarrow \eta^2 = 1 \text{ or } \eta = \pm 1$$

or

$$\psi(-x) = \pm\psi(x)$$

We say that ψ has *even/odd* parity or *parity* $\eta = \pm 1$.
The assumption above is valid for any normalisable ψ (Sheet 1 question 8).
More generally, consider linear combinations of states

$$\psi_\pm(x) = \lambda\left(\psi(x) \pm \psi(-x)\right)$$

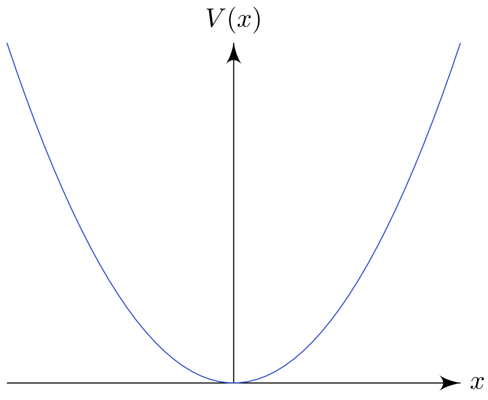
(with λ const) also eigenstates of H with eigenvalues E

$$\psi_\pm(-x) = \pm\psi_\pm(x)$$

so parity ± 1 by construction. For bound states, one of these combinations vanishes.

3.3 Harmonic Oscillator

Particle of mass m in a potential



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

($\omega = \sqrt{k/m}$ to compare with chapter 1 and sheet 1, question 5)
Classically, in general solution

$$x = A\cos\omega(t - t_0)$$

In QM, seek all normalisable solutions of SE:

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

To simplify, put

$$y = \left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}} \qquad \text{dimensionless}$$

SE becomes

$$-\frac{\mathrm{d}^2\psi}{\mathrm{d}y^2} + y^2\psi = \varepsilon\psi \qquad \text{with } \varepsilon = \frac{2E}{\hbar\omega}$$

Behaviour for $y^2 >> \varepsilon$ suggests setting

$$\psi = f(y)e^{-\frac{1}{2}y^2} \qquad \text{(wlog)}$$

and then SE holds iff

$$\frac{\mathrm{d}^2 f}{\mathrm{d}y^2} - 2y\frac{\mathrm{d}f}{\mathrm{d}y} + (\varepsilon - 1)f = 0$$

[y^2 term now absent, by construction]
Now seek series solution

$$f(y) = \sum_{r\geq 0} a_r y^r$$

and substitute

$$\sum_{r\geq 0}\left\{(r+2)(r+1)a_{r+2} + (\varepsilon - 1 - 2r)a_r\right\}y^r = 0$$

$$\iff a_{r+2} = \frac{2r+1-\varepsilon}{(r+2)(r+1)}a_r \qquad r \geq 0$$

This gives two linearly independent series solutions consisting of all even or all odd powers, with overall constants a_0 and a_1

Consider each series separately and examine behaviour of $f(y)$ when y is large. Unless coeffs vanish,

$$\begin{array}{rlll} \text{for even series} & a_{2p}/a_{2p-2} & \sim \frac{1}{p} & p \to \infty \\ \text{for odd series} & a_{2p+1}/a_{2p-1} & \sim \frac{1}{p} & p \to \infty \end{array}$$

which matches behaviour of $y^\alpha e^{y^2}$ for some ∞
eg

$$\sum \frac{1}{p!}y^{2p}, \quad \sum \frac{1}{p!}y^{2p+1}$$

Such behaviour for $f \Rightarrow \psi \sim$ (poly in y) $e^{\frac{1}{2}y^2}$ not normalisable

Hence ψ is a normalisable solution iff series for f terminates, giving a polynomial. This happens iff

$$\varepsilon = 2n + 1 \qquad \text{for } n = 0, 1, 2, \cdots$$

Solutions:

$$\begin{cases} a_{r+2} = \frac{2r-2n}{(r+2)(r+1)} a_r & \text{if } n \text{ even} \\ a_r = 0 & \text{if } n \text{ odd} \end{cases}$$

Solutions

$$f(y) = h_n(y) \text{ poly of degree } n \text{ with}$$

$$h_n(-y) = (-1)^n h_n(y)$$

eg.

$$\begin{aligned} &h_0(y) = a_0 \qquad \varepsilon = 1 \\ &h_1(y) = a_1 y \qquad \varepsilon = 3 \\ &h_2(y) = a_0(1 - 2y^2) \qquad \varepsilon = 5 \\ &h_3(y) = a_1 a_1 (y - \frac{2}{3} y^3) \qquad \varepsilon = 7 \end{aligned}$$

The ODE for f is called *Hermite's equation*, and solutions are *Hermite polynomials*

Restoring constants- harmonic oscillator eigenvalues and eigenfunction are

$$E_n = \hbar\omega(n + \frac{1}{2}) \quad \text{and} \quad \psi_n(x) = h_n\left(\left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}} x\right) e^{-\frac{1}{2}\left(\frac{m\omega}{\hbar}\right)x^2}$$

for $n = 0, 1, 2, \cdots$

There are many important applications of these results.

(i) Any smooth potential can be approximated by an oscillator near a minimum x_0:

$$V(x) \simeq V(x_0) + \frac{1}{2} V''(x_0)(x - x_0)^2 + \cdots$$

frequency

$$\omega = \sqrt{V''(x_0)/m}$$

(ii) Systems with many degrees of freedom e.g. crystals can be analysed by reducing to *normal modes* of oscillation

(iii) Quantised EM fields: one oscillator for each mode of vibration with nth state of this oscillator interpreted as n photons with $E_n - E_0 = n\hbar\omega$

Underlies full explaination (QFT) of wave/particle duality

4 Expectation and Uncetainty

4.1 Hermitian Operators

Recall definition:

$$(\phi, \psi) = \int_{-\infty}^{\infty} \phi(x)^* \, \mathrm{d}x$$

which obeys

$$(\phi, \alpha\psi) = \alpha(\phi, \psi) = (\alpha^*\phi, \psi)$$

and

$$(\phi, \psi) = (\psi, \phi)^*$$

Regrading this as an inner product on wavefns, define the norm $||\psi||$ of a wavefn ψ by

$$||\psi||^2 = (\psi, \psi) = \int_{-\infty}^{\infty} |\psi(x)|^2 \, \mathrm{d}x$$

so ψ normalised iff $||\psi|| = 1$.
An operator Q is *hermitian* if

$$(\psi, Q\psi) = (Q\psi, \psi) \qquad \forall \text{ normalisiable } \psi, \phi$$

or

$$\int_{-\infty}^{\infty} \phi^* Q\psi \, \mathrm{d}x = \int_{-\infty}^{\infty} (Q\phi)^* \psi \, \mathrm{d}x$$

This implies

$$(\psi, Q\psi) = (Q\psi, \psi) = (\psi, Q\psi)^*$$

or

$$\langle Q \rangle_\psi = \langle Q \rangle_\psi^*$$

The operators $\hat{x}$, $\hat{p}$ and $H = \frac{\hat{p}^2}{2m} + V(\hat{x})$ are hermitian for V real.

Proof.

$$\begin{aligned} &(\phi, \hat{x}\psi) = (\hat{x}\phi, \psi) \\ \iff &\int_{-\infty}^{\infty} \phi(x)^*(x\psi(x)) \, \mathrm{d}x \\ \iff &\int_{-\infty}^{\infty} (x\psi(x))^* \phi(x) \, \mathrm{d}x \end{aligned}$$

x real

$$= (\phi, \hat{p}\psi) = (\hat{p}\phi, \psi)$$
$$\iff \int_{-\infty}^{\infty} \phi^*(-i\hbar\psi') \, \mathrm{d}x$$
$$\iff \int_{-\infty}^{\infty} (-i\hbar\phi')^* \psi(x) \, \mathrm{d}x$$

by parts, since $-i\hbar \left[\phi^*\psi\right]_{-\infty}^{\infty}$
To show

$$(\phi, H\psi) = (H\phi, \psi)$$

consider k.e and p.e terms separately
ke
$(\phi, \psi'') = -(\phi', \psi') = (\phi'', \psi)$
pe $(\phi, V(\hat{x})\psi) = (V(\hat{x})\phi, \psi)$ since V real.
This gives better understanding why $< \hat{x} >, < \hat{p} >$ and $< H >$ are real □

4.2 Ehrenfest's Theorem - QM is like classical mechanics

Consider normalised $\Psi(x, t)$ satisfying time-dep SE

$$i\hbar\dot{\Psi} = H\Psi = \left(\frac{1}{2m}\hat{p}^2 + V(\hat{x})\right)\Psi = -\frac{\hbar^2}{2m}\Psi'' + V(x)\Psi$$

The expectation values $< \hat{x} >_\Psi = (\Psi, \hat{x}\Psi)$ and $< \hat{p} >_\Psi = (\Psi, \hat{p}\Psi)$ depend on t through Ψ

Ehrenfest's Thm states

$$\frac{\mathrm{d}}{\mathrm{d}t} < \hat{x} >_\Psi = \frac{1}{m} < \hat{p} >_\Psi$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t} < \hat{p} >_\Psi = - < V'(\hat{x}) >_\Psi$$

quantum counterparts of classical eqns of motion.

Proof.

$$\frac{\mathrm{d}}{\mathrm{d}t} < \hat{x} >_\Psi = (\dot{\Psi}, \hat{x}\Psi) + (\Psi, \hat{x}\dot{\Psi})$$

$$= (\frac{1}{i\hbar}H\Psi, \hat{x}\Psi) + (\Psi, \hat{x}\frac{1}{i\hbar}H\Psi) \qquad \text{SE}$$

$$= \frac{1}{i\hbar}(H\Psi, \hat{x}\Psi) + \frac{1}{i\hbar}(\Psi, \hat{x}H\Psi)$$

$$= \frac{1}{i\hbar}(\Psi, H\hat{x}\Psi) + \frac{1}{i\hbar}(\Psi, \hat{x}H\Psi)$$

$$= \frac{1}{i\hbar}(\Psi, (\hat{x}H - H\hat{x})\Psi)$$

Now

$$
\begin{aligned}
(\hat{x}H - H\hat{x})\Psi &= -\frac{\hbar^2}{2m}(x\Psi'' - (x\Psi)'') + (xV - Vx)\Psi \\
&= -\frac{\hbar^2}{2m}\Psi' = \frac{i\hbar}{m}\hat{p}\Psi \quad \text{as req}
\end{aligned}
$$

Similarly,

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t} < \hat{p} > &= (\dot{\Psi}, \hat{p}\Psi) + (\Psi, \hat{p}\dot{\Psi}) \\
&= (+\frac{1}{i\hbar}H\Psi, \hat{p}\Psi) + (\Psi, \hat{p}\frac{1}{i\hbar}H\Psi) \\
&= \frac{1}{i\hbar}(\Psi, (\hat{p}H - H\hat{p})\Psi)
\end{aligned}
$$

But

$$
\begin{aligned}
(\hat{p}H - H\hat{p})\Psi &= -i\hbar\left(-\frac{\hbar^2}{2m}\right)((\psi'')' - (\psi')'') \\
&= -i\hbar\left((V(x)\Psi)' - V(x)\Psi'\right) \\
&= -i\hbar V'(x)\Psi \qquad \text{as req}
\end{aligned}
$$

In each case it is the *commutator* that appears:

$$\hat{x}H - H\hat{x} \text{ and } \hat{p}H - H\hat{p})\Psi$$

□

4.3 Heisenberg's Uncertainty Relation - QM is NOT like classical mechanics

Statement: If ψ is any normalised state (at fixed time) define the *uncertainty m* position and momentum $(\Delta x)_\psi$ and $(\Delta p)_\psi$ by

$$(\Delta x)^2_\psi = \langle(\hat{x} - \langle\hat{x}\rangle_\psi)^2\rangle_\psi = \langle\hat{x}^2\rangle_\psi - \langle\hat{x}\rangle^2_\psi$$

$$(\Delta p)^2_\psi = \langle(\hat{p} - \langle\hat{p}\rangle_\psi)^2\rangle_\psi = \langle\hat{p}^2\rangle_\psi - \langle\hat{p}\rangle^2_\psi$$

These quantify the 'spread' of possible results. Heisenberg's Uncertainty Relation or Principle, states

$$(\Delta x)_\psi(\Delta p)_\psi \geq \frac{\hbar}{2}$$

Interpretation: we can never reduce combined uncertainty in position and momentum below this threshold.

Note $X = \hat{x} - \alpha$ and $P = \hat{p} - \beta$ both hermitian for any real constants α and β. This implies

$$(\psi, X^2\psi) = (X\psi, X\psi) = ||X\psi||^2 \geq 0$$

and

$$(\psi, P^2\psi) = (P\psi, P\psi) = ||P\psi||^2 \geq 0$$

Choosing $\alpha =< \hat{x} >_\psi$ and $\beta =< \hat{p} >_\psi$ we deduce that $(\Delta x)^2_\psi$ and $(\Delta p)^2_\psi$ are indeed real and positive

Example. Gaussian

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

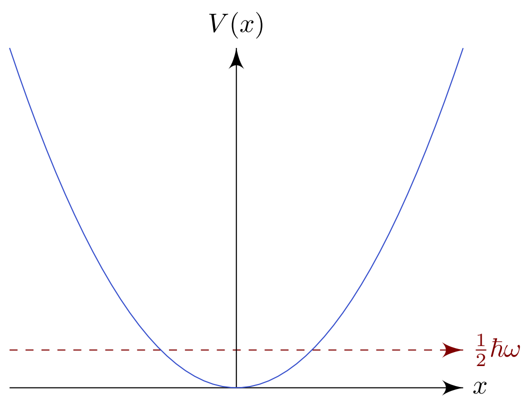
has $\langle\hat{x}\rangle_\psi = \langle\hat{p}\rangle_\psi = 0$
and $(\Delta x)^2_\psi = \frac{\alpha}{2}$ and $(\Delta p)^2_\psi = -\frac{\hbar^2}{2\alpha}$
So

$$(\Delta x)_\psi(\Delta p)_\psi = \frac{\hbar}{2}$$

minimum allowed by Heisenberg.
Furthermore, this is ground state of the Harmonic oscillator for

$$\alpha = \frac{\hbar}{m\omega}$$

Classically, lowest energy from oscillator is when $x = p = 0$.
In QM can't have exact values for x and p in this way, and minimum energy $E_0 = \frac{1}{2}\hbar\omega$ consistent with this.
Particle of mass m in a potential



(a)
Statement:

$$(\Delta x)_\psi(\Delta p)_\psi \geq \frac{\hbar}{2}$$

for any normalisable state ψ

$$(\Delta x)^2_\psi = (X\psi, X\psi)$$

$$(\Delta p)^2_\psi = (P\psi, P\psi)$$

$$X = \hat{x} - <\hat{x}>_\psi$$
$$P = \hat{p} - <\hat{p}>_\psi$$

(b)

Proof. The uncertainty relation follows from the *canonical commutation relation*

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

This holds since

$$\begin{aligned}(\hat{x}\hat{p} - \hat{p}\hat{x})\psi &= x(-i\hbar\psi') + i\hbar(x\psi)' \\ &= i\hbar\psi\end{aligned}$$

as required.
For any normalised ψ, consider

$$\begin{aligned}||(X + i\lambda P)\psi||^2 &= ((X + i\lambda P)\psi, (X + i\lambda P)\psi) \\ &= (X\psi, X\psi) + i\lambda(X\psi, P\psi) - i\lambda(P\psi, X\psi) + \lambda^2(P\psi, P\psi) \geq 0 \text{ for any real } \lambda\end{aligned}$$

But then

$$(\Delta x)^2_\psi + i\lambda(X\psi, P\psi) - i\lambda(P\psi, X\psi) + \lambda^2(\Delta p)^2_\psi \geq 0$$

and

$$\begin{aligned}(X\psi, P\psi) - (P\psi, X\psi) &= (\psi, XP\psi) - (\psi) \text{ since } X \text{ and } P \text{ are Hermitian} \\ &= (\psi, [X, P]\psi) \\ &= (\psi, i\hbar\psi) \\ &= i\hbar\end{aligned}$$

Since $[X, P] = [\hat{x}, \hat{p}] = i\hbar$
Hence

$$(\Delta x)^2_\psi + \lambda^2(\Delta p)^2_\psi - \lambda\hbar \geq 0 \text{ for any real } \lambda$$

In fact, by inspection, $(\Delta x)^2_\psi$ and $(\Delta p)^2_\psi > 0$.
Choosing $\lambda = (\Delta x)_\psi/(\Delta p)_\psi$ then gives the desired result.

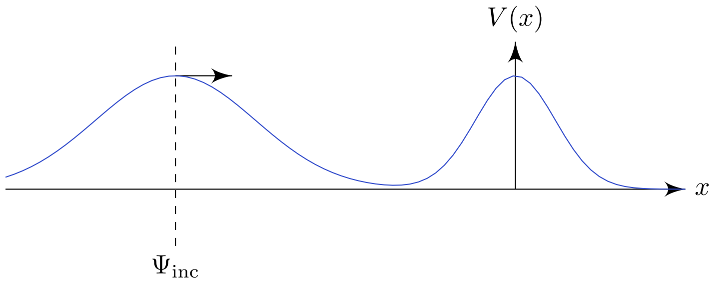
□

5 Scattering in One Dimension

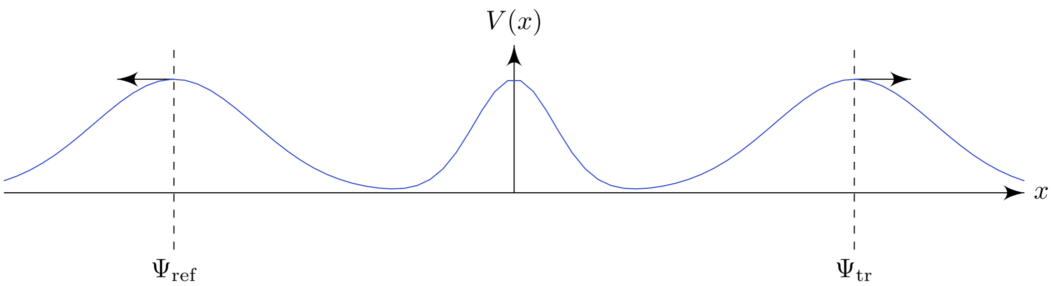
Many interesting physical processes involve a particle fired at a target and being *scattered* (What is the probability of scattering a particular direction?)

In one dimension, we can consider an incident wavepacket Ψ_{inc} interacting with a potential which then evolves into a reflected and a transmitted wavepacket.

"Early times"



"Late times"



Solving the t-dep SE for such a problem is difficult. Seek instead a stationary state solution

5.1 Momentum Eigenstates and Particle Beams

Recall eigenstates of $\hat{p} = -i\hbar\frac{\partial}{\partial x}$ are

$$\psi = Ce^{ikx} \text{ with } \hat{p}\psi = p\psi, \text{ eval } p = \hbar k$$

and these are *not* normalisable on $-\infty < x < \infty$.

Could impose *periodic boundary conditions* $\phi(x + l) = \phi(x)$ and restrict to an interval or "box" $-\frac{l}{2} \leq x \leq \frac{l}{2}$. Then eigenstates can be normalised and we can take $l \to \infty$ after completing calculations.

A convenient alternative is to allow *non-normalisable* but bounded wavefunctions. For $V = 0$:

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

stationary state with $E = \hbar^2k^2/2m$

Interpretation:

(i) beam of particles, each with momentum and $p = \hbar k$ and energy $E = -\hbar^2 k^2/2m$.

(ii) average particle density (number per unit length) is $|C|^2$.

(iii) *Flux* on particles is given by the current

$$\begin{aligned} J &= -\frac{i\hbar}{2m}(\Psi^*\Psi' - \Psi'^*\Psi) \qquad \text{(number passing a given point per unit time)} \\ &= |C|^2 \frac{\hbar k}{m} \qquad \text{(number density times velocity)} \end{aligned}$$

Moreover, superposition of beams

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

$p = \hbar k$, $p = -\hbar k$ same energy.

$$\Rightarrow J(x,t) = |C_+|^2 \frac{\hbar k}{m} + |C_-|^2 \left(-\frac{\hbar k}{m}\right) \qquad \text{(cross terms cancel)}$$

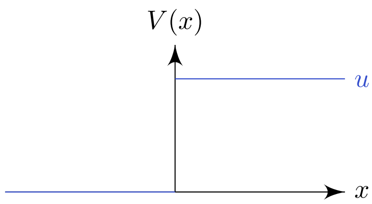
(iv) Probabilities are calculated by comparing fluxes.

To justify assumptions and interpretations using beams, we can refer back to one-particle description in a box.

5.2 Potential Step

Consider solution $\Psi(x,t) = \phi(x)e^{-iEt/\hbar}$ to SE with potential

$$V(x) = \begin{cases} 0 & \text{if } x \leq 0 \\ u & \text{if } x > 0 \end{cases}$$



ϕ satifies t dep SE
ϕ, ϕ' continuous at $x = 0$
Current

$$J = -\frac{i\hbar}{2m}(\psi^*\psi' - \psi'^*\psi)$$

(i) $E > U$

Set

$$E = \frac{\hbar^2 k^2}{2m} \qquad E - U = \frac{\hbar^2 l^2}{2m} \quad (k, l > 0)$$

SE becomes

$$\phi'' + k^2\phi = 0 \qquad \phi'' + l^2\phi = 0$$

$$x < 0 \qquad x > 0$$

$$\Rightarrow \phi = Ie^{ikx} + Re^{-ikx} \qquad \phi = Te^{ilx}$$

(No e^{-ilx} term $\iff$ no particles sent from right)

Match at $x = 0$

$$\phi \text{ continuous } I + R = T$$
$$\phi' \text{ continuous } ikI - ikR = ilT$$

$$\Rightarrow R = \frac{k-l}{k+l} I \qquad T = \frac{2k}{k+l} I$$

Current

$$\begin{aligned} J &= J_{\text{inc}} + J_{\text{ref}} \\ &= (|I|^2 - |R|^2)\frac{\hbar k}{m} \qquad (x < 0) \end{aligned}$$

and

$$J = |T|^2 \frac{\hbar l}{m} \qquad (x > 0)$$

Probability of reflection

$$P_{\text{ref}} = \frac{|J_{\text{ref}}|}{|J_{\text{inc}}|} = \frac{|R|^2}{|I|^2} = \left(\frac{k-l}{k+l}\right)^2$$

Probability of transmission

$$P_{\text{tr}} = \frac{|J_{\text{tr}}|}{|J_{\text{inc}}|} = \frac{|T|^2}{|I|^2}\frac{l}{k} = \frac{4kl}{(k+1)^2}$$

(ii) $0 < E < U$

Set

$$E = \frac{\hbar^2 k^2}{2m} \qquad U - E = \frac{\hbar^2 \lambda^2}{2m} \qquad (k, \lambda > 0)$$

SE becomes

$$\phi'' + k^2\phi = 0 \qquad \phi'' - \lambda^2\phi = 0$$

$$x < 0 \qquad x > 0$$

Interpret as inc, ref beams with

$$\begin{aligned} J &= J_{\text{inc}} + J_{\text{ref}} \\ &= |I|^2 \frac{\hbar k}{m} + |R|^2 \left(-\frac{\hbar k}{m}\right) \end{aligned}$$

for $x < 0$, and $J = 0$ for $x > 0$.

Match solutions at $x = 0$

$$\phi \text{ continuous } I + R = c$$
$$\phi' \text{ continuous } ikI - ikR = -\lambda c$$

$$\Rightarrow R = \frac{k - i\lambda}{k + i\lambda} I \qquad c = \frac{2k}{k + i\lambda} I$$

Probability of reflection

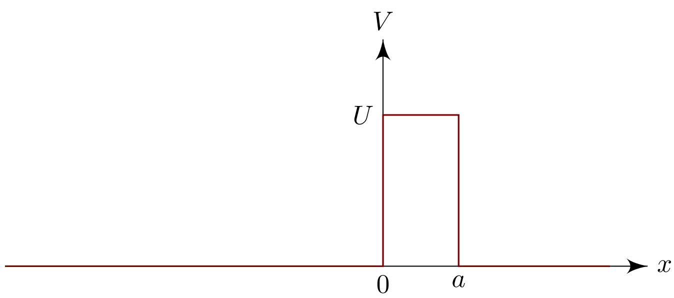
$$P_{\text{ref}} = \frac{|J_{\text{ref}}|}{|J_{\text{inc}}|} = \frac{|R|^2}{|I|^2} = 1$$

All particles reflected: consistent with $J_{\text{tr}} = 0$.

Note that in case (i), non-zero probability of reflection, contrary to classical explanation. In case (ii) all particles reflected but $\psi \neq 0$ for $(x > 0)$.

5.3 Potential Barrier and Tunneling

Consider the following potential:



$$V(x) = \begin{cases} 0 & x \leq 0 \\ U & 0 < x < a \\ 0 & x \geq a \end{cases}$$

We consider a stationary state with energy E with $0 < E < U$. We set the constants

$$E = \frac{\hbar^2 k^2}{2m}, \quad U - E = \frac{\hbar^2 \kappa^2}{2m}.$$

Then the Schrödinger equations become

$$\begin{aligned} \psi'' + k^2\psi &= 0 && x < 0 \\ \psi'' - \kappa^2\psi &= 0 && 0 < x < a \\ \psi'' + k^2\psi &= 0 && x > a \end{aligned}$$

So we get

$$\begin{aligned} \psi &= Ie^{ikx} + Re^{-ikx} && x < 0 \\ \psi &= Ae^{\kappa x} + Be^{-\kappa x} && 0 < x < a \\ \psi &= Te^{ikx} && x > a \end{aligned}$$

Matching ψ and ψ' at $x = 0$ and a gives the equations

$$\begin{aligned} I + R &= A + B \\ ik(I - R) &= \kappa(A - B) \\ Ae^{\kappa a} + Be^{-\kappa a} &= Te^{ika} \\ \kappa(Ae^{\kappa a} - Be^{-\kappa a}) &= ikTe^{ika}. \end{aligned}$$

We can solve these to obtain

$$\begin{aligned} I + \frac{\kappa - ik}{\kappa + ik}R &= Te^{ika}e^{-\kappa a} \\ I + \frac{\kappa + ik}{\kappa - ik}R &= Te^{ika}e^{\kappa a}. \end{aligned}$$

After ~~lots of~~ *some* algebra, we obtain

$$T = Ie^{-ika}\left(\cosh \kappa a - i\frac{k^2 - \kappa^2}{2k\kappa}\sinh \kappa a\right)^{-1}$$

To interpret this, we use the currents

$$j = j_{\text{inc}} + j_{\text{ref}} = (|I|^2 - |R|^2)\frac{\hbar k}{m}$$

for $x < 0$. On the other hand, we have

$$j = j_{\text{tr}} = |T|^2\frac{\hbar k}{m}$$

for $x > a$. We can use these to find the transmission probability, and it turns out to be

$$P_{\text{tr}} = \frac{|j_{\text{tr}j}|}{|j_{\text{inc}}|} = \frac{|T|^2}{|I|^2} = \left[1 + \frac{U^2}{4E(U - E)}\sinh^2 \kappa a\right]^{-1}.$$

This demonstrates *quantum tunneling*. There is a non-zero probability that the particles can pass through the potential barrier even though it classically does not have enough energy. In particular, for $\kappa a \gg 1$, the probability of tunneling decays as $e^{-2\kappa a}$. This is important, since it allows certain reactions with high potential barrier to occur in practice even if the reactants do not classically have enough energy to overcome it.

5.4 General features of stationary states

We are going to end the chapter by looking at the difference between bound states and scattering states in general.

Consider the time-independent Schrödinger equation for a particle of mass m

$$H\psi = -\frac{\hbar^2}{2m}\psi'' + V(x)\psi = E\psi,$$

with the potential $V(x) \to 0$ as $x \to \pm\infty$. This is a second order ordinary differential equation for a complex function ψ, and hence there are two complex constants in general solution. However, since this is a linear equation, this implies that 1 complex constant corresponds to changing $\psi \mapsto \lambda\psi$, which gives no change in physical state. So we just have one constant to mess with.

As $|x| \to \infty$, our equation simply becomes

$$-\frac{\hbar^2}{2m}\psi'' = E\psi.$$

So we get

$$\psi \sim \begin{cases} Ae^{ikx} + Be^{-ikx} & E = \frac{\hbar^2 k^2}{2m} > 0 \\ Ae^{\kappa x} + Be^{-\kappa x} & E = -\frac{\hbar^2 \kappa^2}{2m} < 0. \end{cases}$$

So we get two kinds of stationary states depending on the sign of E. These correspond to bound states and scattering states.

Bound state solutions, $E < 0$

If we want ψ to be normalizable, then there are 2 boundary conditions for ψ:

$$\psi \sim \begin{cases} Ae^{\kappa x} & x \to -\infty \\ Be^{-\kappa x} & x \to +\infty \end{cases}$$

This is an overdetermined system, since we have too many boundary conditions. Solutions exist only when we are lucky, and only for certain values of E. So bound state energy levels are quantized. We may find several bound states or none.

Definition (Ground and excited states)**.** The lowest energy eigenstate is called the *ground state*. Eigenstates with higher energies are called *excited states*.

Scattering state solutions, $E > 0$

Now ψ is not normalized but bounded. We can view this as particle beams, and the boundary conditions determines the direction of the incoming beam. So we have

$$\psi \sim \begin{cases} Ie^{ikx} + Re^{-ikx} & x \to -\infty \\ Te^{ikx} & x \to +\infty \end{cases}$$

This is no longer overdetermined since we have more free constants. The solution for any $E > 0$ (imposing condition on one complex constant) gives

$$j \sim \begin{cases} j_{\mathrm{inc}} + j_{\mathrm{ref}} \\ j_{\mathrm{tr}} \end{cases} = \begin{cases} |I|^2 \frac{\hbar k}{m} - |R|^2 \frac{\hbar k}{m} & x \to -\infty \\ |T|^2 \frac{\hbar k}{m} & x \to +\infty \end{cases}$$

We also get the reflection and transmission probabilities

$$\begin{aligned} P_{\mathrm{ref}} &= |A_{\mathrm{ref}}|^2 = \frac{|j_{\mathrm{ref}}|}{|j_{\mathrm{inc}}|} \\ P_{\mathrm{tr}} &= |A_{\mathrm{tr}}|^2 = \frac{|j_{\mathrm{tr}}|}{|j_{\mathrm{inc}}|}, \end{aligned}$$

where

$$\begin{aligned} A_{\mathrm{ref}}(k) &= \frac{R}{I} \\ A_{\mathrm{tr}}(k) &= \frac{T}{I} \end{aligned}$$

are the reflection and transmission *amplitudes*. In quantum mechanics, "amplitude" general refers to things that give probabilities when squared.

6 Axioms of Quantum Mechanics

We now consider quantum systems more generally, with abstract states ψ, ψ (at fixed time) or $\Psi(t), \Phi(t)$ - no longer restricted to one dimension. We will describe any such system in terms of axioms and then recover (P1),(P2),(P3).

6.1 States and Operators

Axiom (A1): State's not of a quantum system correspond to non-zero elemnets of complex vector space V, with ψ and ϕ physically equivalent for $\alpha \neq 0$. Furthermore,

(i) A complex inner product (ψ, ϕ) is defined on V with

$$
\begin{aligned}
(\phi, \alpha_1\psi_1 + \alpha_2\psi_2) &= \alpha_1(\phi, \psi_1) + \alpha_2(\phi, \psi_2) \\
(B_1\phi_1 + B_2\phi_2, \psi) &= B_1^*(\phi_1, \psi) + B_2^*(\phi_2, \psi) \\
(\phi, \psi) &= (\psi, \phi)^* \\
||\psi^2|| := (\psi, \psi) &\geq 0 \qquad \text{and } = 0 \text{ iff } \psi = 0
\end{aligned}
$$

(ii) V is *complete*: well-behaved series (Cauchy sequences) converge. V typically infinite dimensional, a Hilbert space.

An *operator* (or linear operator) is a linear map $V \to V$

$$A(\alpha\psi + \beta\phi) = \alpha A\psi + \beta A\phi$$

Axiom(A2): A measurable quantity or *observable* corresponds to *Hermitian* operator on V. Mathematical elaboration: for any vector A, the *hermitian conjugate* $A^\dagger$ is defined by

$$(A^\dagger, \psi) = (\phi, A\psi) \qquad \forall \phi, \psi$$

It follows that

$$(\alpha A + \beta B)^\dagger = \alpha^* A^\dagger + \beta^* B^\dagger$$

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

An operator Q is *hermitian* if $Q^\dagger = Q$ (also called self-adjoint)
Axiom (A3): The state of the system $\Psi(t)$ obeys the Schrödinger Equation

$$i\hbar\dot{\Psi} = H\Psi$$

where H is a hermitian operator, the *Hamilotian.*
This holds *except* at the instant when a measurement is made (see below)

6.2 Observables and Measurements

A state $\chi (\neq 0)$ is an *eigenstate* of an operator Q with eigenvalue λ if

$$Q\chi = \lambda\chi$$

The set of all eigenvalues of Q is called the *spectrum.*

6.2.1 Key Results for Hermitian Operators

Let Q be hermitian ($Q^\dagger = Q$). Then

(i) Eigenvalues of Q are real

Proof. if $Q\chi = \lambda\chi$ then

$$\begin{aligned} &(\chi, Q\chi) = (Q\chi, \chi) \qquad (Q^\dagger = Q) \\ \Rightarrow\ &(\chi, \lambda\chi) = (\lambda\chi, \chi) \\ \Rightarrow\ &\lambda(\chi, \chi) = \lambda^*(\chi, \chi) \end{aligned}$$

□

(ii) Eigenstates of Q with different eigenvalues are orthogonal wrt. the inner product.

Proof.

$$\left\{ \begin{aligned} Q\chi &= \lambda\chi \\ Q\phi &= \mu\phi \end{aligned} \right. \text{ then}$$

$$\begin{aligned} &(\phi, Q\chi) = (Q\phi, \chi) \\ \Rightarrow\ &(\phi, \lambda\chi) = (\mu\phi, \chi) \\ \Rightarrow\ &\lambda(\phi, \chi) = \mu(\phi, \chi) \end{aligned}$$

So $\lambda \neq \mu \Rightarrow (\phi, \chi) = 0$

□

(iii) Any state can be expressed as a linear combination (in general an finite sum) of eigenstates of Q. Eigenstates of Q provide a *basis* for V, or set of eigenstates is *complete*.

We will not attempt to justify (iii) or to discuss issues of convergence.

6.2.2 Measurement Axioms

Consider an observable Q with discrete spectrum and normalised eigenstates and eigenvalues labelled by n, such that

$$Q\chi_n = \lambda_n\chi_n \qquad (\chi_m, \chi_n) = \delta_{mn}$$

From part (a) any state can be written

$$\psi = \sum_n \alpha_n\chi_n \qquad \text{with } \alpha_n = (\chi_n, \psi)$$

Assume that the eigenvalues are distinct ($\lambda_n \neq \lambda_m$ for $m \neq n$). Suppose Q is measured when the system is in a normalised state ψ as above. Then

Axiom (M1): The outcome of the measurement is some eigenvalue of Q
Axiom (M2): The probability of obtaining λ_n is

$$P_n = |\alpha_n|^2 \qquad \text{where } \alpha_n = (\chi_n, \psi) \text{is called the } \textit{amplitude}$$

Axiom (M3): The measurement is instantaneous and it forces the system into the state χ_n: this is the state immediately after the result λ_n is obtained.

This implies that if Q is measured again immediately afterwards, then λ_n is obtained again with probability one

Note

(i) ψ normalised $\Rightarrow$

$$\begin{aligned}(\psi, \psi) &= (\sum_n \alpha_n \chi_n, \sum_m \alpha_m \chi_m) \\ &= \sum_{n,m} \alpha_n^* \alpha_m (\chi_n, \chi_m) \\ &= \sum_n |\alpha_n|^2 \\ &= \sum_n P_n = 1\end{aligned}$$

(ii) Postulate (P3) follows immediately: if $\alpha_k = 1$ and $\alpha_n = 0$ $n \neq k$, then λ_k is obtained with probability 1. $(\psi = \lambda_k)$

Example. (Harmonic Oscillator, see 3.3) with $Q = H$, $\chi_n = \psi_n$, $\lambda_n = E_n = \hbar\omega(n + \frac{1}{2})$ for $n = 0, 1, 2, \cdots$

Suppose

$$\psi = \frac{1}{\sqrt{6}}(\psi_0 + 2\psi_1 - i\psi_4)$$

is state of system.

$\alpha_0 = \frac{1}{\sqrt{6}}$, $\alpha_1 = \frac{2}{\sqrt{6}}$, $\alpha_4 = \frac{-i}{\sqrt{6}}$ and $\alpha_n = 0$ else.

Measuring energy gives result:

$E_0 = \frac{1}{2}\hbar\omega$ with probability $P_0 = \frac{1}{6}$ or $E_1 = \frac{3}{2}\hbar\omega$ with probability $P_1 = \frac{2}{3}$ or $E_4 = \frac{9}{2}\hbar\omega$ with probability $P_4 = \frac{1}{6}$ and probability 0 for any other result.

6.2.3 Expressions for Expectation and Uncertainty

(i) The expectation value of Q in a normalised state ψ is

$$\langle Q \rangle_\psi = (\psi, Q\psi) = \sum_n \lambda_n P_n$$

(usual definition of mean). All notation as in part 6.2.2 above

Proof.

$$\psi = \sum_m \alpha_m \chi_m \Rightarrow Q\psi = \sum_m \alpha_m \lambda_m \chi_m$$
$$\Rightarrow (\psi, Q\psi) = \sum_{m,n} (\alpha_n \chi_n, \alpha_m \lambda_m \chi_m) = \sum_n |\alpha_n|^2 \lambda_n \text{ as expected}$$

□

This justifies (P2): Note: $\langle Q \rangle_\psi$ is the average result of a large number of measurements of Q (N, with $N \to \infty$) with the system prepared in state ψ each time. (contrast this with (M3)).

Example. (Harmonic Oscillator with details as above)

$$\langle H \rangle_\psi = \sum_n E_n P_n = (\frac{1}{2} \times \frac{1}{6} + \frac{3}{2} \times \frac{2}{3} + \frac{9}{2} \times \frac{1}{6}) \hbar\omega = \frac{11}{6} \hbar\omega$$

(ii) The uncertainty $(\Delta Q)_\psi$ is given by

$$(\Delta Q)_\Psi = \langle (Q - \langle Q \rangle_\psi)^2 \rangle_\psi = \langle Q^2 \rangle_\psi - \langle Q \rangle_\psi^2 = \sum_n (\lambda_n \langle Q \rangle_\psi)^2 P_n$$

Proof. Check directly form first expression above □

6.3 Discrete and Continuous Spectra

In statement measurement axioms we assumed spectrum of Q discrete. For a particle in 1d, spectra of $\hat{p}$ and H may be continuous, but can be made discrete as in section 5.1 : impose periodic boundary conditions ($\psi(x) = \psi(x + l)$ and confine to box $-l/2 \leq x \leq 1/2$)

Example. $Q = \hat{p} = -i\hbar \frac{\mathrm{d}}{\mathrm{d}x}$ (particle in 1d)
eigenstates $\chi_n(x) = \frac{1}{\sqrt{l}} e^{ik_n x}$ with $k_n = \frac{2\pi n}{l}$, $n \in \mathbb{Z}$, and eigenvalues $\lambda_n = \hbar k_n$. These states are indeed orthonormal.

$$(\chi_m, \chi_n) = \int_{-l/2}^{l/2} \chi_m(x)^* \chi_n(x) \, \mathrm{d}x = \delta_{mn}$$

Expansion of a general state in terms of eigenstates:

$$\psi(x) = \sum_n \alpha_n \chi_n(x) \text{ with } \alpha_n(\chi_n, \psi) = \int_{-l/2}^{l/2} \frac{1}{\sqrt{l}} e^{-ik_n x} \psi(x) \, \mathrm{d}x$$

ie a complex Fourier series with Fourier coefficients.

6.3.1 Alternative Approach (Non Examiniable)

Extend from discrete to continuous spectra by replacing discrete label n with continuous label ξ and $\sum_n \to \int \mathrm{d}\xi$, $\delta_{mn} \to \delta(\xi - \nu)$.

Then orthonormal eigenstates of Q satisfy

$$Q\chi_\xi = \lambda_\xi \chi_\xi \quad \text{with} \quad (\chi_\xi, \chi_\iota) = \delta(\xi - \eta)$$

Expansion in terms of eigenstates becomes

$$\psi = \int \alpha_\xi \chi_\xi \, \mathrm{d}\xi \quad \text{with} \quad \alpha_\xi = (\chi_\xi, \psi)$$

$P_\xi = |\alpha_\xi|^2$ is now probability density with

$$\int_a^b P_\xi \, \mathrm{d}\xi \text{ probability that result corresponds } a \leq \xi \leq b$$

Example. (i) $Q = \hat{p}$, have $\xi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$, $-\infty < p < \infty$. ($\lambda_p = p$). Note

$$(\chi_p, \chi_q) = \frac{1}{2\pi\hbar} \int e^{i(p-q)x/\hbar} \, \mathrm{d}x = \delta(p - q)$$

Now

$$\psi(x) = \int_{-\infty}^{\infty} \alpha_p \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} \, \mathrm{d}p$$

with

$$\alpha_p = \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi\hbar}} e^{-ipx/\hbar} \psi(x) \, \mathrm{d}x$$

Fourier representation transform

(ii) $Q = \hat{x}$ have eigenstates $\chi_\xi(x) = \delta(x - \xi)$ with eigenvalue $\lambda_\xi = \xi$ since $\hat{x} X_\xi(x) = x\delta(x - \xi) = \xi\delta(x - \xi) = \xi\chi_\xi(x)$

Then

$$\begin{aligned}
\psi(x) &= \int_{-\infty}^{\infty} \alpha_\xi \chi_\xi(x) \, \mathrm{d}\xi \\
&= \int_{-\infty}^{\infty} \alpha_\xi \delta(x - \xi) \, \mathrm{d}\xi \\
&= \alpha_x
\end{aligned}$$

So $\int_a^b P_\xi \, \mathrm{d}\xi = \int_a^b |\alpha_\xi|^2 \, \mathrm{d}\xi = \int_a^b |\psi(\xi)|^2 \, \mathrm{d}\xi$

probability of measuring position to be in range $a \leq x \leq b$

Hence we recover (P1)

6.4 Evolution in Time

6.4.1 Stationary States

Consider energy eigenstates ψ_n with

$$H\psi_n = E_n\psi_n \text{ and } (\psi_m, \psi_n) = \delta_{mn}$$

Then $\psi_n e^{iE_n t/\hbar}$ is a solution of t-dep SE for any n. This, or ψ_n, called a stationary state. Given any initial state (not necc stationary) we can expand

$$\Psi(0) = \sum_n \alpha_n \psi_n \qquad \text{with } \alpha_n = (\psi_n, \Psi(0))$$

By linearity, the solution of the SE is

$$\Psi(t) = \sum_n \alpha_n \psi_n e^{-iE_n t/\hbar}$$

6.4.2 General Form of Ehrenfest's Theorem

If Q is any observable (with no explicit time dependence) for a quantum system with state $\Psi(t)$, then

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle Q\rangle_{\Psi(t)} = \langle\ \frac{1}{i\hbar}[Q, H]\ \rangle_{\Psi(t)}$$

where $[Q, H] = QH - HQ$, the commutator.

Proof. Use SE and follow the same steps as for particle in 1d. □

This closely resembles equation of motion in Hamiltonian formalism

6.5 Degeneracy and Simultaneous Measurements

6.5.1 Degeneracy

For an observable Q, the number of linearly independent states with eigenvalue λ is called the *degeneracy* of λ; this is the dimension of the *eigenspace* $V_\lambda = \{\psi : Q\psi = \lambda\psi\}$. Also say eigenvalue λ is non-degenerate iff the degeneracy $= 1$. The eigenvalues are degenerate iff the degeneracy > 1.

Also say *states* are degenerate if they have the same eigenvalue.

Physically - cannot distinguish degenerate states by measuring Q alone. We are free to chose any orthonormal basis of states for each V_λ.

Consider discussion leading to (M1), (M2), (M3) and use same notation. If there is degeneracy then:

(M2)' Probability of measuring λ is $\sum_{n:\lambda_n=\lambda} P_n = \sum_{n:\lambda_n=\lambda} |\alpha_n|^2$.

(M3)' State after such a measurement is

$$(\text{ const }) \sum_{n:\lambda_n=\lambda} \alpha_n \chi_n$$

Measurement projects onto the eigenspace V_λ

6.5.2 Commuting Observables and Simultaneous Measurements

Observables A and B (hermitian operators) can be measured simultaneously iff there exist a basis for V (space of states) consisting of *simultanous* or *joint* eigenstates χ_n which are simply eigenstates of both operators.

$$A\chi_n = \lambda_n \chi_n \text{ and } B_n \chi_n = \mu_n \chi_n$$

Measurement axioms $\Rightarrow$ with system in state χ_n we can measure A, B in any order, in rapid succession and get results λ_n, μ_n (respectively) with probability 1 each time.

A neccessary and sufficient condition for A and B to be simultaneously measurable is

$$[A, B] = AB - BA = 0$$

Proof. Necessity: For any joint eigenstate,

$$AB\chi_n = BA\chi_n = \lambda_n \mu_n \chi_n \Rightarrow [A, B]\chi_n = 0$$

Since this holds for all n, and χ_n form a basis for V, we deduce that $[A, B] = 0$.

Sufficiency: For any eigenvalue λ of A, consider the eigenspace $V_\lambda = \{\psi \mid A\psi = \lambda\psi\}$, ie. the subspace of V containing all the corresponding eigenstates. If $[A, B] = 0$ then

$$A\psi = \lambda\psi \Rightarrow A(B\psi) = B(A\psi) = B(\lambda\psi) = \lambda(B\psi)$$

Hence, for every λ, B maps V_λ to itself. Now V is the direct sum of eigenspaces V_λ over all possible eigenvalues λ (since V is spanned by eigenstates of A).

Furthermore, *any* choice of basis for each V_λ gives a choice of basis for the entire space V. But since B is Hermitian on V, it is also Hermitian as an operator on each subspace of V_λ.

It follows that V_λ has a basis of eigenstates of B, all with a common eigenvalue λ under A, by definition, and so all of which are joint eigenstates. Since this holds for every V_λ, this provides a basis of joint eigenstates for V, as required. □

A simple case of the argument for sufficiency applies if the eigenvalues of A are non-degenerate. Then each V_λ is one-dimensional and, since B maps V_λ to itself, we must have $B\psi = \mu\psi$ for some μ.

A related result in the *Generalised Uncertainty Relation/Principle*

$$\langle \Delta A \rangle_\psi \langle \Delta B \rangle_\psi \geq \frac{1}{2} |\langle [A, B] \rangle_\psi|$$

Any number of observables $A, B, \cdots, Q$ can be measured simultaneously if every pair commutes. A *complete commuting set* of observables is one for which the eigenvalues specify the basis states uniquely.

7 Quantum Mechanics in Three Dimensions

7.1 Introduction

- Quantum state of particle in 3d is a wavefunction

$$\begin{array}{cc} \psi(\mathbf{x}) \quad \text{or} & \Psi(\mathbf{x}, t) \\ \text{at fixed time} & \text{as } t \text{ varies} \end{array}$$

- Inner product

$$(\phi, \psi) = \int \phi(\mathbf{x})^* \psi(\mathbf{x}) \, \mathrm{d}^3\mathbf{x}$$

(integrate over all space if limits left out)

- If ψ normalised

$$(\psi, \psi) = \int |\psi(\mathbf{x})|^2 \, \mathrm{d}^3\mathbf{x} = 1$$

then

$$|\psi(\mathbf{x})|^2 \delta V$$

is the probability of measuring particle to be in small volume δV at x.

- Position and Momentum operators

$$\hat{\mathbf{x}} = (\hat{x}_1, \hat{x}_2, \hat{x}_3)$$

$$\hat{\mathbf{p}} = (\hat{p}_1, \hat{p}_2, \hat{p}_3)$$

$$= -i\hbar\nabla = -i\hbar \left(\frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \frac{\partial}{\partial x_3} \right)$$

- Canonical commutation relations

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

- Uncertainty relation

$$(\Delta x_i)(\Delta p_i) \geq \hbar/2 \qquad \text{fixed } i \text{(no sum)}$$

- Structureless particle $\Rightarrow$ all observables are functions of position and momentum. For particle of mass m in potential V have Hamiltonian

$$\begin{aligned} H &= \frac{1}{2m}\hat{\mathbf{p}}^2 + V(\hat{\mathbf{x}}) \\ &= -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x}) \end{aligned}$$

Example. Free particle ($V = 0$), consider $\psi = Ce^{i\mathbf{k}\cdot\mathbf{x}}$ (plain waves).

Joint eigenstates of momentum ops:

$$\hat{p}_i\psi = \hbar k_i \psi$$

and Hamiltonian

$$H\psi = -\frac{\hbar^2\mathbf{k}^2}{2m}\psi$$

These wavefunctions not normalisable but can be used in scattering problems.

– Time -dep SE

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

– Probability current in 3d

$$\mathbf{J} = -\frac{i\hbar}{2m}(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*)$$

satisfies

$$\frac{\partial}{\partial t}|\Psi(\mathbf{x},t)|^2 = -\nabla\cdot J \qquad \text{from SE}$$

This imples that

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_V \Psi(\mathbf{x},t)|^2\mathrm{d}^3\mathbf{x} &= \int_V -\nabla\cdot\mathbf{J}\mathrm{d}^3\mathbf{x}\\ &= -\int_{\delta V}\mathbf{J}\cdot\mathrm{d}\mathbf{S} \quad \text{by Divergence Thm}\end{aligned}$$

for any fixed volume V. With boundary conditions such that $|\Psi| \to 0$ suff rapidly as $|\mathbf{x}| \to \infty$, get

$$\frac{\mathrm{d}}{\mathrm{d}t}|\Psi(\mathbf{x},t)|^2\ \mathrm{d}^3\mathbf{x} = 0$$

– Seek stationary state/energy eigenfunction solutions for various V

$$\Psi(\mathbf{x},t) = \psi(\mathbf{x})e^{-iEt/\hbar}, \quad \text{where } H\psi = E\psi$$

7.2 Separable Solutions in Cartesian Coordinates

Consider t-indep SE in 2d with

$$H\psi = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right) + V(x_1,x_2)\psi = E\psi$$

For a potential of the form

$$V(x_1,x_2) = U_2(x_1) + U_2(x_2)$$

then

$$H = H_1 + H_2$$

with

$$H_i = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_i^2} + U_i(x_i) \qquad i = 1, 2$$

Look for separable solutions

$$\psi = \chi_1(x_1)\chi_2(x_2)$$

SE $\Rightarrow$

$$\underbrace{\left(-\frac{\hbar^2}{2m}\frac{\chi_1''}{\chi_1} + U_1\right)}_{=E_1} + \underbrace{\left(-\frac{\hbar^2}{2m}\frac{\chi_2''}{\chi_2} + U_2\right)}_{=E_2} = E$$

Since each term is independent of x_1 and x_2, there are separation constants E_1 and E_2 as shown. Note

$$H_1\chi_1 = E_1\chi_1 \text{ and } H_2\chi_2 = E_2\chi_2$$

Also, $[H_1, H_2] = 0$ so method amounts to finding joint eigenstates of H_1 and H_2, with $E = E_1 + E_2$.

Example. $U_i(x_i) = \frac{1}{2}m\omega^2 x_i^2$
Then
$H_i = H_0(x_i)$ with H_0 the oscillator Hamiltonian
where $H_0\psi_n = \hbar\omega(n + 1/2)\psi_n$, $n = 0, 1, 2, \cdots$

$$\begin{aligned}
\chi_1 &= \psi_{n_1}(x_1) \\
\chi_2 &= \psi_{n_2}(x_2) \\
E_i &= \hbar\omega(n_i = 1/2) \\
E &= E_1 + E_2 = \hbar\omega(n_1 + n_2 + 1)
\end{aligned}$$

for $\psi(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2)$.
Ground state $E = \hbar\omega$, $\psi = \psi_0(x_1)\psi_0(x_2)$.
1^{st} excited states, $E = 2\hbar\omega$, $\psi = \psi_1(x_1)\psi_0(x_2)$ or $\psi_0(x_1)\psi_1(x_2)$ with degeneracy 2

7.3 Angular Momentum

7.3.1 Definitions

Angular momentum in QM is a vector of operators

$$\mathbf{L} = \hat{\mathbf{x}} \times \hat{\mathbf{p}} = -i\hbar\mathbf{x} \times \nabla$$

or in components

$$L_i = \varepsilon_{ijk}\hat{x}_j\hat{p}_k = -i\hbar\varepsilon_{ijk}x_j\frac{\partial}{\partial x_k}$$

ie.

$$L_3 = \hat{x}_1\hat{p}_2 - \hat{x}_2\hat{p}_1 = -i\hbar\left(x_1\frac{\partial}{\partial x_2} - x_2\frac{\partial}{\partial x_1}\right)$$

The *total* angular momentum operator is

$$L^2 = \mathbf{L}^2 = L_iL_i = L_1^2 + L_2^2 + L_3^2$$

These operators are hermitian
eg.

$$\begin{aligned}
L_3^\dagger &= (\hat{x}_1\hat{p}_2 - \hat{x}_2\hat{p}_1)^\dagger \\
&= \hat{p}_2^\dagger\hat{x}_1^\dagger - \hat{p}_1^\dagger\hat{x}_2^\dagger \\
&= \hat{p}_2\hat{x}_1 - \hat{p}_1\hat{x}_2 \\
&= \hat{x}_1\hat{p}_2 - \hat{x}_2\hat{p}_1
\end{aligned}$$

In the above, we used the general result

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

Furthermore,

$$\begin{aligned}
(\mathbf{L}^2)^\dagger &= (L_1^2)^\dagger + (L_2^2)^\dagger + (L_3^2)^\dagger \\
&= L_1^2 + L_2^2 + L_3^2 \\
&= \mathbf{L}^2
\end{aligned}$$

7.3.2 Commutation Relations

(i)

$$[L_i, L_j] = i\hbar\varepsilon_{ijk}L_k$$

ie. $[L_1, L_2] = i\hbar L_3$ and cyclic perms

(ii) $[\mathbf{L}^2, L_i] = 0$

Interpretation: cannot measure different components of $\mathbf{L}$ simultaneously, eg. L_1 and L_2, but can measure simultaneously eg. L_3 and $\mathbf{L}^2$

(iii) Other useful commutation relations are

$$[L_i, \hat{x}_j] = i\hbar\varepsilon_{ijk}\hat{x}_k$$

and

$$[L_i, \hat{p}_j] = i\hbar\varepsilon_{ijk}\hat{p}_k$$

7.3.3 Proof of commutation relations

(i) Direct approach (can let everything act on a general function to check)

$$
\begin{aligned}
L_1 L_2 &= (-i\hbar)^2 \left(x_2 \frac{\partial}{\partial x_3} - x_3 \frac{\partial}{\partial x_2}\right)\left(x_3 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial x_3}\right) \\
&= -\hbar^2 \left(x_2 \frac{\partial}{\partial x_3} x_3 \frac{\partial}{\partial x_1} - x_2 x_1 \frac{\partial^2}{\partial x_3^2} - x_3^2 \frac{\partial^2}{\partial x_2 \partial x_1} + x_3 x_1 \frac{\partial^2}{\partial x_2 \partial x_3}\right)
\end{aligned}
$$

First term gives $-\hbar^2\left(x_2 \frac{\partial}{\partial x_1} + x_2 x_3 \frac{\partial^2}{\partial_3 \partial x_1}\right)$

Finding $L_2 L_1$ similarly, and subtracting,

$$
L_1 L_2 - L_2 L_1 = -\hbar^2 \left(x_2 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial x_2} = i\hbar L_3\right)
$$

as required.

(ii) Use (i) and the commutator identity

$$
[A, B, C] = [A, B]C + B[A, C]
$$

(compare Liebnitz property)

$$
\begin{aligned}
[L_i, \mathbf{L}^2] &= [L_i, L_j L_j] \\
&= [L_i, L_j]L_j + L_j[L_i, L_j] \\
&= i\hbar\varepsilon_{ijk}(L_k L_j + L_j L_k) \\
&= 0
\end{aligned}
$$

as ε is antisymmetric, acting on a symmetric thing.

(iii) Use canonical commutation relations and commutator identity

$$
[AB, C] = [A, C]B + A[B, C]
$$

$$
\begin{aligned}
[L_i, \hat{x}_j] &= [\varepsilon_{iab}\hat{x}_a \hat{p}_b, \hat{x}_j] \\
&= \varepsilon_{iab}\left([\hat{x}_a, \hat{x}_j]\hat{p}_b + \hat{x}_a[\hat{p}_b, \hat{x}_j]\right) \\
&= \varepsilon_{iab}\hat{x}_a(-i\hbar\delta_{bj}) \\
&= i\hbar\varepsilon_{ija}\hat{x}_a
\end{aligned}
$$

as required. momentum work, similarly
Note: (iii) allows an alternative proof of (i) by calculating

$$[L_i, L_j] = [L_i, \varepsilon_{jab}\hat{x}_a\hat{p}_b]$$

and evaluating

7.3.4 Spherical Polars and Spherical Harmonics

Define r, θ, φ by usual relations

$$\begin{aligned} x_1 &= r\sin\theta\cos\varphi \\ x_2 &= r\sin\theta\sin\varphi \\ x_3 &= r\cos\theta \end{aligned}$$

Routine application of the chain rule gives (eventually)

$$L_3 = -i\hbar\frac{\partial}{\partial\varphi}$$

and

$$L_\pm := L_1 \pm iL_2 = \pm\hbar e^{\pm i\varphi}\left(\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\varphi}\right)$$

and

$$\mathbf{L}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

Note angular momentum operators only involve θ and φ.
Note:

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{1}{\hbar^2 r^2}\mathbf{L}^2$$

So $\mathbf{L}^2$ is the angular part of ∇^2.
Because

$$[L_3, \mathbf{L}^2] = 0$$

there are simultaneous eigenfunction of these operators

$$Y_{e_m}(\theta, \varphi)$$

with $e = 0, 1, 2, \cdots$ and $m = 0, \pm 1, \pm 2, \cdots, \pm l$
where L_3 has eigenvalue $\hbar m$ and $\mathbf{L}^2$ has eigenvalue $\hbar^2 l(l+1)$

The solutions are *spherical harmonics*

$$Y_{e_m} = (\text{ const })e^{im\varphi} P_l^m(\cos\theta)$$

This is just a label on P, (not P to the n^{th} power), the associated Legendre function.

[see handout]

Familiar case: $m = 0$,

$$Y_{l_0} = (\text{ const }) = P_l(\cos\theta)$$

In QM we can *construct* other solutions ($m \neq 0$) in form:

$$Y_{l\pm r} = (\text{const}) L_\pm^r P_l$$

eg.

$$\begin{aligned} Y_{1\pm 0} &= (\text{ const }) \cos\theta \\ Y_{1\pm 1} &= (\text{ const }) e^{\pm i\varphi} \sin\theta \end{aligned}$$