0. INTRODUCTION

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

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

with dimensions $[\hbar] = \mathrm{M\,L^2T^{-1}}$ = [position]×[momentum] = [energy]×[time].

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 circumstances.

• *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. A famous example is the *Heisenberg uncertainty 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 (0.1, 0.2 and 0.3) provide some physical background and summarise key experimental evidence for these novel features of QM.

0.1 Light Quanta

An electromagnetic (EM) wave, e.g. 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 wavelength, λ, or wavenumber, k, according to

$$E = \; h\nu \;=\; \hbar\omega\,,$$
$$p \;= h/\lambda = \; \hbar k\,.$$

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

$$c \;=\; \omega/k \;=\; \nu\lambda \qquad \text{or} \qquad E \;=\; cp$$

and so the relations above 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 or EM radiation (γ) of frequency ω 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.

Figure 1

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.

These 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.

Figure 2

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

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

Figure 3

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

0.2 The Bohr Model of the Atom

The *Rutherford model* of the atom was proposed to explain the results of scattering experiments (e.g. 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 $m_p \gg m_e$ it is a good approximation to assume that 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

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\,, \qquad \mathbf{F}(\mathbf{r}) = -\nabla V = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r^2}\,\hat{\mathbf{r}}\,.$$

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

$$E = \frac{1}{2}m_e v^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\,,$$

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 correspond to photons 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*:

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

with only these discrete values 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.

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

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

Figure 4

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

$$r_n = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}\,n^2\,, \qquad v_n = \frac{e^2}{4\pi\epsilon_0\hbar}\frac{1}{n}\,, \qquad E_n = -\tfrac{1}{2}m_e\Big(\frac{e^2}{4\pi\epsilon_0\hbar}\Big)^2\frac{1}{n^2}\,, \qquad n = 1, 2, \dots\,.$$

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

$$\hbar\omega \;=\; E_{n'} - E_n \;=\; \tfrac{1}{2}m\Big(\frac{e^2}{4\pi\epsilon_0\hbar}\Big)^2\Big(\frac{1}{n^2} - \frac{1}{n'^2}\Big)\,.$$

Figure 5

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 $r_1 \approx 5.29\times10^{-11}\,\mathrm{m}$, 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 (ν or ω 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

$$L = rp = n\hbar \qquad \Longleftrightarrow \qquad n\lambda = 2\pi r\,.$$

The Bohr condition therefore says that the circumference of the orbit is exactly an integral number of de Broglie wavelengths (e.g. $n = 3$ in Fig. 6).

Figure 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 first that one slit is open and the other is closed, as in Figure 7. We cannot say with certainty where any particular electron will be detected, but after many electrons have been emitted, the number detected varies with transverse position according to the distributions shown.

Figure 7

If *both* slits are open, however, then the electrons produce (perhaps unexpectedly) an interference pattern (Fig. 8).

Figure 8

This matches the interference pattern obtained for waves, of wavelength λ, say, incident on a barrier, as shown in Figure 9. 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 (amplitude)^2 of the superposed waves varies as in Figure 8, as P varies.

Figure 9

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 (amplitude)^2 of a wave.

Some Constants and Units

- Planck's Constant: $\hbar = 1.05\times10^{-34}$ Js , or $h = 2\pi\hbar = 6.63\times10^{-34}$ Js
- Speed of light: $c = 3.00\times10^{8}$ ms^{-1} ; Wavelength of visible light (approx) 4×10^{-7}m to 7×10^{-7}m
- Unit of electric charge: $e = 1.60\times10^{-19}$ C ; Unit of energy: electron-volt, 1 eV $= 1.60\times10^{-19}$ J
- Fine structure constant: $\alpha = e^2/4\pi\epsilon_0\hbar c \approx 1/137$ (dimensionless)
- Electron mass: $m_e = 9.11\times10^{-31}$ kg ; Proton mass: $m_p = 1.67\times10^{-27}$ kg
- Bohr radius: $r_1 = 4\pi\epsilon_0\hbar^2/m_e e^2 = \hbar/m_e c\alpha = 5.29\times10^{-11}$ m

Wave Behaviour

We will refer to any real or complex valued function with periodicity in time and/or space as a *wave*. The following remarks summarise a few useful definitions and ideas.

- A function of time t obeying $f(t+T) = f(t)$ has *period* T, *frequency* $\nu = 1/T$, and *angular* or *circular frequency*

$$\omega = 2\pi\nu = 2\pi/T \ .$$

Familiar examples are $f(t) = \cos\omega t$, $\sin\omega t$ or $\exp\pm i\omega t$. It is also customary to refer to ω as the frequency, provided this leads to no confusion.

A function of position x (in one dimension) obeying $f(x+\lambda) = f(x)$ has *wavelength* λ and *wavenumber*

$$k = 2\pi/\lambda$$

Examples are $f(x) = \cos kx$, $\sin kx$ or $\exp\pm ikx$. The analogous functions of a position vector $\mathbf{x}$ with periodicity in three dimensions are $f(\mathbf{x}) = \exp i\mathbf{k}\cdot\mathbf{x}$ where $\mathbf{k}$ is the *wave vector*, and the wavelength is then $\lambda = 2\pi/|\mathbf{k}|$. We shall refer to such functions as *plane waves*.

- The wave equation in one dimension for a function $f(x,t)$ is

$$\frac{\partial^2 f}{\partial t^2} - c^2\frac{\partial^2 f}{\partial x^2} = 0$$

where c is some constant. This has solutions which are periodic in both position and time:

$$f_\pm(x,t) \ = \ A_\pm \exp(\ \pm ikx - i\omega t\ ) \qquad (*)$$

provided that the wavelength and frequency are related by

$$\omega = ck \qquad \text{or} \qquad \lambda\nu = c \ .$$

Such solutions represent waves which move or *propagate* with speed c to the right or left, according to the sign in $(*)$ (assuming ω, $k > 0$). The constant $A_\pm$ is the *amplitude* of the wave.

In electromagnetic (EM) waves, the field components obey the three dimensional wave equation, obtained by replacing $\partial^2/\partial x^2$ by ∇^2 above. This has solutions of an analogous form

$$f(\mathbf{x},t) \ = \ A\exp(\ i\mathbf{k}\cdot\mathbf{x} \ - \ i\omega t\ ) \qquad \text{with} \qquad \omega = c|\mathbf{k}| \ .$$

Such a wave propagates in the direction of $\mathbf{k}$, with speed c, now the speed of light.

• Other kinds of waves arise as solutions of other *governing equations* which may differ significantly from the standard wave equation. A function does not have to satisfy the standard wave equation in order to be usefully thought of as a wave! The *Schrödinger Equation* is one example of an alternative governing equation; it is the central equation in QM and we will study it in some depth. (In other physical applications, e.g. waves in real fluids, we should expect the wave equation to be modified by friction or dissipative terms.)

• Many different governing equations give rise to propagating solutions of the form $(*)$, provided the frequency is chosen to be a suitable function of the wavenumber, $\omega(k)$. Moreover, if the governing equation is *linear* in f, then any solutions f_1 and f_2 can be combined to give a new solution:

$$f = f_1 + f_2$$

This is the *Principle of Superposition* and it is responsible for much behaviour we tend to think of as *wave-like*.

• *Interference* or *diffraction* occurs when waves from different sources merge, or when parts of a wave recombine after passing around or through some obstacle. When a number of such waves are superposed, they may interfere *constructively*, increasing the size of the amplitude, or *destructively*, diminishing the amplitude. The result is an interference or diffraction pattern which depends on the sources or the obstacles.

When light is passed through a number of narrow slits, the resulting diffraction pattern provides conclusive evidence that light is a wave. Passing higher energy waves, such as X-rays, through matter gives a way of determining the crystalline arrangement of atoms from the resulting diffraction patterns.

A Few Historical Highlights

• 1801-03: Interference/diffraction experiments by Young show that light is a wave

• 1862-4: Maxwell identifies light as an EM (electromagnetic) wave

• 1897: Thompson discovers the electron, the first elementary particle

• 1900: Planck introduces the energy-frequency relation, with h as a new physical constant, and derives the *black body spectrum* (the distribution of energy with frequency for EM radiation in thermal equilibrium)

• 1905: Einstein imparts clearer physical meaning to photons, using them to explain the *photoelectric effect*, and other experimental results

• 1911: Based on scattering experiments, Rutherford proposes a model of the atom with most of its mass concentrated in a small, compact *nucleus*

• 1913: Bohr proposes an atomic model with electrons orbiting a nucleus and with quantisation of their angular momentum, using this to derive observed line spectra

• 1923: Compton scattering of X-rays on electrons confirms that photons are relativistic particles of zero rest mass

• 1923-24: de Broglie proposes *wave-particle duality* for matter, as for radiation

• 1925-30: The emergence of *Quantum Mechanics*, through work of Heisenberg, Born, Jordan, Dirac, Pauli, Schrödinger, and others

• 1927-28: Diffraction experiments of Davisson, Germer and Thompson confirm that electrons behave as waves as well as particles

Solving the Schrödinger Equation with Zero Potential

Consider the time-dependent Schrödinger Equation (SE) for $\Psi(x,t)$, the wavefunction for a free particle (zero potential), subject to an initial condition:

$$-\frac{\hbar^2}{2m}\frac{\partial}{\partial x^2}\Psi \;=\; i\hbar\frac{\partial}{\partial t}\Psi \qquad \text{with} \qquad \Psi(x,0)=\psi(x)\;. \tag{$*$}$$

This can be solved by expanding the initial wavefunction in terms of momentum eigenstates, otherwise known as a Fourier representation:

$$\psi(x) \;=\; (\hbar/2\pi)^{1/2}\int_{-\infty}^{\infty}\tilde{\psi}(k)\,e^{ikx}\,\mathrm{d}k \qquad \text{where} \qquad \tilde{\psi}(k) \;=\; (1/2\pi\hbar)^{1/2}\int_{-\infty}^{\infty}\psi(x)\,e^{-ikx}\,\mathrm{d}x\;.$$

(The constants, including $\hbar$, are conventional for Fourier transforms in QM.) Now, an eigenstate of momentum, with eigenvalue $\hbar k$, is also an eigenstate of the Hamiltonian, with energy $E=\hbar^2k^2/2m$ (because the potential vanishes); so

$$\exp(ikx)\,\exp(-i\hbar k^2t/2m)$$

is a solution of the SE for any k. Since the SE is linear, we can deduce from the Fourier representation for ψ that the solution to $(*)$ is

$$\Psi(x,t)=(\hbar/2\pi)^{1/2}\int_{-\infty}^{\infty}\tilde{\psi}(k)\,e^{ikx}\,e^{-i\hbar k^2t/2m}\,\mathrm{d}k\,. \tag{$**$}$$

Gaussian Wavepackets and the Uncertainty Relation

• Consider a normalised Gaussian wavefunction at time $t=0$:

$$\psi(x) \;=\; (1/\alpha\pi)^{1/4}\,\exp(-x^2/2\alpha)$$

with α a real positive constant. The expectation values of position and momentum in this state are

$$\langle\hat{x}\rangle \;=\; \int_{-\infty}^{\infty}x\,|\psi(x)|^2\,\mathrm{d}x \;=\; 0 \qquad \text{and} \qquad \langle\hat{p}\rangle \;=\; -i\hbar\int_{-\infty}^{\infty}\psi(x)^*\frac{\mathrm{d}}{\mathrm{d}x}\psi(x)\,\mathrm{d}x \;=\; 0\;.$$

The first integral vanishes because ψ is an even function of x, and the second because the integrand is a total derivative, since ψ is a real function in this case.

• The uncertainty in x and p are calculated using the standard formulas

$$(\Delta x)^2 \;=\; \langle\hat{x}^2\rangle-\langle\hat{x}\rangle^2 \;=\; \int_{-\infty}^{\infty}x^2\,|\psi(x)|^2\,\mathrm{d}x \;=\; \frac{1}{(\alpha\pi)^{1/2}}\int_{-\infty}^{\infty}x^2\,\exp\Big(-\frac{x^2}{\alpha}\Big)\,\mathrm{d}x \;=\; \frac{\alpha}{2}$$

and

$$(\Delta p)^2 \;=\; \langle\hat{p}^2\rangle-\langle\hat{p}\rangle^2 \;=\; \int_{-\infty}^{\infty}\hbar^2\,|\psi'(x)|^2\,\mathrm{d}x \;=\; \frac{\hbar^2}{(\alpha\pi)^{1/2}}\int_{-\infty}^{\infty}\frac{x^2}{\alpha^2}\,\exp\Big(-\frac{x^2}{\alpha}\Big)\,\mathrm{d}x \;=\; \frac{\hbar^2}{2\alpha}\;.$$

The wavefunction can be interpreted as a particle which is localised around $x=0$, on a length scale $\alpha^{1/2}$. The combined uncertainty in position and momentum is as small as possible in this example, since the bound given by the Uncertainty Principle is saturated:

$$(\Delta x)(\Delta p)=\tfrac{1}{2}\hbar\;.$$

• There are similar wavefunctions with non-zero expectation values for position or momentum. For

$$\psi(\,x-c\,) \;=\; (1/\alpha\pi)^{1/4}\exp\big(-(x-c)^2/2\alpha\big)$$

we have $\langle\hat{x}\rangle = c$ and $\langle\hat{p}\rangle = 0$, representing a particle localised around $x = c$ (any real constant). For

$$\phi(x) \;=\; (1/\alpha\pi)^{1/4}\exp(\,i(mu/\hbar)x\,)\exp(\,-x^2/2\alpha\,)$$

we find $\langle\hat{x}\rangle = 0$ but $\langle\hat{p}\rangle = mu$, where u is a real constant which corresponds to a velocity. This shows that $\phi(x)$ represents a moving particle, even before considering the evolution of the wavefunction and probability distribution in time.

Time Evolution of Wavepackets

• Consider $(*)$ with $\psi(x)$ the Gaussian wavefunction above.

$$\tilde{\psi}(k) \;=\; \frac{1}{(2\pi\hbar)^{1/2}(\alpha\pi)^{1/4}}\int_{-\infty}^{\infty}\exp\Big(-\frac{x^2}{2\alpha}\Big)\,\exp(\,-ikx\,)\,\mathrm{d}x \;=\; \frac{1}{\hbar^{1/2}}\Big(\frac{\alpha}{\pi}\Big)^{1/4}\exp\Big(-\frac{\alpha k^2}{2}\Big)$$

which follows by completing the square in the exponential:

$$\frac{1}{2\alpha}x^2 + ikx \;=\; \frac{1}{2\alpha}(\,x + i\alpha k\,)^2 \;+\; \frac{1}{2}\alpha k^2$$

and shifting the variable of integration. (Such an *imaginary* shift in the *real* variable x can be justified using Cauchy's Theorem; see e.g. Complex Methods/Analysis.) Substituting into $(**)$ gives a solution

$$\begin{aligned}\Psi(x,t) \;&=\; \frac{1}{(2\pi)^{1/2}}\Big(\frac{\alpha}{\pi}\Big)^{1/4}\int_{-\infty}^{\infty}\exp\Big(-\frac{\alpha k^2}{2}\Big)\,\exp\Big(-i\frac{\hbar k^2}{2m}t\Big)\,\exp(\,ikx\,)\,\mathrm{d}k\\ &=\; \Big(\frac{\alpha}{\pi}\Big)^{1/4}\frac{1}{\gamma(t)^{1/2}}\,\exp\Big(-\frac{x^2}{2\gamma(t)}\Big)\qquad\text{where}\qquad \gamma(t) = \alpha + i\frac{\hbar t}{m}\;.\end{aligned}$$

The integral over k has been evaluated by again completing a square,

$$\frac{1}{2}\Big(\,\alpha + i\frac{\hbar t}{m}\,\Big)k^2 \;-\; ikx \;=\; \frac{1}{2}\gamma\Big(\,k - \frac{ix}{\gamma}\,\Big)^2 + \;\frac{1}{2\gamma}x^2\,,$$

and shifting the variable of integration. From the solution, we find

$$(\Delta x)^2 \;=\; \frac{\hbar}{2\alpha}\,|\gamma(t)|^2 \quad\text{and}\quad (\Delta p)^2 \;=\; \frac{\hbar}{2\alpha} \quad\Rightarrow\quad (\Delta x)(\Delta p) \;=\; \frac{\hbar}{2}\Big(\,1 + \frac{\hbar^2t^2}{m^2\alpha^2}\,\Big)^{1/2} \;\geq\; \frac{\hbar}{2}\;.$$

• Now consider $(*)$ with an initial wavefunction $\phi(x)$ instead. Observing that

$$\tilde{\phi}(k) \;=\; \tilde{\psi}\Big(\,k - \frac{mu}{\hbar}\,\Big)\;,$$

the solution $\Phi(x,t)$ can be calculated from $(**)$ in a similar way: we need only complete squares in the exponentials before using standard results for Gaussian integrals (although the algebra is now slightly more complicated). The result is

$$\Phi(x,t) \;=\; \Psi(\,x-ut,\,t\,)\,\exp\Big(\,i\frac{mu}{\hbar}x\,\Big)\,\exp\Big(\,-i\frac{mu^2}{2\hbar}t\,\Big)\,.$$

It can also be verified, by substitution, that $\Phi(x,t)$ is a solution of the time-dependent SE if $\Psi(x,t)$ is. (This is an expression of Galilean invariance for the non-relativistic SE with zero potential.)

Standard Gaussian Integrals:

$$\int_{-\infty}^{\infty}\exp(\,-\tfrac{1}{2}\beta x^2\,)\,\mathrm{d}x \;=\; \Big(\frac{2\pi}{\beta}\Big)^{1/2}\;,\quad \int_{-\infty}^{\infty}x^2\exp(\,-\tfrac{1}{2}\beta x^2\,)\,\mathrm{d}x \;=\; \Big(\frac{2\pi}{\beta^3}\Big)^{1/2}\;,\quad \text{for }\;\mathrm{Re}(\beta) > 0\,.$$

Commuting Operators and Simultaneous Measurements

Consider a quantum system with space of states V. We assume throughout that the eigenstates of any observable, or hermitian operator, provide a basis for the space on which the operator acts. Recall also (section 6.2) that eigenvalues of an observable are real, that eigenstates with different eigenvalues are orthogonal, and that these results underpin the measurement axioms.

• Let A and B be observables. A state χ is a *simultaneous* or *joint* eigenstate of A and B if

$$A\chi = \lambda\chi \qquad \text{and} \qquad B\chi = \mu\chi \ .$$

If the system is in state χ and measurements of A or B are made in rapid succession, in any order, then the results obtained will be λ or μ, respectively, with probability 1 each time. (The time intervals that elapse between successive measurements must be small enough that the evolution of the state in time can be ignored.)

In light of this, observables A and B are said to be *simultaneously measurable* if V has a basis of joint or simultaneous eigenstates χ_n:

$$A\chi_n \,=\, \lambda_n\chi_n \ , \qquad B\chi_n \,=\, \mu_n\chi_n \qquad \text{with} \qquad (\chi_m, \chi_n) = \delta_{mn} \ .$$

(An operator is also said to be *diagonalisable* if there exists a basis of eigenstates, and A and B are *simultaneously diagonalisable* if there exists a basis of joint eigenstates.)

• A necessary and sufficient condition for observables A and B to be simultaneously measurable is that they commute:

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

This was stated in section 6.5 and it can be established as follows.

Necessity. For any joint eigenstate,

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

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 $V_\lambda = \{\psi : A\psi = \lambda\psi\}$, i.e. the subspace of V containing all the corresponding eigenstates. If $[A, B] = 0$, then

$$A\psi = \lambda\psi \qquad \Rightarrow \qquad A(B\psi) \,=\, B(A\psi) \,=\, B(\lambda\psi) \,=\, \lambda(B\psi) \ .$$

Hence, for every λ, B maps V_λ to itself. Now V is the direct sum of the 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 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 special 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.

• The fact that observables must commute if they are to be simultaneously measureable is also reflected in the *generalised uncertainty relation*

$$(\Delta A)(\Delta B) \,\geq\, \tfrac{1}{2}|\,\langle\,[A, B]\,\rangle\,| \ .$$

The proof of this is set as an exercise on Example Sheet 3.

Angular Momentum Eigenfunctions

• The operators L_3 and L^2 are hermitian and satisfy $[L_3, L^2] = 0$ implying that they have simultaneous or joint eigenstates Y. It is convenient to write the eigenvalues so that

$$L_3\, Y \;=\; \hbar m\, Y\,, \qquad L^2\, Y \;=\; \hbar^2 \ell(\ell{+}1)\, Y\ .$$

• In spherical polar coordinates r, θ, φ,

$$L_3 \;=\; -i\hbar \frac{\partial}{\partial \varphi}\ , \qquad L^2 = -\hbar^2 \Big(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} \;+\; \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\Big)\ ,$$

and simultaneous eigenstates can be found in separable form:

$$Y(\theta,\varphi) \;=\; \Phi(\varphi)\, P(u) \qquad \Rightarrow \qquad \frac{\mathrm{d}\Phi}{\mathrm{d}\varphi} \;=\; im\Phi\ , \qquad -\frac{\mathrm{d}}{\mathrm{d}u}(1-u^2)\frac{\mathrm{d}P}{\mathrm{d}u} + \frac{m^2}{1-u^2}P \;=\; \ell(\ell+1)P\ ,$$

where $u = \cos\theta$. The first of these separated ODEs has solutions

$$\Phi_m(\varphi) \;=\; e^{im\varphi}$$

where m must be an integer for the eigenfunction to be single-valued. The second ODE is the *associated Legendre Equation*. When $m = 0$ it reduces to the usual *Legendre Equation* with solutions $P_\ell(u)$, the *Legendre polynomials* of degree ℓ; these are the solutions which are well-behaved at $u = \pm 1$ or $\theta = 0, \pi$ (see IB Methods). For more general m, the solutions defined on $-1 \le u \le 1$ are

$$P_\ell^m(u) = (1-u^2)^{|m|/2}\frac{\mathrm{d}^{|m|}}{\mathrm{d}u^{|m|}}P_\ell(u)\ , \qquad |m| \le \ell\ ,$$

known as *associated Legendre functions*, with ℓ a non-negative integer.

• In summary, the joint eigenfunctions of L_3 and L^2 are the *spherical harmonic* functions:

$$Y_{\ell m}(\theta,\varphi) \;=\; (\text{const})\, e^{im\varphi}\, P_\ell^m(\cos\theta) \qquad \text{with} \qquad \begin{array}{l} \ell \;=\; 0,\, 1,\, 2,\, \ldots\ , \\ m \;=\; 0,\, \pm1,\, \pm2,\, \ldots,\, \pm\ell\,. \end{array}$$

Spherically Symmetric Potentials

• If the Hamiltonian H of a quantum system satisfies

$$[\, L_3,\, H\,] \;=\; [\, L^2,\, H\,] \;=\; 0 \qquad (*)$$

then there exist energy eigenstates $\psi_{\ell m}(\mathbf{x})$ that are also joint eigenstates of L_3 and L^2:

$$H\,\psi_{\ell m} \;=\; E\,\psi_{\ell m}\ , \qquad L^2\,\psi_{\ell m} \;=\; \hbar^2\ell(\ell{+}1)\,\psi_{\ell m}\ , \qquad L_3\,\psi_{\ell m} \;=\; \hbar m\,\psi_{\ell m}\ .$$

• For a particle of mass μ moving in a spherically symmetric potential $V(r)$ the Hamiltonian is

$$H \;=\; \frac{1}{2\mu}\hat{\mathbf{p}}^2 \;+\; V \;=\; -\frac{\hbar^2}{2\mu}\nabla^2 \;+\; V(r) \;=\; -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r \;+\; \frac{1}{2\mu r^2}L^2 \;+\; V(r)$$

(the L^2 term is the rotational kinetic energy and is proportional to the angular part of ∇^2). The condition $(*)$ follows immediately from the expressions above for L_3 and L^2 (it is also easy to verify using Cartesian coordinates). Joint eigenstates of H, L^2 and L_3 can then be found as separable wavefunctions:

$$\psi_{\ell m}(\mathbf{x}) \;=\; R(r)Y_{\ell m}(\theta,\varphi) \qquad \text{with} \qquad -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}(rR) \;+\; \Big(\frac{\hbar^2}{2\mu r^2}\ell(\ell+1) + V(r)\Big)R \;=\; ER\ .$$

The equation satisfied by $\chi(r) = rR(r)$ is known as the *radial Schrödinger equation*. The energy eigenvalues E will depend on ℓ, in general, but will be independent of m as a consequence of the rotational invariance of H.

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