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

$$(\Delta x)^2 \;=\; \frac{\hbar}{2\alpha}\,|\gamma(t)|^2 \quad\text{and}\quad (\Delta p)^2 \;=\; \frac{\hbar}{2\alpha}\;.$$

• 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.)

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, B maps V_λ to itself, for any λ. 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 well-behaved solutions 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 conclusion, the joint eigenfunctions of L_3 and L^2 are the *spherical harmonic* functions:

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

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.

Comments to: J.M.Evans@damtp.cam.ac.uk