

QUANTUM 20/20

Fundamentals, Entanglement, Gauge Fields, Condensates and Topology

Ian R. Kenyon

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Preface

In writing this book the intention has been to provide support for lecture courses on general quantum physics for university undergraduates in the final year(s) of a physics degree programme. The audience would be expected to have taken the courses in introductory quantum physics and in basic quantum mechanics that are normally met in the first or second years of a physics degree programme. The first chapter is a review of the basic quantum mechanics needed for getting the best out of the text. Instructors are then free to concentrate on a group of chapters, or select components from all chapters, whichever suits their needs.

Thanks to the sheer variety and rapid advance of research across the discipline, the average course in the later years of a physics degree programme is designed to address one area of physics. Instead, this text covers key themes of quantum physics, taking the perspective achieved after more than a century of research, and emphasizing the effectiveness and the subtlety of quantum concepts in explaining diverse physical phenomena. The book is used to bring out these unifying ideas and illustrate them with important examples from modern experiments and applications.

The themes developed in the text, and listed next, are the essence of quantum physics.

One theme contrasts boson condensation and fermion exclusivity. Bose– Einstein condensation is basic to superconductivity, superfluidity and gaseous BEC. Fermion exclusivity leads to compact stars and to atomic structure, and thence to the band structure of metals and semiconductors with applications in material science, modern optics and electronics.

A second theme is that a wavefunction at a point, and in particular its phase is unique (ignoring a global phase change). If there are symmetries, conservation laws follow and quantum states which are eigenfunctions of the conserved quantities. By contrast with no particular symmetry topological effects occur such as the Bohm–Aharonov effect: also stable vortex formation in superfluids, superconductors and BEC, all these having quantized circulation of some sort. The quantum Hall effect and quantum spin Hall effect are *ab initio* topological.

A third theme is entanglement: a feature that distinguishes the quan-

tum world from the classical world. This property led Einstein, Podolsky and Rosen to the view that quantum mechanics is an incomplete physical theory. Bell proposed the way that any underlying local hidden variable theory could be, and was experimentally rejected. Powerful tools in quantum optics, including near-term secure communications, rely on entanglement. It was exploited in the the measurement of CP violation in the decay of beauty mesons.

A fourth theme is the limitations on measurement precision set by quantum mechanics. These can be circumvented by quantum nondemolition techniques and by squeezing phase space so that the uncertainty is moved to a variable conjugate to that being measured. The boundaries of precision are explored in the measurement of g-2 for the electron, and in the detection of gravitational waves by LIGO; the latter achievement has opened a new window on the universe.

The fifth and last theme is quantum field theory. This is based on local conservation of charges. It reaches its most impressive form in the quantum gauge theories of the strong, electromagnetic and weak interactions, culminating in the discovery of the Higgs. Where particle physics has particles condensed matter has a galaxy of pseudoparticles that exist only in matter and are always in some sense special to particular states of matter. Emergent phenomena in matter are successfully modelled and analysed using quasi-particles and quantum theory. Lessons learned in that way on spontaneous symmetry breaking in superconductivity were the key to constructing a consistent quantum gauge theory of electroweak processes in particle physics.

Care has been taken to maintain a level of presentation accessible to undergraduates reading physics, and to provide exercises and solutions to reinforce the learning process.

Solutions to the exercises are accessible via the OUP webpage link for this text.

Acknowledgements

I thank two Heads of the School of Physics and Astronomy at Birmingham University, Professors Andy Schofield and Martin Freer, and also Professor Paul Newman, Head of the Elementary Particle Physics Group at Birmingham, for their support and encouragement during the lengthy preparation of this textbook. Dr Sonke Adlung, the senior science editor at Oxford University Press, has always been unfailingly helpful and courteous in dealing with the many aspects of the preparation, and my thanks go to him for making my path easier. I am also grateful to his colleagues at Oxford University Press and SPi Global for the smooth management of copy editing, layout, production, and publicity.

Many colleagues have been more than generous in finding time in busy lives to read and comment on material for which they have a particular interest and expertise. My thanks go to Professor Ted Forgan, who was kind enough to read the chapters dealing with metals and semiconductors: his guidance and suggestions on particular points were very helpful. Thanks too, to Professor Peter Jones for reading the chapter on Transitions and his helpful comments on suitability. I am indebted to both Dr Rob Smith and Dr Martin Long, who generously found time on numerous occasions for patient explanations on condensed matter physics: their insights clarified many difficult points. In addition, Rob went the extra mile in reading the chapter on superconductivity, unearthing an embarassing number of subtle misunderstandings. I am under a further obligation to him for reading and commenting on the chapter on symmetry and topology. Thanks to Dr Elizabeth Blackburn for reading and making useful comments on the chapter on photon physics. I am very much indebted to Professor Vinen, who read and cross-questioned me on the liquid helium and superfluidity chapter, subjects about which he is a world authority. Dr Giovanni Barontini indoctrinated me in the subtleties of atomic Bose–Einstein condensates, and afterwards reviewed the chapter on BEC with great care: his input was indispensable. I much appreciate the interaction with Dr Hannah Price, who considerably sharpened my understanding of the quantum Hall effects, in particular, the role of topological quantization. Professor Alberto Vecchio took valuable time off from discovering gravitational waves to look over the chapter on quantum measurement, for which I am most grateful. I much appreciate Dr Alastair Rae offering to read three chapters where he has particular expertise: those on entanglement, the EPR controversy, and quantum measurement. He helped me appreciate a number of important points that had escaped my attention. My colleagues in the particle physics group have helped enormously in many ways. Kostas Nikolopoulos and Miriam Watson provided access to AT-LAS publications and event displays. In addition, Miriam and Chris Hawkes took on the task of reading and commenting on the chapters on particle physics. Their valuable critique is highly appreciated. Thanks too, to David Charlton and Mark Colclough who looked over sections where their expertise was particularly useful. Ian Styles of the Computer Science Department scrutinized the chapter relating to the potential for quantum cryptography and computing, for which I am most grateful. I am equally grateful to Dr Brooker who carefully searched the whole text for errors on behalf of Oxford University Press. Last, and definitely not least, I thank Mark Slater warmly for rescuing the text from a problem with missing fonts in the figures, which could have required the redrawing of 120 figures: his prompt and expert help was invaluable.

The input from all these colleagues removed misunderstandings on my part, helped me to clarify arguments, and brought points to my attention that I would otherwise have missed. The responsibility for any remaining errors should be laid at my door.

My thanks also go to the authors and publishers who have allowed me to use published figures, or adaptations of figures, or tables, each acknowledged individually in the text. I am grateful on this account to the American Physical Society, the American Society for the Advancement of Science, the American Chemical Society, the Royal Society, Elsevier publishers, Springer Nature, and Springer Verlag.

In producing some 290 diagrams I made almost exclusive use of the ROOT package developed by Dr Rene Brun and Dr Fons Rademakers and described in *ROOT – An Object Oriented Data Analysis Framework*, which appeared in the Proceedings of AIHENP '96 Workshop, Lausanne, Nuclear Instruments and Methods in Physics Research A389(1997)81-6. ROOT can be accessed at http://root.cern.ch. I also thank Dr Brun for help while learning to use this sophisticated tool.

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The cover picture shows one end of a double dipole magnet from the CERN LHC. Two counter-rotating beams are steered around a 27 km closed path inside an evacuated tube by 1232 such magnets. For around 90 per cent of the year the particles in the beams are protons; for the remainder of the year heavy ions (such as lead). The beams are brought into collision at four locations on this circuit: around three of these interaction points the ATLAS, CMS, and LHCb detectors were built to study the products of proton-proton collisions at 13 TeV energy; around the fourth the ALICE detector was built, explicitly to study heavy ion collisions. In operation, the dipole current is carried by a *superconducting condensate* of Cooper pairs. Liquid helium flowing through the magnet coils provides the necessary cooling to 1.9 K. The flow is dissipation-free thanks to the superfluid condensate component of ultra-cold liquid helium. A final condensate is the *Higgs condensate* in the vacuum, whose particle excitations were discovered by the ATLAS and CMS experiments. See Chapters 14, 15 and 19 respectively.

Review of basic quantum physics



1.1 Introduction

This chapter reviews the evidence for quantization, and basic quantum mechanics, including Schrödinger's equation. The material should provide a refresher and a reference for students who have had exposure to a first course on quantum physics. The uncertainty principle, wave packets, wavefunction collapse and the no-cloning theorem are discussed. State vectors in Hilbert space are introduced. A summary of useful formulae from special relativity and electromagnetism closes the chapter.

1.2 The fundamental evidence

The three pieces of compelling evidence for the quantum nature of electromagnetic radiation were provided by the black body radiation spectrum, the photoelectric effect and Compton scattering. They are reviewed briefly here. The black body radiation spectrum, that is, the radiation in thermal equilibrium within a closed volume, whose walls are at a constant temperature, is shown in Figure 1.1 for three temperatures. The ingredients for calculating this spectrum are the count of distinct modes of oscillation of the electromagnetic field, and the energy per mode in thermal equilibrium. Of these, the mode density per unit frequency per unit volume $\rho(f)$ is given by¹

$$\rho(f)df = [8\pi f^2/c^3]df, \qquad (1.1)$$

for frequency f, including both polarizations. Classical and quantum predictions differ on how the energy per mode is assigned: in classical thermodynamics all modes have energy $k_{\rm B}T$, where T K is the temperature and $k_{\rm B}$ is Boltzmann's constant, $1.381 \, 10^{-28} \, \mathrm{J \, K^{-1}}$. The predicted energy spectrum therefore diverges at high frequencies and short wavelenths, as shown in Figure 1.1. This was the *ultraviolet catastrophe*. Planck, in a step that signalled the birth of quantum physics, proposed that in each mode electromagnetic radiation is emitted and absorbed in



Fig. 1.1 Black body radiation spectra at 3000 K, 4000 K and 5000 K. Planck's quantum predictions which are indicated with full lines fit the data. The classical prediction for 3000 K is shown with a broken line.

¹This is derived in Appendix B, eqn. B.12, together with similar mode calculations.

Quantum 20/20: Fundamentals, Entanglement, Gauge Fields, Condensates and Topology. Ian R. Kenyon. © 2020. Published in 2020 by Oxford University Press. DOI: 10.1093/oso/9780198808350.001.0001 energy packets, the quanta, of magnitude

$$E = hf = \hbar\omega, \tag{1.2}$$

where ω is the angular frequency of the radiation and h is known as Planck's constant; \hbar is simply $h/2\pi$. The rest of the quantum calculation proceeds as follows. If there are ℓ quanta in the mode its energy is $\ell h f$. The probability of ℓ quanta in any mode within the enclosure is then given by the Boltzmann distribution $\exp[-\ell h f/(k_{\rm B}T)]$. Evaluating the mean number gives

$$\overline{\ell} = 1 / [\exp(hf/k_{\rm B}T) - 1].$$
(1.3)

Multiplying this expression by the density of modes given in eqn. 1.1, the energy spectrum of black body radiation is predicted to be^2

$$W(f)df = (8\pi h f^3/c^3)df / [\exp(hf/k_{\rm B}T) - 1], \qquad (1.4)$$

with W(f) in J m⁻³ Hz⁻¹. This expression fits the the observed black body spectra at all temperatures with one value of h, namely 6.626 10⁻³⁴ J s. When $hf/k_{\rm B}T$ is very small, the quantum formula reduces to the classical expression.

The *photoelectric effect* occurs when visible or ultraviolet light falls on a clean metal or an alkali metal surface causing electrons to be emitted. By 1902, Lenard had shown that for each such metal there exists a threshold frequency below which no photoelectrons are produced, however high the intensity of the incoming radiation. Classically, the electrons would continuously acquire energy from incident radiation and eventually break free from the surface, at any radiation frequency.

In 1905, Einstein proposed that in the photoelectric effect a single electron absorbs one quantum of energy from the radiation and escapes from the surface. Then electrons located at the surface will emerge with kinetic energy equal to

$$KE_{max} = hf - \phi, \qquad (1.5)$$

where ϕ is the *work function* of the metal surface. Electrons originating deeper in the metal lose further energy through collisions on their way out. Einstein's proposal provides the required cut-off, with no photoelectron emission for radiation of frequencies below $f_{\rm co} = \phi/h$.

Millikan showed that the maximum kinetic energy of the *photoelec*trons fitted Einstein's predicted linear relation. He extracted a value of Planck's constant from the data, which agreed with that found from the fit to the black body spectrum. Forrester, Gudmundson and Johnson in 1955 studied the photoelectric effect using light modulated at high frequencies and observed that the detector signal followed the modulation faithfully, showing that any delay was much less than the modulation

²In a material of refractive index n there would be an additional factor n^3 in the numerator.

period of 10^{-10} s. According to the classical view, there would be a delay before photoemission because the wave energy is supposed to be spread uniformly over the whole surface, rather than being concentrated in quanta that interact with individual atoms.

Compton followed through the consequences of the quantization of radiation, realizing that when X-rays scatter from matter the underlying process is the scattering of one quantum of electromagnetic radiation off one electron that is initially at rest. Then treating the photon-electron collision as an elastic two body collision, Compton arrived at an expression for the wavelength change of the scattered radiation

$$\lambda - \lambda_0 = (h/mc)(1 - \cos\theta), \tag{1.6}$$

where m is the electron mass and θ the angle through which the photon scatters. Compton found that the shift in wavelength fitted his prediction precisely in magnitude, in its dependence on the scattering angle and in its independence of the target material.

1.3 De Broglie's hypothesis

In 1924, de Broglie realized that if electromagnetic waves possess particle properties, then all material particles such as electrons must possess wave properties. Equally, the relations connecting the wave and particle properties of electromagnetic radiation apply also to material particles. Thus the frequency of the wave f associated with a particle of total energy E would be given by Planck's relation

$$E = hf. \tag{1.7}$$

The parallel relation for the momentum of a photon, p, also extends to material particles

$$p = h/\lambda. \tag{1.8}$$

This is called the *de Broglie* relation, and λ is known as the *de Broglie* wavelength of material particles. De Broglie's ideas were confirmed in 1926 when electron diffraction was observed from crystals.

Wave particle duality extends to gravitational effects. Einstein's general theory of relativity assigns an inertial mass of E/c^2 to a photon of energy E.

1.4 The Bohr model of the atom

In 1911, Rutherford's colleagues used α -particles (bare ⁴He nuclei) to bombard thin metal foils and observed that substantial numbers were



scattered into the backward hemisphere and some almost straight backward. Rutherford showed that these observations could only be consistently explained if the object within the atom that scatters the α -particles carries most of the atomic mass, has positive charge and is very much smaller than the atom. This scatterer is the nucleus, which is typically 10^{-15} m across. The electrons circulate around it in orbits extending to 10^{-10} m from the nucleus.

Classically the electrons in such an atom would accelerate into the nucleus and radiate over a broad range of wavelengths. In fact, isolated atoms radiate at discrete wavelengths, the spectral lines. Hydrogen has a particularly simple atomic structure, with one electron orbiting a single proton nucleus. Its spectrum consists of spectral lines whose wavelengths are given by a single formula³

$$1/\lambda = R_{\rm H}(1/n^2 - 1/p^2), \tag{1.9}$$

where n and p are positive integers with the restriction that p > n. $R_{\rm H}$ is a constant known as the *Rydberg constant*, with value 1.09678 10⁷m⁻¹. Part of the spectrum is shown in Figure 1.2

In Bohr's model of 1913, the electrons are pictured as travelling in stable circular orbits around the nucleus. Here, his model is applied to the hydrogen atom, for which it works best. The transition from an orbit of higher energy to one of lower energy is accompanied by a photon

Fig. 1.2 The energy levels in the hydrogen atom are displayed together with transitions producing the Lyman and Balmer series. For clarity only the first few transitions are drawn. The spectral lines are shown in the lower panel. Each series converges to a limit: in the case of upward transitions the limit is reached when the electron just escapes from the atom with zero kinetic energy.

³The fine and hyperfine structure of spectral lines are discussed in the next chapter.

being emitted. Equally, an electron in a lower energy orbit can absorb a photon and jump to a higher energy orbit. In both cases, the photon energy exactly matches the energy difference between the electron states ΔE : the photon frequency, f, is thus given by

$$hf = \Delta E. \tag{1.10}$$

Bohr discovered the quantization condition that one complete electron orbit contains an integral number n of de Broglie wavelengths; any other orbit would interfere destructively with itself. This is a condition on the phase of a stable quantum state: in a closed loop the phase must change by an integral number of multiples of 2π . This simple, but powerful, phase condition has applicability beyond the Bohr model and will be met repeatedly. Bohr's only other requirement was that the Coulomb attraction of the nucleus provides the centripetal force to maintain the electron in its stable orbit. This leads to an expression for the energy of the *n*th orbit as

$$E_n = -(e^2/4\pi\varepsilon_0)^2 (m/2n^2\hbar^2), \qquad (1.11)$$

where -e is the electron charge, m its mass and ε_0 the permittivity of free space. From this result the photon energy emitted/absorbed in a transition between the pth and nth orbit is

$$\Delta E = Rhc[1/n^2 - 1/p^2], \qquad (1.12)$$

where p > n is required for this to be positive. R is $me^4/[4\pi c(4\pi\varepsilon_0)^2\hbar^3]$ so this reproduces the main features of the hydrogen spectrum with Rbeing equal to the experimental Rydberg constant. The radius of the innermost orbit, called the *Bohr radius*, is

$$a_0 = 4\pi\varepsilon_0 \hbar^2 / (me^2). \tag{1.13}$$

Despite its undoubted success in the case of hydrogen, Bohr's model fails to explain the spectrum of neutral helium. Its hybrid nature is also very unsatisfying and it lacks any means for calculating transition rates. Further progress in understanding required the quantum mechanics developed by Born, Heisenberg and Schrödinger.

1.5 Wave–particle duality

The connection between the particle and wave properties for electromagnetic radiation, and for material particles, is statistical. Thus the probability of finding a photon in a given volume dV is determined by the instantaneous energy density, I, of the electromagnetic wave over the same volume

$$P \mathrm{d}V = I \mathrm{d}V / \int I \mathrm{d}V, \qquad (1.14)$$

where P is called the *probability density*. The integral is taken over the whole of space to ensure that the total probability of the photon being



Fig. 1.3 Distribution of photons in the detection plane in Young's two slit experiment for 10, 1000 and 20 000 photons. The broken curves indicate the classical interference pattern.

found somewhere is unity.

Young's two slit experiment will be used to illustrate the statistical interpretation. Suppose the observation screen is a pixelated detector with granularity much finer than the fringe widths, and that all the pixels are equally efficient in detecting photons. Further, suppose that an extremely low intensity source is used, so that at any given moment there is only ever a single photon within the volume between source and Figure 1.3 shows typical histograms of the photon distribuscreen. tion across the detector after 10, 1000 and 20000 photons have been detected. For comparison the calculated wave intensity is superposed. An individual photon may hit anywhere across the screen, other than locations where the wave intensity is precisely zero. Only the probability for arriving at each pixel is known, and the probabilities of reaching a given pixel are identical for each and every photon emerging from the source slit. The distribution with few photons is extremely ragged, but as the number increases the resemblance becomes ever closer to the wave intensity. If the number of photons expected to strike a pixel is n, then the statistical uncertainty in this number is \sqrt{n} . Thus the *fractional* uncertainty is $1/\sqrt{n}$, which falls with increasing n.

The laws of classical physics are deterministic: statistical analysis is used only in dealing with systems containing very large numbers of particles, as in the kinetic theory of gases. By contrast, statistical behaviour is fundamental to quantum systems.

1.6 The uncertainty principle

Heisenberg considered the uncertainty when simultaneous measurements are made of a position component y and corresponding momentum p_y and arrived at the limit

$$\Delta p_y \Delta y \ge \hbar/2, \tag{1.15}$$

known as Heisenberg's *uncertainty principle*. The equality would only be achieved if the distributions of momentum and position were Gaussian, and there were no instrumental errors. The uncertainty principle applies to each dimension separately, from which it follows that simultaneous measurements of the vector position \mathbf{r} and vector momentum \mathbf{p} have uncertainties that satisfy

$$\Delta p_x \Delta p_y \Delta p_z \Delta x \Delta y \Delta z \ge \hbar^3 / 8. \tag{1.16}$$

The product on the left-hand side of this equation can be pictured as a volume element in a six-dimensional space-momentum *phase space*.

Spatial coordinates and time are treated in a unified way within the special theory of relativity: they define a single space-time location (ct, x, y, z). Similarly, energy and momentum form an energymomentum four-vector $(E/c, p_x, p_y, p_z)$, which transforms exactly like a space-time vector under a Lorentz boost from one inertial frame to another. This implies that there must exist an energy-time uncertainty relation

$$\Delta E \Delta t \ge \hbar/2. \tag{1.17}$$

The interpretation differs subtly from that for space-momentum because Δt is the time taken to measure the energy, and ΔE is the resulting uncertainty in this measurement. To be precise, a quantity such as $\Delta \chi$ is the standard deviation of the measurements of χ on a set of similarly prepared states, that is, on an *ensemble*.

1.7 Outline of quantum mechanics

Experiment shows that the laws of conservation of energy, momentum and angular momentum are universal.

The behaviour of electrons or other particles is described by a complex wavefunction that contains all possible information that exists about the system. This wavefunction, $\Psi(q_n, t)$, is a function of time and all the independent variables, written as a set $\{q_n\}$. These variables include the spatial coordinates and its spin (intrinsic angular momentum) state. The interpretation of the wavefunction will always be that the probability for finding a system with variables in a range $dV = dq_1 dq_2 \cdots$ around q_1 , q_2, \cdots is

$$P(q_1, q_2, \cdots) \,\mathrm{d}V = \Psi^* \Psi \mathrm{d}V. \tag{1.18}$$

The wavefunction used is normalized, meaning that a numerical factor is inserted so that integrating PdV over the full range of the independent variables gives unity.

Quantities that are measurable for a particle or a system of particles are known as *observables*. Position, momentum, orbital angular momentum, polarization and energy are all observables. These are therefore *real*, rather than complex, quantities. Each observable has a corresponding operator that acts on the wavefunction describing the system considered. The operators for momentum and the total energy are indicated by placing hats over the respective symbols for the observables

$$\hat{p} = -i\hbar \frac{\partial}{\partial x}, \quad \hat{H} = +i\hbar \frac{\partial}{\partial t}.$$
 (1.19)

Their action is most easily demonstrated by considering a free electron moving in the *x*-direction. This has a plane wavefunction.

$$\Phi_k = (1/\sqrt{L}) \exp\left[i(kx - \omega t)\right], \qquad (1.20)$$

where L is the range in x to which the electron is restricted and can be increased to infinity as required. Then

$$\hat{p}\Phi_k = \hbar k \Phi_k = p\Phi_k, \quad \hat{H}\Phi_k = \hbar \omega \Phi_k = E\Phi_k.$$
 (1.21)

Plane waves provide a simple example for discussion and finite realistic wavepackets are all linear sums of plane waves. Plane sinusoidal waves extend to infinity and the range L is needed to give a normalizable wavefunction. The values of measurable quantities are correctly predicted when the limit $L \to \infty$ is taken. On occasion care is needed when taking the limit.

The quantities p and E appearing on the right-hand side, without hats, are the values that can be obtained in measurements of the momentum and kinetic energy respectively. This prediction of an exact value for the momentum of a plane wave does not violate the uncertainty principle because the location is undetermined.

Operators are complex and the quantities measured are real, so it follows that the waves for electrons and other material particles must themselves be complex, unlike magnetic and electric fields, which are always real. We now come to the equation that is the equivalent for non-relativistic electrons of the wave equation for electromagnetic waves.

1.8 Schrödinger's equation

Starting from the equation for conservation of energy for non-relativistic motion in a potential V,

$$E = V + p^2/2m$$

Schrödinger constructed an operator equation acting on a wavefunction. The total energy and the momentum are replaced by the operator forms from eqn. 1.19, giving

$$i\hbar\partial\Psi(\mathbf{r},t)/\partial t = V(\mathbf{r},\mathbf{t})\Psi(\mathbf{r},t) - (\hbar^2/2m)\nabla^2\Psi(\mathbf{r},t).,$$
 (1.22)

This is Schrödinger's time-dependent equation for non-relativistic motion in a potential $V(\mathbf{r}, \mathbf{t})$. Solutions for the motion in square, harmonic and Coulomb potentials are calculated in Chapter 2.

In the case of a static potential the solution factorizes to give

$$\Psi(\mathbf{r},t) = \psi(\mathbf{r}) \exp\left(-iEt/\hbar\right),\tag{1.23}$$

which, when substituted in Schrödinger's equation, gives its *time inde*pendent form

$$E\psi(\mathbf{r}) = V(\mathbf{r})\psi(\mathbf{r}) - (\hbar^2/2m)\nabla^2\psi(\mathbf{r}), \qquad (1.24)$$

where E is the electron total energy, kinetic plus potential.

Schrödinger's equation is linear in ψ so that the superposition principle applies to wavefunctions that satisfy the equation: adding these wavefunctions with constant coefficients produces another valid wavefunction. There are several crucial differences between, on the one hand, Maxwell's equations for electromagnetic waves, and on the other, Schrödinger's equation for electron waves. Schrödinger's equation is non-relativistic, and complex, so the electron waves are complex and not directly measurable: Maxwell's equations are relativistic, and the electromagnetic fields are directly measurable. A basic understanding of atomic states and their radiation is achieved by applying Schrödinger's equation.

Any solution of Schrödinger's equation must satisfy several simple requirements. Firstly, the wavefunction must be finite and continuous everywhere. If instead the wavefunction jumped discontinuously, the derivative, and hence the momentum, would become infinite. Similarly, the first derivative must be continuous everywhere to avoid an infinite term in the energy. These requirements on continuity are essential tools when joining up solutions of Schrödinger's equation at boundaries where the potential changes.

The non-relativistic density of particles is

$$\rho = \Psi^* \Psi, \tag{1.25}$$

so that

$$\partial \rho / \partial t = \Psi^* \partial \Psi / \partial t + [\partial \Psi^* / \partial t] \Psi.$$
 (1.26)

There is a corresponding vector flux, or current, **j**, defined to be the number of particles crossing unit area in unit time. That is the real part of $\Psi^*[\mathbf{p}/m]\Psi$:

$$\mathbf{j} = (i\hbar/2m)(\Psi\nabla\Psi^* - \Psi^*\nabla\Psi). \tag{1.27}$$

Flux and density obey the standard continuity equation

$$\partial \rho / \partial t + \nabla \cdot \mathbf{j} = 0, \qquad (1.28)$$

which ensures that the number of particles is conserved.

1.9 Eigenstates

The wavefunctions that are solutions of Schrödinger's equation are known as energy *eigenfunctions*. The corresponding energies are called energy *eigenvalues* and the electron is said to be in an *eigenstate* of energy. An eigenstate may be an eigenstate of several observables with each taking unique values for a given eigenstate. These are then known as *compatible* or *simultaneous* observables: examples are the energy, the angular momentum and a component of the angular momentum of an electron in a hydrogen atom. The measurement of an observable leaves the electron in an eigenstate of that variable and its compatible variables. As explained later, the eigenvalues of energy are discrete when the potential localizes the electron in a potential well, but continuous from zero up to any conceivable positive value when an electron is free.

The existence and the properties of eigenstates generalize to systems of electrons and other material particles. Such a system has a set of eigenstates $\{\phi_i\}$ of observables, such as A, with eigenvalues $\{a_i\}$, respectively. With the standard notation the operator corresponding to Ais \hat{A} , and this acts on the wavefunction ϕ_i in the following way:

$$\hat{A}\phi_i = a_i\phi_i,\tag{1.29}$$

meaning that any measurement of the observable A on the eigenstate ϕ_i always gives the eigenvalue a_i .

An intrinsic property of eigenstates is their *orthogonality* in the sense that the overlap integrals between the wavefunctions of any pair of them over all the free variables vanish. Suppose ϕ_i and ϕ_j are two such eigenfunctions of an electron; then

$$\int \phi_j^* \phi_i \, \mathrm{d}V = 0, \quad \text{if } j \neq i. \tag{1.30}$$

Eigenfunctions are usually normalized for convenience so that

$$\int \phi_j^* \phi_i \mathrm{d}V = \delta_{ji},\tag{1.31}$$

where δ_{ji} is the Kronecker δ defined by

$$\delta_{ji} = 0 \text{ for } j \neq i; \ \delta_{ji} = 1 \text{ for } j = i.$$
(1.32)

In the case of a free particle $\phi(x) = \exp(ikx)$, where k is a continuous variable rather than an integer label, then

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \phi^*(x')\phi(x) dk = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp[i(kx - kx')] dk = \delta(x - x').$$
(1.33)

where δ is the *Dirac delta function* This has the property that for any function f(x)

$$\int f(x)\delta(x-x')\mathrm{d}x = f(x'), \qquad (1.34)$$

provided the range of integration includes the point x = x'; otherwise it vanishes. The Dirac δ -function $\delta(x - x')$ is effectively an infinitely narrow and tall spike at x = x' such that the area under this spike is exactly unity.

1.10 Observables and expectation values

In the more general case that a system is not in an eigenstate of an observable, the value that is obtained by measuring the observable can only be predicted statistically. Quantum mechanics predicts the *expectation value* of an observable A, which is written $\langle \hat{A} \rangle$, is obtained using the equation

$$\langle \hat{A} \rangle = \int \psi^* \hat{A} \psi \, \mathrm{d}V, \qquad (1.35)$$

where ψ is normalized. The equation is to be interpreted in this way. This is the average value found if A is measured on a large number of systems which have been prepared in exactly the same way so that they have identical wavefunctions ψ – such a hypothetical collection of systems is called an *ensemble*. In the case of an eigenstate of the observable A the expectation value is simply the eigenvalue of A for that eigenstate. Any wavefunction ψ of a system which has an observable A can always be expanded as a linear superposition of the normalized eigenfunctions $\{\phi_i\}$ of A. Assuming for simplicity that the eigenvalues are discrete,

$$\psi = \sum_{i} c_i \phi_i. \tag{1.36}$$

Then the expectation value of A in a state with wavefunction ψ is

$$\langle \hat{A} \rangle = \sum_{j} c_{j}^{*} c_{j} a_{j}.$$
(1.37)

where $c_j^* c_j$ is the probability that the system is found to be in the eigenstate ϕ_j with eigenvalue a_j of A. When the eigenvalues are continuous, as for example the momentum $\hbar k$ of a free electron described by eqn. 1.20,

$$\psi = \int c(k)\phi_k \,\mathrm{d}k,\tag{1.38}$$

and

$$\langle \hat{A} \rangle = \int c^*(k) c(k) a(k) \,\mathrm{d}k, \qquad (1.39)$$

where a(k) is the value obtained when A is measured on the eigenstate with momentum k. In particular $c^*(k)c(k) dk$ is the probability that the measurement gives a momentum eigenvalue lying between k and k + dk.

All measurements yield real values so that the expectation value of an observable, A, is always real; hence it equals its complex conjugate so that

$$\int \psi^* \hat{A} \psi dV = \int (\hat{A} \psi)^* \psi \, dV.$$
(1.40)

Operators with this mathematical property are called *hermitean*.

Eigenstates of a system are usually eigenstates of several observables, and it requires knowledge of all of these to completely specify an eigenstate. Here we consider the case where there are just two of these *compatible* observables, A and B. There is a set of eigenfunctions $\{\phi\}$ for which

$$\hat{A}\phi_j = a_j\phi_j; \ \hat{B}\phi_j = b_j\phi_j.$$

Suppose some eigenfunctions are degenerate, that is to say they share the same eigenvalue for A, while each has an eigenvalue of B different from that of all the others. A measurement of A may then leave the system in a state described by a superposition of the degenerate eigenfunctions. A subsequent measurement of B will result in the wavefunction collapsing into a single eigenfunction from this superposition, for example ϕ_k . Further measurements thereafter of A and B yield a_k and b_k respectively. The expectation value for the product of compatible observables

$$\int \psi^* \hat{A} \hat{B} \psi \, \mathrm{d}V = \sum_j c_j^* c_j a_j b_j = \int \psi^* \hat{B} \hat{A} \psi \, \mathrm{d}V,$$

holds true whatever arbitrary state ψ of the system is being considered. Consequently the expectation value of $\hat{A}\hat{B} - \hat{B}\hat{A}$ always vanishes. This operator is called the *commutator* of A and B and is written with square brackets $[\hat{A}, \hat{B}]$. In the case of compatible observables

$$[\hat{A}, \hat{B}] = 0: \tag{1.41}$$

 \hat{A} and \hat{B} are said to commute.

Pairs of conjugate variables like \hat{p}_x and \hat{x} are not compatible observables. It follows from eqn. 1.19 that

$$[x, p_x]\psi = x(-i\hbar\partial/\partial x)\psi + i\hbar\partial(x\psi)/\partial x$$

= $-ix\hbar(\partial\psi/\partial x) + i\hbar(\partial x/\partial x)\psi + i\hbar x(\partial\psi/\partial x)$
= $i\hbar\psi.$ (1.42)

There are corresponding relations for the commutators of other pairs of conjugate variables.

1.11 Collapse of the wavefunction

A most surprising feature of quantum mechanics has been left for discussion here. Any measurement of the observable A on a system in a superposition of eigenstates of A with wavefunction $\psi = \sum_i \phi_i$ gives some eigenvalue a_j . The system is thereafter in the eigenstate with wavefunction ϕ_j , and no longer in the state with wavefunction ψ . A second measurement of the observable A will again give a_j , and so would further measurements. The result of the first measurement is profoundly different from anything met in classical mechanics. There is a discontinuity: up to the exact moment of the measurement the system is evolving according to the wavefunction ψ and immediately afterwards its wavefunction has become ϕ_j . This step is known as the *collapse of the wavefunction*. It is clearly a very drastic step because, for example when a photon is absorbed on an atom in the photoelectric effect, the photon wavefunction over all space collapses simultaneously.

1.12 Schrödinger's cat

Schrödinger highlighted a logical difficulty arising out of the collapse of the wave function. A cat is locked in a box together with a mechanism which will release a lethal gas if and when a single radioactive nucleus decays. It is then argued that the wavefunction of the contents of the box should contain two terms: the first term describing an undisturbed mechanism and a live cat; the second describing an activated mechanism and a dead cat. Later Schrödinger opens the box and observes the contents. At this instant the wavefunction of the contents collapses to either one that contains a live cat, or to another that contains a dead cat. A popular resolution of this paradox of having a cat simultaneously alive and dead is through what is called *decoherence*. Broadly speaking any interaction of a quantum system with its surroundings, for example gas molecules striking the cat, is supposed to cause the collapse its wavefunction.⁴ A counter view is that the interactions only cause loss of phase coherence between the macroscopic states and leave them superposed.⁵

1.13 No-cloning theorem

Quantum mechanics forbids the creation of exact replicas of arbitrary quantum states. If it were possible to do so then one observable could be measured on the original and the conjugate observable measured on the clone, both with high precision. As a result, both observables would be precisely known for the parent quantum state, which would violate the uncertainty principle. Suppose we attempt to clone a state labelled '1', which is an arbitrary superposition of two pure states

$$\psi(1) = \alpha \psi_a(1) + \beta \psi_b(1), \qquad (1.43)$$

where α and β are some unknown constants. Then making a copy labelled '2' gives

$$Copy[\psi(1)] = \alpha Copy[\psi_a(1)] + \beta Copy[\psi_b(1)]$$

= $\alpha \psi_a(1)\psi_a(2) + \beta \psi_b(1)\psi_b(2)$ (1.44)

whereas true cloning⁶ would produce $\psi(1)\psi(2)$.

1.14 Wavepackets

Wavepackets considered here are finite wavetrains of electromagnetic waves emitted by a source, and contain a number of photons determined by the physical situation. Wavepackets exist equally for any particle species. In free space wavepackets travel without change of shape because all the frequency components travel at the same velocity, c. However, in dispersive media the velocity depends on the frequency. For example the electric field

$$E(z,t) = \int \epsilon(\omega) \exp[i(kz - \omega t)] \,\mathrm{d}\omega, \qquad (1.45)$$

k being the wavenumber and $\epsilon(\omega)$ is the wave distribution in angular frequency centred on ω_0 . This is portrayed at a given location in the upper plot of Figure 1.4. Rewriting this waveform to first order in $(\omega - \omega_0)$

$$E(z,t) = \exp[i(k_0 z - \omega_0 t)] \int \epsilon(\omega) \exp[i(\omega - \omega_0)(z \, \mathrm{d}k/\mathrm{d}\omega - t)] \,\mathrm{d}\omega, \quad (1.46)$$

⁶Obviously a single pure state can be copied but we have to know that it is a pure state in the first place. It is cloning of an arbitrary and therefore unknown quantum state that is forbidden. See W. K. Wootters and W. H. Zurek, *Nature* 299, 802 (1982).

⁴See, for example, 'Decoherence and the the Transition from Quantum to Classical' by W. H. Zurek, *Physics Today*, October 1991.

⁵See A. Bassi, K. Lochan, S. Satin, T. P. Singh, and H. Ulbricht, *Reviews of Modern Physics* 85, 471 (2013).



Fig. 1.4 The time and angular frequency distributions for a Gaussian wavepacket. In this case the full width at half maximum is 2.36 times the standard deviation.

In the case of microwaves of much lower frequency, it is the electric field that is detected. Very large numbers of photons make up the signal detected, so that a classical analysis is generally adequate. where ω_0 and k_0 are the central values. The first term describes the rapidly oscillating waves within the envelope that have the *wave velocity* $v_w = \omega_0/k_0$. The integral describes the envelope. Its maximum is located where all the waves are in phase, that is, where $z dk/d\omega = t$. Thus the envelope has the group velocity, $v_g = d\omega/dk$. Photons, and energy and information, all travel at the group velocity. Suppose the wave velocity is less than the group velocity, then to an observer moving at the group velocity the waves would appear to travel backward within the envelope in the upper plot.

Measurements on photons from identically prepared wavepackets must satisfy time/angular frequency and position/wave-vector uncertainty relations:

$$\Delta t \Delta \omega \ge 1/2, \quad \Delta x \Delta k \ge 1/2,$$
 (1.47)

where Δx , etc. are standard deviations in measurements. The most convenient wavepackets for use in analysis are Gaussian in shape, and approximations to this shape are met often enough to be of practical interest. An example is drawn in Figure 1.4, first as a function of time at a fixed location and then as a function of angular frequency: these are both amplitude plots. The corresponding intensity plots, proportional to the probability of finding a photon, are shown in Figure 1.5. These are also Gaussians, narrower than the amplitude envelopes by a factor $\sqrt{2}$. Only the envelope is shown because detectors of light, which typically have nanosecond resolution, cannot follow the wave oscillations under the envelope at 10^{14} Hz. Explicitly the intensity distributions are

$$I(t - t_0) = \frac{1}{\sqrt{2\pi\sigma_t}} \exp[-(t - t_0)^2 / (2\sigma_t^2)], \qquad (1.48)$$

$$I(\omega - \omega_0) = \frac{1}{\sqrt{2\pi\sigma_\omega}} \exp[-(\omega - \omega_0)^2 / (2\sigma_\omega^2)].$$
(1.49)

These are related through Fourier transforms

$$I(\omega) = \int_{-\infty}^{\infty} I(t) \exp(i\omega t) dt,$$

$$I(t) = \int_{-\infty}^{\infty} I(\omega) \exp(-i\omega t) d\omega.$$
(1.50)

These distributions have standard deviations σ_{ω} and σ_t related by $\sigma_{\omega}\sigma_t = 1/2$. Projections of the wavepacket in position and wave-vectors are also Gaussian and these too are Fourier transforms of one another.

When measurements are made on photons from a Gaussian wavepacket, taking the errors in the detectors to be negligible, the distributions would have standard deviations σ_t and σ_{ω} . In this special case of Gaussian wavepackets with negligible intrinsic measurement errors, we have uniquely an equality

$$\Delta\omega\Delta t = \sigma_{\omega}\sigma_t = 1/2. \tag{1.51}$$

In any other conditions, with intrinsic errors and/or a non-Gaussian wavepacket, $\Delta\omega\Delta t$ is larger.

1.15 State vectors

States of systems have so far been described by wavefunctions. A more flexible description is provided by *state vectors*, which are indispensable when dealing with quantum fields. State vectors are presented here using the notation introduced by Dirac. For a system with a set of orthonormal wavefunctions $\{\phi_i\}$, any normalized wavefunction can be expanded as

$$\psi = \sum_{i} c_i \phi_i, \qquad (1.52)$$

in which the c_i s are complex coefficients. Then the integral

$$\int \psi^* \psi \, \mathrm{d}V = \sum_{ij} c_i^* c_j \int \phi_i^* \phi_j \, \mathrm{d}V = \sum_i c_i^* c_i.$$
(1.53)

The right-hand side of this equation can be expressed in matrix notation as

$$\begin{pmatrix} c_1^* & c_2^* & c_3^* & \cdots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \cdot \\ \cdot \end{pmatrix}$$
, (1.54)

which is identical to the scalar product of two vectors with coordinate lengths referred to the same set of orthogonal axes $(c_1^*, c_2^*, c_3^*, \cdots)$ and (c_1, c_2, c_3, \cdots) . We define the unit vector along the *i*th axis to be $|\phi_i\rangle$. This space is known as a *Hilbert space* and all the vectors, including $|\phi_i\rangle$, are called *kets*. The state vector for the column matrix above is then a ket,

$$|\psi\rangle = \sum_{i} c_i \, |\phi_i\rangle,\tag{1.55}$$

an equation equivalent to eqn. 1.52. Another type of state vector is needed to correspond to the row matrix in eqn. 1.54. These are called *bra vectors*, and are written $\langle \psi |$ and $\langle \phi_i |$. Note that the vectors $|\psi \rangle$ and $\langle \psi |$ describe *exactly* the same state.⁷ For the bra vectors

$$\langle \psi | = \sum_{i} c_i^* \langle \phi_i |. \tag{1.56}$$

The scalar product $\langle \phi_i | \phi_j \rangle$ is the overlap of these states given by

$$\langle \phi_i | \phi_j \rangle = \int \phi_i^* \phi_j \, \mathrm{d}V = \delta_{ij}.$$
 (1.57)

Correspondingly,

$$\langle \psi | \phi_i \rangle = c_i^*, \text{ and } \langle \phi_i | \psi \rangle = c_i.$$
 (1.58)

Then the state vectors $|\psi\rangle$ and $\langle\psi|$ can be expanded in this way

$$|\psi\rangle = \sum_{i} \langle \phi_i |\psi\rangle |\phi_i\rangle, \text{ and } \langle \psi| = \sum_{i} \langle \psi |\phi_i\rangle \langle \phi_i|.$$
 (1.59)



Fig. 1.5 The time and angular frequency intensity distributions for the Gaussian wavepacket amplitudes shown in 1.4.

⁷The Hilbert spaces containing the bra and ket vectors are actually separate vector spaces known as dual spaces. If wavefunctions were real then only one vector space would suffice. We can rewrite the first equation as

$$|\psi\rangle = \sum_{i} |\phi_{i}\rangle\langle\phi_{i}|\psi\rangle, \qquad (1.60)$$

which demonstrates that

where I is the identity matrix. This useful result is called the *closure* relation. The expectation value of an observable A in the state described by $|\psi\rangle$ is given by

$$\langle \hat{A} \rangle = \int \psi^* \hat{A} \psi \, \mathrm{d}V = \sum_{ij} c_i^* c_j \, \langle \phi_i | \hat{A} | \phi_j \rangle, \qquad (1.62)$$

which contains matrix elements $A_{ij} = \langle \phi_i | \hat{A} | \phi_j \rangle$. Observables are real and A_{ij} is hermitian: $A_{ij}^* = A_{ji}$. The complex conjugate transpose of a matrix A is written A^{\dagger} so that for observables $A^{\dagger} = A$.

The state vector $|\mathbf{r}\rangle$ describes a state whose wavefunction is a delta function at the point \mathbf{r} in space. In this case the connection between the spatial wavefunction and the state vector is

$$\psi(\mathbf{r}) = \langle \mathbf{r} | \psi \rangle. \tag{1.63}$$

In momentum space the wavefunction would be

$$\psi(\mathbf{p}) = \langle \mathbf{p} | \psi \rangle, \tag{1.64}$$

where $|\mathbf{p}\rangle$ is a delta function at momentum \mathbf{p} . In the case of free particles the Hilbert space with unit vectors $|\mathbf{r}\rangle$ has infinite dimensions. Rephrasing eqn. 1.63 is useful: when a state vector is projected onto eigenstates of, for example, \mathbf{r} the outcome is a wavefunction, in this case $\psi(\mathbf{r})$.

Rotations can be made in Hilbert space which leave any product of state vectors $\langle \psi | \xi \rangle$ unaffected. These transformations differ from rigid rotations in cordinate space because the length of a vector in Hilbert space is a complex number. Suppose U is such a *unitary transformation*,

$$\langle \psi | \xi \rangle = \langle U \psi | U \xi \rangle. \tag{1.65}$$

From this it follows that

$$U^{\dagger}U = I \text{ and } U^{\dagger} = U^{-1}.$$
 (1.66)

Energy being an observable and real, the corresponding operator, the Hamiltonian operator \hat{H} is Hermitian. Hence the time evolution operator $\exp(-i\hat{H}t)$ is unitary:

$$\left[\exp(-i\hat{H}t)\right]^{\dagger} = \exp(i\hat{H}^{\dagger}t) = \exp i\hat{H}t, \qquad (1.67)$$

so that states originally orthogonal remain orthogonal and retain their separate identities.

1.16 Special relativity and electromagnetism

The space-time four-vector for a point at \mathbf{r} at time t is (ct,\mathbf{r}) or X with components

$$X_0 = ct, \quad X_1 = x, \quad X_2 = y, \quad X_3 = z.$$
 (1.68)

The energy-momentum four-vector for a system of energy E and momentum \mathbf{p} is $P = (E/c, \mathbf{p})$. Under a Lorentz transformation from one inertial frame to another (primed) frame with relative velocity $v = \beta c$ parallel to the x(x')-axis four-vectors all transform in the same way:

where $\gamma = \sqrt{1/(1-\beta^2)}$. Quantities like X and P are four-vector representations of the Lorentz group. For four-vectors we introduce the subscript labelling 0, 1, 2, 3 for the time component, x-component, y-component, z-component respectively. We also introduce the *Einstein convention* that if a subscript is repeated it should be summed over, $a_{\mu}b_{\mu}$ is to be read $a_0b_0 - a_1b_1 - a_2b_2 - a_3b_3$. The scalar product of four-vectors is defined by

$$A \cdot B = g_{\mu\nu} A_{\mu} B_{\nu}, \tag{1.70}$$

The *metric tensor* appearing here is

$$g_{\mu\nu} = \begin{bmatrix} +1 & 0 & 0 & 0\\ 0 & -1 & 0 & 0\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & -1 \end{bmatrix},$$
 (1.71)

where the indices run from 0 to 3. These products are scalar representations of the Lorentz group and are invariant under Lorentz transformations. The scalar product of (ct, \mathbf{r}) with itself is:

$$X^{2} = c^{2}t^{2} - x^{2} - y^{2} - z^{2} = c^{2}t^{2} - r^{2}.$$
 (1.72)



Fig. 1.6 Section through the light cones at one point in space-time showing one spatial dimension. A representation for two spatial dimensions can be obtained by rotating the image around the time axis.

This is the new form of Pythagoras' theorem after taking special relativity into account. If X^2 is positive the separation in space-time is *time-like*, if it is negative the separation is *space-like* and if it is zero the separation is *light-like*. No signals can travel over space-like separations, since signals would then be travelling faster than light. Figure 1.6 illustrates by the gray shading the regions of the past that can influence an event (at the centre), and the regions of the future that the event can influence.

The scalar product of an energy-momentum four-vector with itself is:

$$s/c^{2} = E^{2}/c^{2} - p_{x}^{2} - p_{y}^{2} - p_{z}^{2} = E^{2}/c^{2} - p^{2}.$$
 (1.73)

In the centre of mass frame of a system the vector sum of the momenta is zero, so s is the centre of mass energy squared. In the case of an isolated particle

$$m^2 c^4 = E^2 - p^2 c^2, (1.74)$$

where m is its rest mass. At low energies such that $cp \ll mc^2$ we can expand this as

$$E = mc^{2} + p^{2}/(2m) + \cdots, \qquad (1.75)$$

and at high energies such that $cp \gg mc^2$, as met for neutrinos,

i

$$E = cp + m^2 c^3 / (2p) + \cdots, \qquad (1.76)$$

and in the limit for the massless photons E = cp. The scalar product of space-time and energy-momentum four-vectors is equally invariant under Lorentz transformations $P \cdot X = Et - \mathbf{p} \cdot \mathbf{r}$. This appears in the wave function of free particles:

$$\Psi(\mathbf{r},t) = \exp[-i(Et - \mathbf{p} \cdot \mathbf{r})] = \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)\hbar], \quad (1.77)$$

where $\mathbf{k} = \mathbf{p}/\hbar$ is the wave-vector and $\omega = E/\hbar$ the angular frequency.

Any quantities that are representations of the Lorentz group are known as *Lorentz covariant*. Relationships between covariant quantities do not change their form under Lorentz transformations and are also Lorentz covariant. Maxwell's equations are a fundamental example.

In the presence of an electromagnetic field the energy and momentum of a particle need to be specified more carefully. Suppose the Lorentz four-vector potential describing the field is $(\phi/c, \mathbf{A})$ with electric and magnetic fields $-\nabla \phi - \partial \mathbf{A}/\partial t$ and $\nabla \wedge \mathbf{A}$. Then the components of a particle's energy-momentum vector become:

$$E/c + q\phi/c$$
 and $m\mathbf{v} = \mathbf{p} - q\mathbf{A}$, (1.78)

with q being the particle's charge. The symbol e is only used in this textbook in the electron's charge -e. The quantity $m\mathbf{v}$ is the usual *physical momentum* of a particle of mass m with velocity \mathbf{v} . The quantity

p is the *canonical momentum* conjugate to the coordinate: in operator form $[x, p_x] = i\hbar$. For completeness note that the corresponding non-relativistic Lagrangean is

$$L = mv^2/2 - q\phi + q\mathbf{A} \cdot \mathbf{v}, \qquad (1.79)$$

and
$$\mathbf{p} = \partial L / \partial \mathbf{v} = m \mathbf{v} + q \mathbf{A}.$$
 (1.80)

The Hamiltonian (energy) is

$$H = [\mathbf{p} - q\mathbf{A}]^2 / (2m) + q\phi. \qquad (1.81)$$

In addition, the current carried by particles of charge q becomes, in the presence of an electromagnetic field, the real part of $(q/m)[\Psi^*(\mathbf{p}-q\mathbf{A})\Psi]$, that is

$$\mathbf{j} = \frac{q}{2m} [\Psi(i\hbar\nabla - q\mathbf{A})\Psi^* - \Psi^*(i\hbar\nabla + q\mathbf{A})\Psi].$$
(1.82)

This reduces to

$$\mathbf{j} = \frac{iq\hbar}{2m} [\Psi \nabla \Psi^* - \Psi^* \nabla \Psi] - \frac{q^2}{m} \mathbf{A} |\Psi|^2.$$
(1.83)

The four-vector potential is not unique: under what is called a *local* gauge transformation the physical electric and magnetic fields are unchanged. With $\alpha(t,\mathbf{r})$ being any smoothly varying scalar function of position and time, the corresponding local gauge transformation is

$$\mathbf{A} \to \mathbf{A} - \nabla \alpha; \quad \phi \to \phi + \partial \alpha / \partial t.$$
 (1.84)

The four-vector form of, for example, the momentum operator is

$$\hat{P} = (\hat{E}/c, \hat{\mathbf{p}}) = i\hbar \left[\frac{\partial}{c\partial t}, -\frac{\partial}{\partial x}, -\frac{\partial}{\partial y}, -\frac{\partial}{\partial z}\right], \quad (1.85)$$

or in shorthand notation: $i\hbar \frac{\partial}{\partial x_{\mu}}$ and $i\hbar \partial_{\mu}$.

The wave equation of electromagnetism in the presence of a current \mathbf{j} , obtained from Maxwell's equations, will also be needed:⁸

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = -\mu_0 \mathbf{j}.$$
 (1.86)

This requires a choice of gauge fields such that

$$\frac{1}{c}\frac{\partial\phi}{\partial t} + \nabla \cdot \mathbf{A} = 0, \qquad (1.87)$$

known as the Lorentz gauge.

Finally a relativistic equivalent of Schrödinger's equation is obtained, starting with eqn. 1.74. The kinematic quantities are replaced by operators and the result applied to a wavefunction ϕ representing a massive material particle. This gives the *Klein–Gordon* equation,

$$m^2 c^4 \phi = -\hbar^2 \partial^2 \phi / \partial t^2 + \hbar^2 c^2 \nabla^2 \phi.$$
(1.88)

⁸Page 410 in *Classical Electrodynamics* by W. Greiner, published by Springer (1996), but using S.I. units. Note the standard use of the symbol ϕ as the wavefunction of a scalar particle and as the electric potential.

All particles must satisfy this equation. However, on its own, because it lacks any reference to spin, it is inadequate to describe relativistic electrons. Dirac's relativistic description of electrons is covered in Appendix G. This takes account of both spin and, equally important, the existence of antiparticles . Paralleling this approach the Klein–Gordan equation provides an adequate description of spinless (scalar) particles.

1.17 Further reading

There are numerous good introductions to quantum mechanics. A welltried example is *Quantum Mechanics*, 5th edition, by A. I. M. Rae, published by Taylor and Francis, London (2007). More sophisticated is *Lectures on Quantum Mechanics*, by the Nobel Laureate Steven Weinberg, published by Cambridge University Press (2012).

Exercises

- (1.1) In the case of a particle having high energy compared to its rest mass energy, show that the appropriate expansion of the energy equation is $E = pc + m^2 c^3/(2p) + \dots$
- (1.2) Where ψ is some scalar that varies smoothly with position, show that the simultaneous transformations of the electromagnetic vector field $(\mathbf{A}, \phi/c)$

 $\begin{array}{ll} \mathbf{A} & \rightarrow \mathbf{A} + \nabla \psi \\ \phi & \rightarrow \phi - \partial \psi / \partial t \end{array}$

do not affect measureable quantities.

- (1.3) Calculate the particle density and flux in a plane wave $\exp[i(\mathbf{k} \cdot \mathbf{r} \omega t)]/\sqrt{V}$ and check that the continuity equation holds.
- (1.4) Evaluate the commutator of the energy and time operators [E, t].
- (1.5) Time dilation has $\Delta t' = \gamma \Delta t$ and the Lorentz contraction has $\Delta x' = \Delta x/\gamma$. In each case spell out what is being measured in which frame. Then deduce these results.
- (1.6) Show that in a rigid rotation in normal space the product of the transformation matrix and its transpose equals the identity matrix.
- (1.7) $|\xi_i\rangle$ is one of a set of orthonormal eigenstates. What is the operator that projects out the contribution of this eigenstate from a normalized state $|\phi\rangle$?

- (1.8) Two lasers illuminate one each of the pair of slits in a Young's two slit interference experiment. They are tuned to the same frequency. Would interference fringes be seen? If so, explain how it is possible when any given photon originates from only one laser?
- (1.9) A light source at a frequency f with a spectral width Δf has lateral dimensions r. What are the dimensions of the volume over which the light is coherent at a distance L from the source? $L \gg r$. Light at one point in the coherence volume has a fixed phase with respect to light at another point in the same coherence volume. Light from two such points can be superposed by means of mirrors, lenses, etc. and will show interference. Light from two points not within the same coherence volume have time varying relative phases and intereference fringes are not seen. Take L to be 1 m, Δf to be 10^{10} Hz, r to be 1 µm, and the wavelength to be 0.5 µm.
- (1.10) A vertically polarized beam of light is incident in sequence on a polaroid that transmits light with its polarization at 45 degrees to the vertical and a polaroid that transmits light that is horizontally polarized. Using quantum mechanics explain how light initially vertically polarized can pass through the second horizontal polarizer.

Solutions to Schrödinger's equation

2

2.1 Introduction

Solutions to Schrödinger's equation are presented for square, harmonic and Coulomb wells. Barrier penetration in nuclear α -decay is used to illustrate the use of the solution for the square well potential. The solution for the harmonic well potential provides a first step toward the quantum theory of electromagnetic fields. Finally, the solution for the Coulomb potential provides the basis for explaining the states of the hydrogen atom. This is supplemented by a discussion of fine and hyperfine splitting of atomic energy levels.

2.2 The square potential well

The potential is drawn in Figure 2.1, it has a value $-V_0$ over the region -a/2 < x < a/2 and is zero elsewhere. Within the attractive well Schrödinger's equation is

$$(-\hbar^2/2m)\mathrm{d}^2\psi/\mathrm{d}x^2 = (E+V_0)\psi \text{ (internal)}, \qquad (2.1)$$

while outside the potential it becomes

$$(-\hbar^2/2m)\mathrm{d}^2\psi/\mathrm{d}x^2 = E\psi \text{ (external)}.$$
 (2.2)

Bound states of the particle, say an electron, for which E is negative and the kinetic energy, $(E + V_0)$, is positive are considered first. A solution inside the well, which is symmetric about the origin is

$$\psi_{\mathbf{i}} = A_{\mathbf{i}} \cos\left(k_{\mathbf{i}}x\right),\tag{2.3}$$

where $k_{\rm i} = \sqrt{2m(E+V_0)}/\hbar$ and $A_{\rm i}$ is some constant. Externally

$$\psi_{\rm e} = A_{\rm e} \exp\left(\mp k_{\rm e} x\right) \tag{2.4}$$

where $k_{\rm e} = \sqrt{-2mE}/\hbar$ and $A_{\rm e}$ is another constant. The upper sign in the exponent is taken for x > a/2 and the lower sign for x < -a/2. The opposite choices of sign for the exponentials would give wavefunctions growing exponentially with the distance from the well. These can be rejected because they grow infinitely.

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Fig. 2.1 The energy levels of eigenstates in the square potential well.

Applying the requirements that the wavefunction and its first derivative are continuous at the wall at x = a/2 gives

$$A_{i} \cos \left(k_{i} a/2\right) = A_{e} \exp \left(-k_{e} a/2\right) \text{ and}$$
$$A_{i} k_{i} \sin \left(k_{i} a/2\right) = k_{e} A_{e} \exp \left(-k_{e} a/2\right).$$

Dividing one equation by the other gives

$$k_{\rm e} = k_{\rm i} \tan\left(k_{\rm i} a/2\right). \tag{2.5}$$

From the definitions of k_i and k_e we also have

$$(k_{\rm i}a/2)^2 + (k_{\rm e}a/2)^2 = ma^2 V_0/(2\hbar^2).$$
(2.6)

The last two equations can be solved simultaneously either by computer or graphically as exhibited in Figure 2.2 where $(k_e a/2)$ is plotted as a function of $(k_i a/2)$ for a given potential V_0 . The relation found in eqn. 2.5 is represented by the full lines, while the quarter circle represents eqn. 2.6 with $ma^2V_0/(2\hbar^2)$ taken to be 100. Simultaneous solutions to eqns. 2.5 and 2.6 lie at the points where these curves intersect.

A second set of wavefunctions that are antisymmetric about the origin also satisfy Schrödinger's equation for the square well. The waves inside the well have the form

$$\psi_{\rm i} = B_{\rm i} \sin\left(k_{\rm i} x\right),\tag{2.7}$$

where B_i is some constant. Outside the well

$$\psi_{\rm e} = B_{\rm e} \exp\left(\mp k_{\rm e} x\right) \tag{2.8}$$

where $B_{\rm e}$ is another constant. For these wavefunctions the continuity conditions lead to a different transcendental equation

$$k_{\rm e} = -k_{\rm i} \cot(k_{\rm i}a/2).$$
 (2.9)

This equation is plotted with broken lines in Figure 2.2. On this plot the simultaneous solutions to eqns. 2.9 and 2.6 lie at the intersections of the broken lines and the quarter circle. Then on Figure 2.1 the energy levels of all seven solutions are shown using full and broken lines for the states with even and odd wavefunctions respectively. Finally the wavefunctions of the four lowest energy (most tightly bound) states are plotted in Figure 2.3.

The preceding analysis shows that bound states are restricted to discrete energies. Only then can the sinusoidal waves inside the well join smoothly onto a wave that decays exponentially outside the well. At other energies the requirement of continuity at the boundary makes it necessary to have a sum of a decaying and an *increasing* exponential outside the well. No matter how little the electron's energy differs from the discrete value picked out by the solution of Schrödinger's equation in Figure 2.2, the exponentially increasing component of the wave outside



Fig. 2.2 Graphical method of solving Schrödinger's equation for the square well potential.

the well will tend to infinity at an infinite distance. Such a wavefunction cannot describe electron states localized in the well. This restriction, in some situations, to states with *discrete* energies is a feature specific to quantum mechanics. Discrete energy states are met in atoms, molecules, nuclei and elementary particles. Particles with positive energies have wavefunctions that are oscillatory both inside and outside the potential well. The continuity conditions at the boundary can now be satisfied at any positive energy and so there is a continuum of allowed states extending from zero energy upwards.

2.2.1 Barrier penetration

In contrast to the classical prediction, electrons and other particles, can penetrate regions where their kinetic energy is negative. The particle wavefunction decays exponentially as it penetrates such a region. When, as in Figure 2.4, the potential barrier is of finite width, the particle's wavefunction penetrates the potential barrier and emerges as an oscillatory wave that travels away from the boundary. Particles can therefore travel through a region where their kinetic energy is negative and penetrate to the far side. This purely quantum process is called *barrier penetration* or *tunnelling*.

The penetration of evanescent electromagnetic waves through interfaces at which total internal reflection is expected is also due to barrier penetration. Its exploitation in monomode optical fibre underpins the telecomms industry: near-infrared radiation is guided along the glass core by total internal reflection between the core and the glass cladding. Nonetheless, around half the energy is carried by the evanescent wave travelling in the cladding. This parallel between the behaviour of electrons and photons can be better appreciated when their wave equations are compared. The electromagnetic wave equation is

$$d^2\psi/dx^2 = -[\omega\mu(x)/c]^2\psi,$$
 (2.10)

with $\mu(x)$ being the refractive index of the material at x and ω the wave's angular frequency. Writing Schrödinger's equation again

$$d^{2}\psi/dx^{2} = -(2m/\hbar^{2})[E - V(x)]\psi, \qquad (2.11)$$

we can recognize the equivalence

$$\mu(x) = \sqrt{2m[E - V(x)]} / (\hbar k), \qquad (2.12)$$

where $k = \omega/c$ is the wave number in vacuum. Barrier penetration corresponds to an imaginary refractive index and hence to decay of the electromagnetic wave. What is expressed here is of general significance: namely, that the electromagnetic wave equation has the same relation to photons that Schrödinger's equation has to non-relativistic electrons.



Fig. 2.3 The four wavefunctions of lowest energy satisfying the square well boundary conditions. The node count is given. Broken lines mark limits of classical motion.



Fig. 2.4 Potential barrier and wavefunction penetration.



Fig. 2.5 The potential seen by the α particle. Its kinetic energy is negative between r_1 and r_2 .

Nuclear species emitting α -particles have a huge range in lifetimes but surprisingly small differences in the energy released: for example ²³⁸U has a half life of 4.4710⁹yr for an energy release of 4.27 MeV, while ²²⁶U has a half life of 0.35s for an energy release of 7.70 MeV. This striking variation in lifetimes can only be explained by quantum barrier penetration. The α -particle is pictured as bouncing to and fro inside the attractive nuclear potential well shown in Figure 2.5. Outside this nuclear potential there is a Coulomb barrier due to the charge on the nucleus. A dotted line indicates the energy of the α -particle which has to penetrate this barrier between radii r_1 and r_2 . The solution to eqn. 2.11 for barrier penetration where the kinetic energy is negative is

$$\psi(r + \mathrm{d}r) = \exp\left(-g\mathrm{d}r\right)\psi(r),\tag{2.13}$$

where $g = \sqrt{(2M/\hbar^2)(V(r) - E)}$ over a region of length dr where the potential is V(r), M is the α -particle mass and E is the energy of the α -particle. Integrating across the barrier

$$\psi(r_2) = \psi(r_1) \exp[-\int_{r_1}^{r_2} g(r) \,\mathrm{d}r] = \psi(r_1) \exp[-G], \qquad (2.14)$$

and the *probability* of transmission through the barrier is

$$T = \exp\left(-2G\right). \tag{2.15}$$

If the α -particle has a velocity v_i inside the nucleus the rate of collisions with the barrier is $[v_i/(2r_1)]$ and the decay probability is

$$P = [v_i/(2r_1)]T = [v_i/(2r_1)] \exp(-2G).$$
(2.16)

The Coulomb potential energy of the α -particle is

$$V(r) = 2Ze^2/(4\pi\varepsilon_0 r), \qquad (2.17)$$

where the atomic number of the daughter nucleus is Z. The energy E equals $V(r_2)$, so we can replace both E and V(r) in eqn. 2.14 to give

$$G = \sqrt{[MZe^2/(\pi\varepsilon_0\hbar^2)]} \int_{r_1}^{r_2} \sqrt{(1/r - 1/r_2)} \,\mathrm{d}r.$$
(2.18)

Making the approximation that r_2 is much larger than r_1 this yields

$$G = \sqrt{[MZe^2/(\pi\epsilon_0\hbar^2)]} \ [\pi\sqrt{r_2}/2 - \sqrt{r_1}].$$
(2.19)

Applying eqn. 2.17 and using the equality of E and $V(r_2)$ again, we have

$$r_2 = 2Ze^2/(4\pi\varepsilon_0 E). \tag{2.20}$$

The radius r_1 varies little between the nuclei considered and this fact allows some simplification from here onward. Then using eqn. 2.16 and substituting for r_2 in G gives

$$P = [v_i/(2r_1)] \exp\{-\sqrt{(M/2E)} [Ze^2/\varepsilon_0\hbar)] + c_1\}, \qquad (2.21)$$