

Advanced Quantum Mechanics

William Royce

May 30, 2024

Part II Physics, The University of Cambridge

Abstract

The abstract (no more than 250 words) makes it possible to assess the interest of a document and makes it easier to identify it in a bibliographic search in databases where the document is referenced.

It is recommended that the summary briefly addresses:

- Main objectives and theme or motivations for the work;
- Methodology used (when necessary for understanding the report);
- Results, analyzed from a global point of view;
- Conclusions and consequences of the results, and link to the objectives of the work.

As this report template is aimed at work that focuses mainly on software development, some of these components may be less emphasized, and information on the work's analysis, design, and implementation may be added.

The abstract should not contain references.

Keywords: Keyword 1 · Keyword 2 · Keyword 3 · Keyword 4

Contents

1	Wave Mechanics and the Schrödinger Equation	1
1.1	Historical Foundations of Quantum Physics	1
1.1.1	Black-body Radiation	1
1.1.2	Photoelectric Effect	2
1.1.3	Compton Scattering	3
1.1.4	Atomic Spectra	3
1.2	Wave Mechanics	4
1.2.1	Maxwell's Wave Equation	5
1.2.2	Schrödinger's Equation	6
1.3	Postulates of Quantum Theory	7
2	Quantum Mechanics in One Dimension	9
2.1	Wave Mechanics of Unbound Particles	10
2.1.1	Particle Flux and conservation of probability	10
2.1.2	Free Particle	10
2.1.3	Potential Step	12
2.1.4	Potential Barrier	12
2.1.5	The Rectangular Potential Well	12
2.2	Wave Mechanics of Bound Particles	12
2.2.1	The Rectangular Potential Well (Continued)	12
2.2.2	The δ -Function Potential Well	12
2.2.3	The δ -Function Model of a Crystal	12
2.3	Wentzel, Kramers and Brillouin (WKB) Method	12
2.3.1	Semi-Classical Approximation to Leading Order	12
2.3.2	Next to Leading Order Correction	12
2.3.3	Connection Formulae, Boundary Conditions and Quantization Rules	12
3	Operator Methods in Quantum Mechanics	13
3.1	Operators	13
3.1.1	Matrix representations of operators	13
3.1.2	Time-evolution operator	13
3.1.3	Uncertainty principle for non-commuting operators	13
3.1.4	Time-evolution of expectation values	13
3.2	The Heisenberg picture	13
3.3	Quantum harmonic oscillator	13
4	Quantum Mechanics in More Than One Dimension	15
4.1	Rigid diatomic molecule	15
4.2	Angular momentum	15
4.2.1	Commutation relations	15
4.2.2	Eigenvalues of angular momentum	15
4.2.3	Representation of the angular momentum states	15
5	Spin	17
5.1	Spinors, spin operators, Pauli matrices	17
5.2	Relating the spinor to the spin direction	17
5.3	Spin precession in a magnetic field	17

5.4	Addition of angular momenta	17
5.4.1	Addition of two spin 1/2 degrees of freedom	17
5.4.2	Addition of angular momentum and spin	17
5.4.3	Addition of two angular momenta $J = 1$	17
6	Motion in a Magnetic Field	19
6.1	Classical mechanics of a particle in a field	19
6.2	Quantum mechanics of a particle in a field	19
6.3	Gauge invariance and the Aharonov-Bohm effect	19
6.4	Free electron in a magnetic field	19
7	Approximation Methods for Stationary States	21
7.1	Time-independent perturbation theory	21
7.1.1	The perturbation series	21
7.1.2	First order perturbation theory	21
7.1.3	Second order perturbation theory	21
7.2	Degenerate perturbation theory	21
7.3	Variational method	21
8	Symmetry in Quantum Mechanics	23
8.1	Observables as generators of transformations	23
8.2	Consequences of symmetries: multiplets	23
8.3	Rotational symmetry in quantum mechanics	23
8.3.1	Scalar operators	23
8.3.2	Vector operators	23
8.4	The Wigner-Eckart theorem for scalar operators	23
8.4.1	Consequences of the Wigner-Eckart theorem (for scalars)	23
8.5	The Wigner-Eckart theorem for vector operators	23
8.5.1	Selection rules for vector operator matrix elements	23
8.5.2	The Landé projection formula	23
8.6	Magnetic dipole moments	23
8.6.1	g-factors	23
8.6.2	Combining magnetic moments	23
9	Identical Particles	25
9.1	Quantum statistics	25
9.2	Space and spin wavefunctions	25
9.3	Physical consequences of particle statistics	25
9.4	Many-body systems	25
9.4.1	Non-interacting Fermi gas	25
9.4.2	Non-interacting Bose gas	25
10	Atomic Structure	27
10.1	The non-relativistic hydrogen atom	27
10.1.1	The Zeeman effect	27
10.2	The “real” hydrogen atom	27
10.2.1	Relativistic correction to the kinetic energy	27
10.2.2	Spin-orbit coupling	27
10.2.3	Darwin term	27
10.2.4	Info: Lamb shift	27

10.2.5	Hyperfine structure	27
10.3	Multi-electron atoms	27
10.3.1	Central field approximation	27
10.3.2	Spin-orbit coupling	27
10.3.3	Info: jj coupling scheme	27
10.3.4	Zeeman effect	27
11	From Molecules to Solids	29
11.1	The H^+2ion	29
11.2	The H_2 molecule	29
11.3	From molecules to solids	29
12	Time-Dependent Perturbation Theory	31
12.1	Time-dependent potentials: general formalism	31
12.1.1	Dynamics of a driven two-level system	31
12.1.2	Paramagnetic resonance	31
12.2	Time-dependent perturbation theory	31
12.3	“Sudden” perturbation	31
12.3.1	Harmonic perturbations: Fermi’s Golden Rule	31
12.3.2	Info: Harmonic perturbations: second-order transitions	31
13	Scattering Theory	33
13.1	Basics	33
13.2	The Born approximation	33
14	Radiative Transitions	35
14.1	Coupling of matter to the electromagnetic field	35
14.1.1	Quantum fields	35
14.1.2	Spontaneous emission	35
14.1.3	Absorption and stimulated emission	35
14.1.4	Einstein’s A and B coefficients	35
14.2	Selection rules	35
14.3	Lasers	35
14.3.1	Operating principles of a laser	35
14.3.2	Gain mechanism	35
15	Field Theory: From Phonons to Photons	37
15.1	Quantization of the classical atomic chain	37
15.1.1	Info: Classical chain	37
15.1.2	Info: Quantum chain	37
15.2	Quantum electrodynamics	37
15.2.1	Info: Classical theory of the electromagnetic field	37
15.2.2	Quantum field theory of the electromagnetic field	37
15.2.3	Fock states	37
15.2.4	Coherent states	37
15.2.5	Non-classical light	37
	Bibliography	39

A	Proofs and Formula Derivations	A.1
A.0.1	Number of Modes	A.1
A.0.2	Probability Current	A.1

List of Tables

List of Figures

CHAPTER 1

Wave Mechanics and the Schrödinger Equation

The formulation of a consistent theory of statistical mechanics, electrodynamics and special relativity during the latter half of the 19th century and the early part of the 20th century had been a triumph of “unification”. However, the undoubted success of these theories gave an impression that physics was a mature, complete, and predictive science. Nowhere was confidence expressed more clearly than in the famous quote made at the time by Lord Kelvin: *There is nothing new to be discovered in physics now. All that remains is more and more precise measurement.* However, there were a number of seemingly unrelated and unsettling problems that challenged the prevailing theories.

1.1 Historical Foundations of Quantum Physics

1.1.1 Black-body Radiation

In 1860, Gustav Kirchhoff introduced the concept of a “black body”, an object that absorbs all electromagnetic radiation that falls upon it – none passes through and none is reflected. Since no light is reflected or transmitted, the object appears black when it is cold. However, above absolute zero, a black body emits thermal radiation with a spectrum that depends on temperature. To determine the spectrum of radiated energy, it is helpful to think of a black body as a thermal cavity at a temperature, T . The energy radiated by the cavity can be estimated by considering the resonant modes. In three-dimensions, the number of modes, per unit frequency per unit volume is given by

$$N(\nu) d\nu = \frac{8\pi\nu^2}{c^3} d\nu, \quad (1.1)$$

where, as usual, c is the speed of light.

The amount of radiation emitted in a given frequency range should be proportional to the number of modes in that range. Within the framework of classical statistical mechanics, each of these modes has an equal chance of being excited, and the average energy in each mode is $k_B T$ (equipartition), where k_B is the Boltzmann constant. The corresponding energy density is therefore given by the Rayleigh-Jeans law,

$$\rho(\nu, T) = \frac{8\pi\nu^2}{c^3} k_B T. \quad (1.2)$$

This result predicts that $\rho(\nu, T)$ increases without bound at high frequencies, ν — the ultraviolet (UV) catastrophe. However, such behaviour stood in contradiction with experiment which revealed that the high-frequency dependence is quite benign. To resolve

difficulties presented by the UV catastrophe, Planck hypothesized that, for each mode ν , energy is quantized in units of $h\nu$, where h denotes the Planck constant. In this case, the energy of each mode is given by

$$\langle \varepsilon(\nu) \rangle = \frac{\sum_{n=0}^{\infty} nh\nu e^{-nh\nu/k_B T}}{\sum_{n=0}^{\infty} \nu e^{-nh\nu/k_B T}} = \frac{h\nu}{e^{h\nu/k_B T} - 1}, \quad (1.3)$$

leading to the anticipated suppression of high frequency modes. From this result one obtains the celebrated Planck radiation formula,

$$\rho(\nu, T) = \frac{8\pi\nu^2}{c^3} \langle \varepsilon(\nu) \rangle = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/k_B T} - 1}. \quad (1.4)$$

This result conforms with experiment, and converges on the Rayleigh-Jeans law at low frequencies, $h\nu/k_B T \rightarrow 0$. Planck's result suggests that electromagnetic energy is quantised: light of wavelength $\lambda = c/\nu$ is made up of quanta each of which has energy $h\nu$. The equipartition law fails for oscillation modes with high frequencies, $h\nu \gg k_B T$.

A quantum theory for the specific heat of matter, which takes into account the quantization of lattice vibrational modes, was subsequently given by Debye and Einstein.

1.1.2 Photoelectric Effect

We turn now to the second ground-breaking experiment in the development of quantum theory. When a metallic surface is exposed to electromagnetic radiation, above a certain threshold frequency, the light is absorbed and electrons are emitted (see figure, right). In 1902, Philipp Eduard Anton von Lenard observed that the energy of individual emitted electrons increases with the frequency of the light. This was at odds with Maxwell's wave theory of light, which predicted that the electron energy would be proportional to the intensity of the radiation.

In 1905, Einstein resolved this paradox by describing light as composed of discrete quanta (photons), rather than continuous waves. Based upon Planck's theory of black-body radiation, Einstein theorized that the energy in each quantum of light was proportional to the frequency. A photon above a threshold energy, the "work function" W of the metal, has the required energy to eject a single electron, creating the observed effect. In particular, Einstein's theory was able to predict that the maximum kinetic energy of electrons emitted by the radiation should vary as

$$\text{K.E.}_{\max} = h\nu - W. \quad (1.5)$$

Later, in 1916, Millikan was able to measure the maximum kinetic energy of the emitted electrons using an evacuated glass chamber. The kinetic energy of the photoelectrons was found by measuring the potential energy of the electric field, eV, needed to stop them. As well as confirming the linear dependence of the kinetic energy on frequency, by making use of his estimate for the electron charge, e , established from his oil drop experiment

in 1913, he was able to determine Planck's constant to a precision of around 0.5%. This discovery led to the quantum revolution in physics and earned Einstein the Nobel Prize in 1921.

1.1.3 Compton Scattering

In 1923, Compton investigated the scattering of high energy X-rays and γ -ray from electrons in a carbon target. By measuring the spectrum of radiation at different angles relative to the incident beam, he found two scattering peaks. The first peak occurred at a wavelength which matched that of the incident beam, while the second varied with angle. Within the framework of a purely classical theory of the scattering of electromagnetic radiation from a charged particle - Thomson scattering - the wavelength of a low-intensity beam should remain unchanged.

Compton's observation demonstrated that light cannot be explained purely as a classical wave phenomenon. Light must behave as if it consists of particles in order to explain the low-intensity Compton scattering. If one assumes that the radiation is comprised of photons that have a well defined momentum as well as energy, $p = \frac{h\nu}{c} = \frac{h}{\lambda}$, the shift in wavelength can be understood: The interaction between electrons and high energy photons (ca. keV) results in the electron being given part of the energy (making it recoil), and a photon with the remaining energy being emitted in a different direction from the original, so that the overall momentum of the system is conserved. By taking into account both conservation of energy and momentum of the system, the Compton scattering formula describing the shift in the wavelength as function of scattering angle θ can be derived,

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{m_e c}(1 - \cos \theta). \quad (1.6)$$

The constant of proportionality $h/m_e c = 0.002426$ nm, the Compton wavelength, characterizes the scale of scattering. Moreover, as $h \rightarrow 0$, one finds that $\Delta\lambda \rightarrow 0$ leading to the classical prediction.

1.1.4 Atomic Spectra

The discovery by Rutherford that the atom was comprised of a small positively charged nucleus surrounded by a diffuse cloud of electrons led naturally to the consideration of a planetary model of the atom. However, a classical theory of electrodynamics would predict that an accelerating charge would radiate energy leading to the eventual collapse of the electron into the nucleus. Moreover, as the electron spirals inwards, the emission would gradually increase in frequency leading to a broad continuous spectra. Yet, detailed studies of electrical discharges in low-pressure gases revealed that atoms emit light at discrete frequencies. The clue to resolving these puzzling observations lay in the discrete nature of atomic spectra. For the hydrogen atom, light emitted when the atom is thermally excited has a particular pattern: Balmer had discovered in 1885 that the emitted wavelengths

follow the empirical law, $\lambda = \lambda_0(1/4 - 1/n^2)$ where $n = 3, 4, 5, \dots$ and $\lambda_0 = 3645.6 \text{ \AA}$. Neils Bohr realized that these discrete values of the wavelength reflected the emission of individual photons having energy equal to the energy difference between two allowed orbits of the electron circling the nucleus (the proton), $E_n - E_m = h\nu$, leading to the conclusion that the allowed energy levels must be quantised and varying as $E_n = -\frac{hcR_H}{n^2}$, where $R_H = 109678 \text{ cm}^{-1}$ denotes the Rydberg constant.

How could the quantum $h\nu$ restricting allowed radiation energies also restrict the allowed electron orbits? In 1913 Bohr proposed that the angular momentum of an electron in one of these orbits is quantised in units of Planck's constant,

$$L = m_e v r = n\hbar, \quad \hbar = \frac{h}{2\pi}. \quad (1.7)$$

But why should only certain angular momenta be allowed for the circling electron? A heuristic explanation was provided by de Broglie: just as the constituents of light waves (photons) are seen through Compton scattering to act like particles (of definite energy and momentum), so particles such as electrons may exhibit wave-like properties. For photons, we have seen that the relationship between wavelength and momentum is $p = h/\lambda$. de Broglie hypothesized that the inverse was true: for particles with a momentum p , the wavelength is

$$\lambda = \frac{h}{p}, \quad \text{i.e. } p = \hbar k \quad (1.8)$$

where k denotes the wavevector of the particle. Applied to the electron in the atom, this result suggested that the allowed circular orbits are standing waves, from which Bohr's angular momentum quantization follows. The de Broglie hypothesis found quantitative support in an experiment by Davisson and Germer, and independently by G. P. Thomson in 1927. Their studies of electron diffraction from a crystalline array of Nickel atoms confirmed that the diffraction angles depend on the incident energy (and therefore momentum).

1.2 Wave Mechanics

de Broglie's doctoral thesis, defended at the end of 1924, created a lot of excitement in European physics circles. Shortly after it was published in the Autumn of 1925, Pieter Debye, a theorist in Zurich, suggested to Erwin Schrödinger that he give a seminar on de Broglie's work. Schrödinger gave a polished presentation, but at the end, Debye remarked that he considered the whole theory rather childish: Why should a wave confine itself to a circle in space? It wasn't as if the circle was a waving circular string; real waves in space diffracted and diffused; in fact they obeyed three-dimensional wave equations, and that was what was needed. This was a direct challenge to Schrödinger, who spent some weeks in the Swiss mountains working on the problem, and constructing his equation.

1.2.1 Maxwell's Wave Equation

For a monochromatic wave in vacuum, with no currents or charges present, Maxwell's wave equation,

$$\boxed{\nabla^2 \mathbf{E} - \frac{1}{c^2} \ddot{\mathbf{E}} = 0}, \quad (1.9)$$

admits the plane wave solution, $\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$, with the linear dispersion relation $\omega = c|\mathbf{k}|$ and c the velocity of light. Here, (and throughout the text) we adopt the convention, $\ddot{\mathbf{E}} = \partial_t^2 \mathbf{E}$. We know from the photoelectric effect and Compton scattering that the photon energy and momentum are related to the frequency and wavelength of light through the relations $E = h\nu = \hbar\omega$, $p = \frac{h}{\lambda} = \hbar k$. The wave equation tells us that $\omega = c|\mathbf{k}|$ and hence $E = c|\mathbf{p}|$. If we think of $e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$ as describing a particle (photon) it would be more natural to write the plane wave in terms of the energy and momentum of the particle as $E_0 e^{i(\mathbf{p} \cdot \mathbf{r} - Et)/\hbar}$. Then, one may see that the wave equation applied to the plane wave describing particle propagation yields the familiar energymomentum relationship, $E^2 = (c\mathbf{p})^2$ for a massless relativistic particle.

This discussion suggests how one might extend the wave equation from the photon (with zero rest mass) to a particle with rest mass m_0 . We require a wave equation that, when it operates on a plane wave, yields the relativistic energy-momentum invariant, $E^2 = (c\mathbf{p})^2 + (m_0 c^2)^2$. Writing the plane wave function $\phi(\mathbf{r}, t) = A e^{i(\mathbf{p} \cdot \mathbf{r} - Et)/\hbar}$, where A is a constant, we can recover the energy-momentum invariant by adding a constant mass term to the wave operator,

$$\left(\nabla^2 - \frac{\partial_t^2}{c^2} - \frac{m_0^2 c^2}{\hbar^2} \right) e^{i(\mathbf{p} \cdot \mathbf{r} - Et)/\hbar} = - \frac{((c\mathbf{p})^2 - E^2 + m_0^2 c^4)}{(\hbar c)^2} e^{i(\mathbf{p} \cdot \mathbf{r} - Et)/\hbar} = 0. \quad (1.10)$$

This wave equation is called the **Klein-Gordon equation** and correctly describes the propagation of relativistic particles of mass m_0 . However, its form is inappropriate for non-relativistic particles, like the electron in hydrogen.

Continuing along the same lines, let us assume that a non-relativistic electron in free space is also described by a plane wave of the form $\Psi(\mathbf{r}, t) = A e^{i(\mathbf{p} \cdot \mathbf{r} - Et)/\hbar}$. We need to construct an operator which, when applied to this wave function, just gives us the ordinary non-relativistic energy-momentum relation, $E = \frac{\mathbf{p}^2}{2m}$. The factor of \mathbf{p}^2 can be recovered from two derivatives with respect to \mathbf{r} , but the only way we can get E is by having a single differentiation with respect to time, i.e.

$$i\hbar \partial_t \Psi(\mathbf{r}, t) = - \frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}, t). \quad (1.11)$$

This is Schrödinger's equation for a free non-relativistic particle. One remarkable feature of this equation is the factor of i which shows that the wavefunction is complex.

How, then, does the presence of a spatially varying scalar potential affect the propagation of a de Broglie wave? This question was considered by Sommerfeld in an attempt to

generalize the rather restrictive conditions in Bohr's model of the atom. Since the electron orbit was established by an inverse square force law, just like the planets around the Sun, Sommerfeld couldn't understand why Bohr's atom had only circular orbits as opposed to Keplerlike elliptical orbits. (Recall that all of the observed spectral lines of hydrogen were accounted for by energy differences between circular orbits.

de Broglie's analysis of the allowed circular orbits can be formulated by assuming that, at some instant, the spatial variation of the wavefunction on going around the orbit includes a phase term of the form $e^{ipq/\hbar}$, where here the parameter q measures the spatial distance around the orbit. Now, for an acceptable wavefunction, the total phase change on going around the orbit must be $2\pi n$, where n is integer. For the usual Bohr circular orbit, where $p = |\mathbf{p}|$ is constant, this leads to quantization of the angular momentum $L = pr = n\hbar$.

Sommerfeld considered a general Keplerian elliptical orbit. Assuming that the de Broglie relation $p = h/\lambda$ still holds, the wavelength must vary as the particle moves around the orbit, being shortest where the particle travels fastest, at its closest approach to the nucleus. Nevertheless, the phase change on moving a short distance Δq should still be $p\Delta q/\hbar$. Requiring the wavefunction to link up smoothly on going once around the orbit gives the **Bohr-Sommerfeld quantization condition**

$$\oint p \, dq = nh, \quad (1.12)$$

where \oint denotes the line integral around a closed orbit. Thus only certain *elliptical* orbits are allowed. The mathematics is non-trivial, but it turns out that every allowed elliptical orbit has the same energy as one of the allowed circular orbits. That is why Bohr's theory gave the correct energy levels. This analysis suggests that, in a varying potential, the wavelength changes in concert with the momentum.

1.2.2 Schrödinger's Equation

Following Sommerfeld's considerations, let us then consider a particle moving in one spatial dimension subject to a "roller coaster-like" potential. How do we expect the wavefunction to behave? As discussed above, we would expect the wavelength to be shortest where the potential is lowest, in the minima, because that's where the particle is going the fastest. Our task then is to construct a wave equation which leads naturally to the relation following from (classical) energy conservation, $E = \frac{p^2}{2m} + V(x)$. In contrast to the free particle case discussed above, the relevant wavefunction here will no longer be a simple plane wave, since the wavelength (determined through the momentum via the de Broglie relation) varies with the potential. However, at a given position x , the momentum is determined by the "local wavelength". The appropriate wave equation is the one-dimensional Schrödinger equation,

$$i\hbar\partial_t\Psi(x,t) = -\frac{\hbar^2\partial_x^2}{2m}\Psi(x,t) + V(x)\Psi(x,t), \quad (1.13)$$

with the generalization to three-dimensions leading to the Laplacian operator ∇^2 in place of ∂_x^2 (cf. Maxwell's equation).

So far, the validity of this equation rests on plausibility arguments and hand-waving. Why should anyone believe that it really describes an electron wave? Schrödinger's test of his equation was the hydrogen atom. He looked for Bohr's "stationary states": states in which the electron was localized somewhere near the proton, and having a definite energy. The time dependence would be the same as for a plane wave of definite energy, $e^{-Et/\hbar}$; the spatial dependence would be a time-independent function decreasing rapidly at large distances from the proton. From the solution of the stationary wave equation for the Coulomb potential, he was able to deduce the allowed values of energy and momentum. These values were exactly the same as those obtained by Bohr (except that the lowest allowed state in the "new" theory had zero angular momentum): impressive evidence that the new theory was correct.

1.3 Postulates of Quantum Theory

Since there remains no "first principles" derivation of the quantum mechanical equations of motion, the theory is underpinned by a set of "postulates" whose validity rest on experimental verification. Needless to say, quantum mechanics remains perhaps the most successful theory in physics.

- **Postulate 1.** The state of a quantum mechanical system is completely specified by a function $\Psi(\mathbf{r}, t)$ that depends upon the coordinates of the particle(s) and on time. This function, called the wavefunction or state function, has the important property that $|\Psi(\mathbf{r}, t)|^2 d\mathbf{r}$ represents the probability that the particle lies in the volume element $d\mathbf{r} \equiv d^d\mathbf{r}$ located at position \mathbf{r} at time t .

The wavefunction must satisfy certain mathematical conditions because of this probabilistic interpretation. For the case of a single particle, the net probability of finding it at some point in space must be unity leading to the normalization condition, $\int_{-\infty}^{\infty} |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} = 1$. It is customary to also normalize many-particle wavefunctions to unity. The wavefunction must also be single-valued, continuous, and finite.

- **Postulate 2.** To every observable in classical mechanics there corresponds a linear, Hermitian operator in quantum mechanics.

If we require that the expectation value of an operator \hat{A} is real, then it follows that \hat{A} must be a Hermitian operator. If the result of a measurement of an operator \hat{A} is the number a , then a must be one of the eigenvalues, $\hat{A}\Psi = a\Psi$, where Ψ is the corresponding eigenfunction. This postulate captures a central point of quantum mechanics – the values of dynamical variables can be quantized (although it is still possible to have a continuum of eigenvalues in the case of unbound states).

- **Postulate 3.** If a system is in a state described by a normalized wavefunction Ψ , then the average value of the observable corresponding to \hat{A} is given by

$$\langle \hat{A} \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\mathbf{r}. \quad (1.14)$$

If the system is in an eigenstate of \hat{A} with eigenvalue a , then any measurement of the quantity A will yield a . Although measurements must always yield an eigenvalue,

the state does not have to be an eigenstate of \hat{A} initially. An arbitrary state can be expanded in the complete set of eigenvectors of \hat{A} ($\hat{A}\Psi_i = a_i\Psi_i$) as $\Psi = \sum_i^n c_i\Psi_i$, where n may go to infinity. In this case, the probability of obtaining the result a_i from the measurement of \hat{A} is given by $P(a_i) = |\langle\Psi_i|\Psi\rangle|^2 = |c_i|^2$. The expectation value of \hat{A} for the state Ψ is the sum over all possible values of the measurement and given by

$$\langle\hat{A}\rangle = \sum_i a_i |\langle\Psi_i|\Psi\rangle|^2 = \sum_i |c_i|^2. \quad (1.15)$$

Finally, a measurement of Ψ which leads to the eigenvalue a_i , causes the wavefunction to “collapse” into the corresponding eigenstate Ψ_i . (In the case that a_i is degenerate, then Ψ becomes the projection of Ψ onto the degenerate subspace). Thus, measurement affects the state of the system.

- **Postulate 4.** The wavefunction or state function of a system evolves in time according to the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi(\mathbf{r}, t), \quad (1.16)$$

where \hat{H} is the Hamiltonian of the system. If Ψ is an eigenstate of \hat{H} , it follows that $\Psi(\mathbf{r}, t) = \Psi(\mathbf{r}, 0)e^{-iEt/\hbar}$.

CHAPTER 2

Quantum Mechanics in One Dimension

Following the rules of quantum mechanics, we have seen that the state of a quantum particle, subject to a scalar potential $V(\mathbf{r}, t)$, is described by the time-dependent Schrödinger equation,

$$\boxed{i\hbar\partial_t\Psi(\mathbf{r}, t) = -\frac{\hbar^2\nabla^2}{2m}\Psi(\mathbf{r}, t) + V(\mathbf{r}, t)\Psi(\mathbf{r}, t).} \quad (2.1)$$

As with all second order linear differential equations, if the potential $V(\mathbf{r}, t)$ is time-independent, the time-dependence of the wavefunction can be separated from the spatial dependence. Setting $\Psi(\mathbf{r}, t) = T(t)\psi(\mathbf{r})$, and separating the variables, the Schrödinger equation takes the form,

$$\frac{\left(-\frac{\hbar^2\nabla^2}{2m}\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r})\right)}{\psi(\mathbf{r})} = \frac{i\hbar\partial_t T(t)}{T(t)} = \text{const.} = E. \quad (2.2)$$

Since we have a function of only \mathbf{r} set equal to a function of only t , they both must equal a constant. In the equation above, we call the constant E (with some knowledge of the outcome). We now have an equation in t set equal to a constant, $i\hbar\partial_t T(t) = ET(t)$, which has a simple general solution, $T(t) = Ce^{-iEt/\hbar}$, where C is some constant. The corresponding equation in \mathbf{r} is then given by the stationary, or **time-independent Schrödinger equation**,

$$\boxed{-\frac{\hbar^2\nabla^2}{2m}\psi(x) + V(x)\psi(x) = E\psi(x).} \quad (2.3)$$

The full time-dependent solution is given by $\Psi(\mathbf{r}, t) = e^{-iEt/\hbar}\psi(\mathbf{r})$ with definite energy, E . Their probability density $|\Psi(\mathbf{r}, t)|^2 = |\psi(\mathbf{r})|^2$ is constant in time – hence they are called stationary states! The operator

$$\boxed{\hat{H} = -\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r})} \quad (2.4)$$

defines the **Hamiltonian** and the stationary wave equation can be written as the eigenfunction equation, $\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$, i.e. $\psi(\mathbf{r})$ is an eigenstate of \hat{H} with eigenvalue E .

To explore its properties, we will first review some simple and, hopefully, familiar applications of the equation to one-dimensional systems. In addressing the one-dimensional geometry, we will divide our consideration between potentials, $V(x)$, which leave the particle free (i.e. unbound), and those that bind the particle to some region of space.

2.1 Wave Mechanics of Unbound Particles

2.1.1 Particle Flux and conservation of probability

In analogy to the Poynting vector for the electromagnetic field, we may want to know the probability current. For example, for a free particle system, the probability density is uniform over all space, but there is a net flow along the direction of momentum. We can derive an equation showing conservation of probability by differentiating the probability density, $P(x, t) = |\Psi(x, t)|^2$, and using the Schrödinger equation, $\partial_t P(x, t) + \partial_x j(x, t) = 0$. This translates to the usual conservation equation if $j(x, t)$ is identified as the probability current,

$$j(x, t) = -\frac{i\hbar}{2m}[\Psi^* \partial_x \Psi - \Psi \partial_x \Psi^*]. \quad (2.5)$$

If we integrate over some interval in x , $\int_a^b \partial_t P(x, t) dx = -\int_a^b \partial_x j(x, t) dx$ it follows that $\partial_t \int_a^b P(x, t) dx = j(x = a, t) - j(x = b, t)$, i.e. the rate of change of probability is equal to the net flux entering the interval.

To extending this analysis to three space dimensions, we use the general form of the continuity equation, $\partial_t P(\mathbf{r}, t) + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0$, from which follows the particle flux,

$$\boxed{\mathbf{j}(\mathbf{r}, t) = -\frac{i\hbar}{2m}[\Psi^*(\mathbf{r}, t) \nabla \Psi(\mathbf{r}, t) - \Psi(\mathbf{r}, t) \nabla \Psi^*(\mathbf{r}, t)]}. \quad (2.6)$$

2.1.2 Free Particle

In the absence of an external potential, the time-dependent Schrödinger equation (2.1) describes the propagation of travelling waves. In one dimension, the corresponding complex wavefunction has the form

$$\Psi(x, t) = Ae^{i(kx - \omega t)}, \quad (2.7)$$

where A is the amplitude, and $E(k) = \hbar\omega(k) = \frac{\hbar^2 k^2}{2m}$ represents the free particle energy dispersion for a non-relativistic particle of mass, m , and wavevector $k = 2\pi/\lambda$ with λ the wavelength. Each wavefunction describes a plane wave in which the particle has definite energy $E(k)$ and, in accordance with the de Broglie relation, momentum $p = \hbar/k = h/\lambda$. The energy spectrum of a freely-moving particle is therefore continuous, extending from zero to infinity and, apart from the spatially constant state $k = 0$, has a two-fold degeneracy corresponding to right and left moving particles.

For an infinite system, it makes no sense to fix the amplitude A by the normalization of the total probability. Instead, it is useful to fix the flux associated with the wavefunction.

Making use of (2.5) for the particle current, the plane wave is associated with a constant (time-independent) flux,

$$j(x, t) = -\frac{i\hbar}{2m}[\Psi^* \partial_x \Psi - \Psi \partial_x \Psi^*] = |A|^2 \frac{\hbar k}{m} = |A|^2 \frac{p}{m}. \quad (2.8)$$

For a given value of the flux j , the amplitude is given, up to an arbitrary constant phase, by $A = \sqrt{mj/\hbar k}$.

To prepare a **wave packet** which is localized to a region of space, we must superpose components of different wave number. In an open system, this may be achieved using a Fourier expansion. For any function,¹ $\psi(x)$, we have the Fourier decomposition,

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(k) e^{ikx} dk, \quad (2.9)$$

where the coefficients are defined by the inverse transform,

$$\psi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) e^{-ikx} dx. \quad (2.10)$$

The normalization of $\psi(k)$ follows automatically from the normalization of $\psi(x)$, $\int_{-\infty}^{\infty} \psi^*(k) \psi(k) dk = \int_{-\infty}^{\infty} \psi^*(x) \psi(x) dx$, and both can represent probability amplitudes. Applied to a wavefunction, $\psi(x)$ can be understood as a wave packet made up of contributions involving definite momentum states, e^{ikx} , with amplitude set by the Fourier coefficient $\psi(k)$. The probability for a particle to be found in a region of width dx around some value of x is given by $|\psi(x)|^2 dx$. Similarly, the probability for a particle to have wave number k in a region of width dk around some value of k is given by $|\psi(k)|^2 dk$. (Remember that $p = \hbar k$ so the momentum distribution is very closely related. Here, for economy of notation, we work with k .)

The Fourier transform of a normalized Gaussian wave packet, $\psi(k) = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha(k-k_0)^2}$ is also a Gaussian,

$$\psi(x) = \left(\frac{1}{2\pi\alpha}\right)^{1/4} e^{ik_0 x} e^{-\frac{x^2}{4\alpha}} \quad (2.11)$$

From these representations, we can see that it is possible to represent a *single* particle, localized in real space as a superposition of plane wave states localized in Fourier space. But note that, while we have achieved our goal of finding localized wave packets, this has been at the expense of having some non-zero width in x and in k .

¹More precisely, we can make such an expansion providing we meet some rather weak conditions of smoothness and differentiability of $\psi(x)$ – conditions met naturally by problems which derive from physical systems!

2.1.3 Potential Step

2.1.4 Potential Barrier

2.1.5 The Rectangular Potential Well

2.2 Wave Mechanics of Bound Particles

2.2.1 The Rectangular Potential Well (Continued)

2.2.2 The δ -Function Potential Well

2.2.3 The δ -Function Model of a Crystal

2.3 Wentzel, Kramers and Brillouin (WKB) Method

2.3.1 Semi-Classical Approximation to Leading Order

2.3.2 Next to Leading Order Correction

2.3.3 Connection Formulae, Boundary Conditions and Quantization Rules

CHAPTER 3

Operator Methods in Quantum Mechanics

3.1 Operators

3.1.1 Matrix representations of operators

3.1.2 Time-evolution operator

3.1.3 Uncertainty principle for non-commuting operators

3.1.4 Time-evolution of expectation values

3.2 The Heisenberg picture

3.3 Quantum harmonic oscillator

CHAPTER 4

Quantum Mechanics in More Than One Dimension

4.1 Rigid diatomic molecule

4.2 Angular momentum

4.2.1 Commutation relations

4.2.2 Eigenvalues of angular momentum

4.2.3 Representation of the angular momentum states

CHAPTER 5

Spin

5.1 Spinors, spin operators, Pauli matrices

5.2 Relating the spinor to the spin direction

5.3 Spin precession in a magnetic field

5.4 Addition of angular momenta

5.4.1 Addition of two spin $1/2$ degrees of freedom

5.4.2 Addition of angular momentum and spin

5.4.3 Addition of two angular momenta $J = 1$

CHAPTER 6

Motion in a Magnetic Field

- 6.1 Classical mechanics of a particle in a field
- 6.2 Quantum mechanics of a particle in a field
- 6.3 Gauge invariance and the Aharonov-Bohm effect
- 6.4 Free electron in a magnetic field

Approximation Methods for Stationary States

7.1 Time-independent perturbation theory

7.1.1 The perturbation series

7.1.2 First order perturbation theory

7.1.3 Second order perturbation theory

7.2 Degenerate perturbation theory

7.3 Variational method

Symmetry in Quantum Mechanics

8.1 Observables as generators of transformations

8.2 Consequences of symmetries: multiplets

8.3 Rotational symmetry in quantum mechanics

8.3.1 Scalar operators

8.3.2 Vector operators

8.4 The Wigner-Eckart theorem for scalar operators

8.4.1 Consequences of the Wigner-Eckart theorem (for scalars)

8.5 The Wigner-Eckart theorem for vector operators

8.5.1 Selection rules for vector operator matrix elements

8.5.2 The Landé projection formula

8.6 Magnetic dipole moments

8.6.1 g-factors

8.6.2 Combining magnetic moments

CHAPTER 9

Identical Particles

9.1 Quantum statistics

9.2 Space and spin wavefunctions

9.3 Physical consequences of particle statistics

9.4 Many-body systems

9.4.1 Non-interacting Fermi gas

9.4.2 Non-interacting Bose gas

CHAPTER 10

Atomic Structure

10.1 The non-relativistic hydrogen atom

10.1.1 The Zeeman effect

10.2 The “real” hydrogen atom

10.2.1 Relativistic correction to the kinetic energy

10.2.2 Spin-orbit coupling

10.2.3 Darwin term

10.2.4 Info: Lamb shift

10.2.5 Hyperfine structure

10.3 Multi-electron atoms

10.3.1 Central field approximation

10.3.2 Spin-orbit coupling

10.3.3 Info: jj coupling scheme

10.3.4 Zeeman effect

CHAPTER 11

From Molecules to Solids

11.1 The H^+ ion

11.2 The H_2 molecule

11.3 From molecules to solids

CHAPTER 12

Time-Dependent Perturbation Theory

12.1 Time-dependent potentials: general formalism

12.1.1 Dynamics of a driven two-level system

12.1.2 Paramagnetic resonance

12.2 Time-dependent perturbation theory

12.3 “Sudden” perturbation

12.3.1 Harmonic perturbations: Fermi’s Golden Rule

12.3.2 Info: Harmonic perturbations: second-order transitions

CHAPTER 13

Scattering Theory

13.1 Basics

13.2 The Born approximation

Radiative Transitions

14.1 Coupling of matter to the electromagnetic field

14.1.1 Quantum fields

14.1.2 Spontaneous emission

14.1.3 Absorption and stimulated emission

14.1.4 Einstein's A and B coefficients

14.2 Selection rules

14.3 Lasers

14.3.1 Operating principles of a laser

14.3.2 Gain mechanism

CHAPTER 15

Field Theory: From Phonons to Photons

15.1 Quantization of the classical atomic chain

15.1.1 Info: Classical chain

15.1.2 Info: Quantum chain

15.2 Quantum electrodynamics

15.2.1 Info: Classical theory of the electromagnetic field

15.2.2 Quantum field theory of the electromagnetic field

15.2.3 Fock states

15.2.4 Coherent states

15.2.5 Non-classical light

Bibliography

APPENDIX A

Proofs and Formula Derivations

A.0.1 Number of Modes

A.0.2 Probability Current

Consider the expression

$$i\hbar \frac{\partial}{\partial t} \int_V P(\mathbf{r}, t) dV = i\hbar \frac{\partial}{\partial t} \int_V \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) dV ; \quad (\text{A.1})$$

apart from the factor $i\hbar$, this is the rate of change of the probability of finding the particle in a closed region (V):