Advanced Quantum Mechanics

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Abstract

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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.

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

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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

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

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_BT (equipartition), where k_B is the Boltzmann constant. The corresponding energy density is therefore given by the Rayleigh-Jeans law,

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

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

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

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

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

This result conforms with experiment, and converges on the Rayleigh-Jeans law at low frequencies, $h\nu/k_B T \to 0$. 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

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

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,

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

The constant of proportionality $h/m_e c = 0.002426\,\mathrm{nm}$, the Compton wavelength, characterizes the scale of scattering. Moreover, as $h \to 0$, one finds that $\Delta\lambda \to 0$ 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 $n = 3, 4, 5, \ldots$ and $\lambda_0 = 3645.6\,\text{Å}$. 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 $R_H = 109678\,\mathrm{cm}^{-1}$ 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,

$$L = m_e vr = n\hbar, \qquad \hbar = \frac{h}{2\pi}. \tag{1.7}$$

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

$$\lambda = \frac{h}{p}, \qquad \text{i.e.}\, p = \hbar k \tag{1.8}$$

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,

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

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, $E^2 = (c\mathbf{p})^2 + (m_0c^2)^2$. Writing the plane wave function $\phi(\mathbf{r}, t) = Ae^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}$, where A is a constant, we can recover the energy-momentum invariant by adding a constant mass term to the wave operator,

$$\left(\nabla^2 - \frac{\partial_t^2}{c^2} - \frac{m_0c^2}{\hbar^2}\right)e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar} = -\frac{((c\mathbf{p})^2 - E^2 + m_0^2c^4)}{(\hbar c)^2}e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar} = 0. \tag{1.10}$$

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 $\Psi(\mathbf{r}, t) = Ae^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}$. 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.

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

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**

$$\boxed{\oint p\,\mathrm{d}q = nh,} \tag{1.12}$$

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,

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

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 $|\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}\mathbf{r}$ represents the probability that the particle lies in the volume element $\mathrm{d}\mathbf{r} \equiv \mathrm{d}^d\mathbf{r}$ 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, $\int_{-\infty}^{\infty} |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}\mathbf{r} = 1$. 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

$$\left\langle \hat{A} \right\rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi \, \mathrm{d}\mathbf{r} \,. \tag{1.14}$$

  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

$$\left\langle \hat{A} \right\rangle = \sum_i a_i |\langle\Psi_i|\Psi\rangle|^2 = \sum_i |c_i|^2. \tag{1.15}$$

  Finally, a measurement of Ψ which leads to the eigenvalue a_i , causes the wavefunction to "collapses" 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

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

  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,

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

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,

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

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**,

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

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

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

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,

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

If we integrate over some interval in x, $\int_a^b \partial_t P(x,t)\,\mathrm{d}x = -\int_a^b \partial_x j(x,t)\,\mathrm{d}x$ it follows that $\partial_t \int_a^b P(x,t)\,\mathrm{d}x = j(x=a,t) - j(x=b,t)$, 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, $\partial_t P(\mathbf{r},t) + \boldsymbol{\nabla} \cdot \mathbf{j}(\mathbf{r},t) = 0$, from which follows the particle flux,

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

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

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

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,

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

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,

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

where the coefficients are defined by the inverse transform,

$$\psi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) e^{-ikx} \, \mathrm{d}x \,. \tag{2.10}$$

The normalization of $\psi(k)$ follows automatically from the normalization of $\psi(x)$, $\int_{-\infty}^{\infty} \psi^*(k)\psi(k)\,\mathrm{d}k = \int_{-\infty}^{\infty} \psi^*(x)\psi(x)\,\mathrm{d}x$, 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 $\mathrm{d}x$ around some value of x is given by $|\psi(x)|^2\,\mathrm{d}x$. Similarly, the probability for a particle to have wave number k in a region of width $\mathrm{d}k$ around some value of k is given by $|\psi(k)|^2\,\mathrm{d}k$. (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,

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

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.

For the Gaussian wave packet, we can straightforwardly obtain the width (as measured by the root mean square – RMS) of the probability distribution, $\Delta x = \left(\langle (x - \langle x \rangle)^2 \rangle\right)^{1/2} = \left(\langle x^2 \rangle - \langle x \rangle^2\right)^{1/2} = \sqrt{\alpha}$, and $\Delta k = \frac{1}{\sqrt{4\alpha}}$. We can again see that, as we vary the width in k-space, the width in x-space varies to keep the following product constant, $\Delta x \Delta k = \frac{1}{2}$. If we translate from the wavevector into momentum $p = \hbar k$, then $\Delta p = \hbar \Delta k$ and

$$\Delta x \Delta p = \frac{\hbar}{2}. \tag{2.12}$$

[1] More 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!

If we consider the width of the distribution as a measure of the "uncertainty", we will prove in section 3.1.3 that the Gaussian wave packet provides the minimum uncertainty. This result shows that we cannot know the position of a particle and its momentum at the same time. If we try to localise a particle to a very small region of space, its momentum becomes uncertain. If we try to make a particle with a definite momentum, its probability distribution spreads out over space.

With this introduction, we now turn to consider the interaction of a particle with a non-uniform potential background. For non-confining potentials, such systems fall into the class of **scattering problems**: For a beam of particles incident on a non-uniform potential, what fraction of the particles are transmitted and what fraction are reflected? In the one-dimensional system, the classical counterpart of this problem is trivial: For particle energies which exceed the maximum potential, all particles are eventually transmitted, while for energies which are lower, all particles are reflected. In quantum mechanics, the situation is richer: For a generic potential of finite extent and height, some particles are always reflected and some are always transmitted. Later in the course we will consider the general problem of scattering from a localised potential in arbitrary dimension. But for now, we will focus on the one-dimensional system, where many of the key concepts can be formulated.

2.1.3 Potential Step

As we have seen, for a time-independent potential, the wavefunction can be factorised as $\Psi(x,t) = e^{-iEt/\hbar}\psi(x)$, where $\psi(x)$ is obtained from the stationary form of the Schrödinger equation,

$$\left[-\frac{\hbar^2\partial_x^2}{2m} + V(x)\right]\psi(x) = E\psi(x), \tag{2.13}$$

and E denotes the energy of the particle. As $|\Psi(x,t)|^2$ represents a probability density, it must be everywhere finite. As a result, we can deduce that the wavefunction, $\psi(x)$, is also finite. Moreover, since E and $V(x)$ are presumed finite, so must be $\partial_x^2\psi(x)$. The latter condition implies that

- both $\psi(x)$ and $\partial_x\psi(x)$ must be continuous functions of x, even if V has a discontinuity.

Consider then the influence of a potential step on the propagation of a beam of particles. Specifically, let us assume that a beam of particles with kinetic energy, E, moving from left to right are incident upon a potential step of height V_0 at position $x = 0$. If the beam has unit amplitude, the reflected and transmitted (complex) amplitudes are set by r and t. The corresponding wavefunction is given by

$$\begin{aligned} \psi_-(x) &= e^{ik_-x} + re^{-ik_-x} \quad && x < 0, \\ \psi_+(x) &= te^{ik_+x} && x > 0, \end{aligned} \tag{2.14}$$

where $k_- = \frac{\sqrt{2mE}}{\hbar}$ and $k_+ = \frac{\sqrt{2m(E-V_0)}}{\hbar}$. Applying the continuity conditions on $\psi(x)$ and $\partial_x\psi(x)$ at the step ($x = 0$), one obtains the relations $1 + r = t$ and $ik_-(1 - r) = ik_+t$

leading to the reflection and transmission amplitudes,

$$r = \frac{k_- - k_+}{k_- + k_-}, \qquad t = \frac{2k_-}{k_- + k_+} \tag{2.15}$$

The reflectivity, R, and transmittivity, T, are defined by the ratios,

$$R = \frac{\text{reflected flux}}{\text{incident flux}}, \qquad T = \frac{\text{transmitted flux}}{\text{incident flux}}. \tag{2.16}$$

With the incident, reflected, and transmitted fluxes given by $|A|^2 \frac{\hbar k_-}{m}$, $|Ar|^2 \frac{\hbar k_-}{m}$, and $|At|^2 \frac{\hbar k_+}{m}$ respectively, one obtains

$$R = \left| \frac{k_- - k_+}{k_- + k_-} \right|^2 = |r|^2, \qquad T = \left| \frac{2k_-}{k_- + k_+} \right|^2 \frac{k_+}{k_-} = |t|^2 \frac{k_+}{k_-} = \frac{4k_- k_+}{(k_- + k_+)^2}. \tag{2.17}$$

From these results one can confirm that the total flux is, as expected, conserved in the scattering process, i.e. $R + T = 1$.

2.1.4 Potential Barrier

Having dealt with the potential step, we now turn to consider the problem of a beam of particles incident upon a square potential barrier of height V_0 (presumed positive for now) and width a. As mentioned above, this geometry is particularly important as it includes the simplest example of a scattering phenomenon in which a beam of particles is "deflected" by a local potential. Moreover, this one-dimensional geometry also provides a platform to explore a phenomenon peculiar to quantum mechanics – **quantum tunneling**. For these reasons, we will treat this problem fully and with some care.

Since the barrier is localised to a region of size a, the incident and transmitted wavefunctions have the same functional form, $e^{ik_1 x}$, where $k_1 = \frac{\sqrt{2mE}}{\hbar}$, and differ only in their complex amplitude, i.e. after the encounter with the barrier, the transmitted wavefunction undergoes only a change of amplitude (some particles are reflected from the barrier, even when the energy of the incident beam, E, is in excess of V_0) and a phase shift. To determine the relative change in amplitude and phase, we can parameterise the wavefunction as

$$\begin{array}{ll} \psi_1(x) = e^{ik_1 x} + re^{-ik_1 x} & x \leq 0 \\ \psi_2(x) = Ae^{ik_2 x} + Be^{-ik_2 x} & 0 \leq x \leq a \\ \psi_3(x) = te^{ik_1 x} & a \leq x \end{array} \tag{2.18}$$

where $k_2 = \frac{\sqrt{2m(E-V_0)}}{\hbar}$. Here, as with the step, r denotes the reflected amplitude and t the transmitted.

Applying the continuity conditions on the wavefunction, ψ, and its derivative, $\partial_x \psi$, at the barrier interfaces at $x = 0$ and $x = a$, one obtains

$$\begin{cases} 1 + r = A + B \\ Ae^{ik_2 a} + Be^{-ik_2 a} = te^{ik_1 a} \end{cases}, \qquad \begin{cases} k_1(1 - r) = k_2(A - B) \\ k_2\left(Ae^{ik_2 a} - Be^{-ik_2 a}\right) = k_1 te^{ik_1 a} \end{cases}. \tag{2.19}$$

Together, these four equations specify the four unknowns, r, t, A and B. Solving, one obtains

$$t = \frac{2k_1k_2e^{-ik_1a}}{2k_1k_2\cos(k_2a) - i\left(k_1^2 + k_2^2\right)^2\sin(k_2a)}, \tag{2.20}$$

translating to a transmissivity of

$$T = |t|^2 = \frac{1}{1 + \frac{1}{4}\left(\frac{k_1}{k_2} - \frac{k_2}{k_1}\right)^2\sin^2(k_2a)}, \tag{2.21}$$

and the reflectivity, $R = 1 - T$. As a consistency check, we can see that, when $V_0 = 0$, $k_2 = k_1$ and $t = 1$, as expected. Moreover, T is restricted to the interval from 0 to 1 as required. So, for barrier heights in the range $E > V_0 > 0$, the transmittivity T shows an oscillatory behaviour with k_2 reaching unity when $k_2a = n\pi$ with n integer. At these values, there is a conspiracy of interference effects which eliminate altogether the reflected component of the wave leading to perfect transmission. Such a situation arises when the width of the barrier is perfectly matched to an integer or half-integer number of wavelengths inside the barrier.

When the energy of the incident particles falls below the energy of the barrier, $0 < E < V_0$, a classical beam would be completely reflected. However, in the quantum system, particles are able to tunnel through the barrier region and escape leading to a non-zero transmission coefficient. In this regime, $k_2 = i\kappa_2$ becomes pure imaginary leading to an evanescent decay of the wavefunction under the barrier and a suppression, but not extinction, of transmission probability,

$$T = |t|^2 = \frac{1}{1 + \frac{1}{4}\left(\frac{k_1}{\kappa_2} - \frac{\kappa_2}{k_1}\right)^2\sinh^2(\kappa_2a)}. \tag{2.22}$$

For $\kappa_2 a \gg 1$ (the weak tunneling limit), the transmittivity takes the form

$$T \simeq \frac{16k_1^2\kappa_2^2}{\left(k_1^2 + \kappa_2^2\right)^2}e^{-2\kappa_2a}. \tag{2.23}$$

Finally, on a cautionary note, while the phenomenon of quantum mechanical tunneling is well-established, it is difficult to access in a convincing experimental manner. Although a classical particle with energy $E < V_0$ is unable to penetrate the barrier region, in a physical setting, one is usually concerned with a thermal distribution of particles. In such cases, thermal activation may lead to transmission *over* a barrier. Such processes often overwhelm any contribution from true quantum mechanical tunneling.

2.1.5 The Rectangular Potential Well

Finally, if we consider scattering from a potential well (i.e. with $V_0 < 0$), while $E > 0$, we can apply the results of the previous section to find a continuum of unbound states with the corresponding **resonance** behaviour. However, in addition to these unbound states, for $E < 0$ we have the opportunity to find bound states of the potential. It is to this general problem that we now turn.

2.2 Wave Mechanics of Bound Particles

In the case of unbound particles, we have seen that the spectrum of states is continuous. However, for bound particles, the wavefunctions satisfying the Schrödinger equation have only particular quantised energies. In the one-dimensional system, we will find that all binding potentials are capable of hosting a bound state, a feature particular to the low dimensional system.

2.2.1 The Rectangular Potential Well (Continued)

As a starting point, let us consider a rectangular potential well similar to that discussed above. To make use of symmetry considerations, it is helpful to reposition the potential setting

$$V(x) = \begin{cases} 0 & x \leq -a \\ -V_0 & -a \leq x \leq a \\ 0 & a \leq x \end{cases}, \tag{2.24}$$

where the potential depth V_0 is assumed positive. In this case, we will look for bound state solutions with energies lying in the range $-V_0 < E < 0$. Since the Hamiltonian is invariant under **parity transformation**, $\left[\hat{H}, \hat{P}\right] = 0$ (where $\hat{P}\psi(x) = \psi(-x)$), the eigenstates of the Hamiltonian $\hat{H}$ must also be eigenstates of parity, i.e. we expect the eigenfunctions to separate into those symmetric and those antisymmetric under parity.

For $E < 0$ (bound states), the wavefunction outside the well region must have the form

$$\psi(x < -a) = Ce^{\kappa x}, \qquad \psi(x > a) = De^{-\kappa x}, \tag{2.25}$$

with $\kappa = \frac{\sqrt{-2mE}}{\hbar}$ while in the central well region, the general solution is of the form

$$\psi(-a < x < a) = A\cos(kx) + B\sin(kx), \tag{2.26}$$

where $k = \frac{\sqrt{2m(E+V_0)}}{\hbar}$. Once again we have four equations in four unknowns. The calculation shows that either A or B must be zero for a solution. This means that the states separate into solutions with even or odd parity.

For the even states, the solution of the equations leads to the quantisation condition, $\kappa = \tan kak$, while for the odd states, we find $\kappa = -\cot kak$. These are transcendental equations, and must be solved numerically. Figure **??** compares $\kappa a = \left(\frac{2mV_0a^2}{\hbar^2} - (ka)^2\right)^{1/2}$ with $ka \tan ka$ for the even states and to $-ka \cot ka$ for the odd states. Where the curves intersect, we have an allowed energy. From the structure of these equations, it is evident that an even state solution can always be found for arbitrarily small values of the binding potential V_0 while, for odd states, bound states appear only at a critical value of the coupling strength. The wider and deeper the well, the more solutions are generated.

2.2.2 The δ-Function Potential Well

Let us now consider perhaps the simplest binding potential, the δ-function, $V(x) = -aV_0\delta(x)$. Here the parameter 'a' denotes some microscopic length scale introduced to make the product $a\delta(x)$ dimensionless.[2] For a state to be bound, its energy must be negative. Moreover, the form of the potential demands that the wavefunction is symmetric under parity, $x \to -x$. (A wavefunction which was antisymmetric must have $\psi(0) = 0$ and so could not be influenced by the δ-function potential.) We therefore look for a solution of the form

$$\psi(x) = A \begin{cases} e^{\kappa x} & x < 0 \\ e^{-\kappa x} & x > 0 \end{cases}, \tag{2.27}$$

where $\kappa = \frac{\sqrt{-2mE}}{\hbar}$. With this choice, the wavefunction remains everywhere continuous including at the potential, $x = 0$. Integrating the stationary form of the Schrödinger equation across an infinitesimal interval that spans the region of the δ-function potential, we find that

$$\partial_x\psi|_{+\epsilon} - \partial_x\psi|_{-\epsilon} = -\frac{2maV_0}{\hbar^2}\psi(0). \tag{2.28}$$

From this result, we obtain that $\kappa = maV_0/\hbar^2$, leading to the bound state energy

$$E = -\frac{ma^2V_0^2}{2\hbar^2}. \tag{2.29}$$

Indeed, the solution is unique. An attractive δ-function potential hosts only one bound state.

2.2.3 The δ-Function Model of a Crystal

Finally, as our last example of a one-dimensional quantum system, let us consider a particle moving in a periodic potential. The **Kronig-Penney model** provides a caricature of a (one-dimensional) crystalline lattice potential. The potential created by the ions is approximated as an infinite array of potential wells defined by a set of repulsive δ-function potentials,

$$V(x) = aV_0 \sum_{n=-\infty}^{\infty} \delta(x - na). \tag{2.30}$$

Since the potential is repulsive, it is evident that all states have energy $E > 0$. This potential has a new symmetry; a translation by the lattice spacing a leaves the potential unchanged, $V(x + a) = V(x)$. The probability density must therefore exhibit the same translational symmetry,

$$|\psi(x + a)|^2 = |\psi(x)|^2 \tag{2.31}$$

which means that, under translation, the wavefunction differs by at most a phase, $\psi(x + a) = e^{i\phi}\psi(x)$. In the region from $(n-1)a < x < na$, the general solution of the Schrödinger equation is plane wave like and can be written in the form,

$$\psi_n(x) = A_n \sin[k(x - na)] + B_n \cos[k(x - na)], \tag{2.32}$$

[2] Note that the dimensions of $\delta(x)$ are $[\text{Length}]^{-1}$.

where $k = \frac{\sqrt{2mE}}{\hbar}$ and, following the constraint on translational invariance, $A_{n+1} = e^{i\phi}A_n$ and $B_{n+1} = e^{i\phi}B_n$. By applying the boundary conditions, one can derive a constraint on k similar to the quantised energies for bound states considered above.

Consider the boundary conditions at position $x = na$. Continuity of the wavefunction, $\psi_n|_{x=na} = \psi_{n+1}|_{x=na}$, translates to the condition, $B_n = A_{n+1}\sin(-ka) + B_{n+1}\cos(-ka)$ or

$$B_{n+1} = \frac{B_n + A_{n+1}\sin(ka)}{\cos(ka)}. \tag{2.33}$$

Similarly, the discontinuity in the first derivative, $\partial_x\psi_{n+1}|_{x=na} - \partial_x\psi_n|_{x=na} = \frac{2maV_0}{\hbar^2}\psi_n(na)$, leads to the condition $k[A_{n+1}\cos(ka) + B_{n+1}\sin(ka) - A_n] = \frac{2maV_0}{\hbar^2}B_n$. Substituting the expression for B_{n+1} and rearranging, one obtains

$$A_{n+1} = \frac{2maV_0}{\hbar^2 k}B_n\cos(ka) - B_n\sin(ka) + A_n\cos(ka). \tag{2.34}$$

Similarly, replacing the expression for A_{n+1} in that for B_{n+1}, one obtains the parallel equation,

$$B_{n+1} = \frac{2maV_0}{\hbar^2 k}B_n\sin(ka) + B_n\cos(ka) + A_n\sin(ka). \tag{2.35}$$

With these two equations, and the relations $A_{n+1} = e^{i\phi}A_n$ and $B_{n+1} = e^{i\phi}B_n$, we obtain the quantisation condition,[3]

$$\boxed{\cos\phi = \cos(ka) + \frac{maV_0}{\hbar^2 k}\sin(ka).} \tag{2.37}$$

As $\hbar k = \sqrt{2mE}$, this result relates the allowed values of energy to the real parameter, ϕ. Since $\cos\phi$ can only take values between -1 and 1, there are a sequence of allowed bands of energy with energy gaps separating these bands.

Such behaviour is characteristic of the spectrum of periodic lattices: In the periodic system, the wavefunctions – known as **Bloch states** – are indexed by a "quasi"- momentum index k, and a band index n where each Bloch band is separated by an energy gap within which there are no allowed states. In a **metal**, electrons (fermions) populate the energy states starting with the lowest energy up to some energy scale known as the **Fermi energy**. For a partially-filled band, low-lying excitations associated with the continuum of states allow electrons to be accelerated by a weak electric field. In a **band insulator**, all states are filled up to an energy gap. In this case, a small electric field is unable to excite electrons across the energy gap – hence the system remains insulating.

2.3 Wentzel, Kramers and Brillouin (WKB) Method

The WKB (or Wentzel, Kramers and Brillouin) approximation describes a "quasi-classical" method for solving the one-dimensional time-independent Schrödinger equation. Note

[3] Eliminating A_n and B_n from the equations, a sequence of cancellations obtains

$$e^{2i\phi} + e^{i\phi}\Big(\frac{2maV_0}{\hbar^2 k}\sin(ka) + 2\cos(ka)\Big) + 1 = 0. \tag{2.36}$$

Then multiplying by $e^{-i\phi}$, we obtain the expression for $\cos\phi$.

that the consideration of one-dimensional systems is less restrictive that it may sound as many symmetrical higher-dimensional problems are rendered effectively one-dimensional (e.g. the radial equation for the hydrogen atom). The WKB method is named after physicists Wentzel, Kramers and Brillouin, who all developed the approach independently in 1926. Earlier, in 1923, the mathematician Harold Jeffreys had developed a general method of approximating the general class of linear, second-order differential equations, which of course includes the Schrödinger equation. But since the Schrödinger equation was developed two years later, and Wentzel, Kramers, and Brillouin were apparently unaware of this earlier work, the contribution of Jeffreys is often neglected.

The WKB method is important both as a practical means of approximating solutions to the Schrödinger equation, and also as a conceptual framework for understanding the classical limit of quantum mechanics. The WKB approximation is valid whenever the wavelength, λ, is small in comparison to other relevant length scales in the problem. This condition is not restricted to quantum mechanics, but rather can be applied to any wave-like system (such as fluids, electromagnetic waves, etc.), where it leads to approximation schemes which are mathematically very similar to the WKB method in quantum mechanics. For example, in optics the approach is called the **eikonal method**, and in general the method is referred to as **short wavelength asymptotics**. Whatever the name, the method is an old one, which predates quantum mechanics – indeed, it was apparently first used by Liouville and Green in the first half of the nineteenth century. In quantum mechanics, λ is interpreted as the de Broglie wavelength, and L is normally the length scale of the potential. Thus, the WKB method is valid if the wavefunction oscillates many times before the potential energy changes significantly

2.3.1 Semi-Classical Approximation to Leading Order

Consider then the propagation of a quantum particle in a slowly-varying one-dimensional potential, $V(x)$. Here, by "slowly-varying" we mean that, in any small region the wave-function is well-approximated by a plane wave, and that the wavelength only changes over distances that are long compared with the local value of the wavelength. We're also assuming for the moment that the particle has positive kinetic energy in the region. Under these conditions, we can anticipate that the solution to the time-independent Schrödinger equation

$$-\frac{\hbar^2\partial_x^2}{2m}\psi(x) + V(x)\psi(x) = E\psi(x), \tag{2.38}$$

will take the form $A(x)e^{\pm ip(x)x}$ where $p(x)$ is the "local" value of the momentum set by the classical value, $p^2/2m + V(x) = E$, and the amplitude, $A(x)$, is slowly-varying compared with the phase factor. Clearly this is a *semi-classical* limit: $\hbar$ has to be sufficiently small that there are many oscillations in the typical distance over which the potential varies.[4]

[4] To avoid any point of confusion, it is of course true that $\hbar$ is a fundamental constant – not easily adjusted! So what do we mean when we say that the semi-classical limit translates to $\hbar \to 0$? The validity of the semi-classical approximation relies upon $\lambda/L \ll 1$. Following the de Broglie relation, we may write this inequality as $h/pL \ll 1$, where p denotes the particle momentum. Now, in this correspondence, both p and L can be considered as "classical" scales. So, formally, we can think of accessing the semi-classical limit by adjusting $\hbar$ so that it is small enough to fulfil this inequality. Alternatively, at fixed $\hbar$, we can access the semi-classical regime by reaching to higher and higher energy scales (larger and larger p) so that the inequality becomes valid.

To develop this idea more rigorously, and to emphasize the rapid *phase* variation in the semi-classical limit, we can parameterise the wavefunction as

$$\phi(x) = e^{i\sigma(x)/\hbar}. \tag{2.39}$$

Here the complex function $\sigma(x)$ encompasses both the amplitude and phase. Then, with $-\hbar^2\partial_x^2\psi(x) = -i\hbar e^{i\sigma(x)/\hbar}\partial_x^2\sigma(x) + e^{i\sigma(x)/\hbar}(\partial_x\sigma)^2$, the Schrödinger equation may be rewritten in terms of the phase function as

$$-i\hbar\partial_x^2\sigma(x) + (\partial_x\sigma)^2 = p^2(x). \tag{2.40}$$

Now, since we're assuming the system is semi-classical, it makes sense to expand $\sigma(x)$ as a power series in $\hbar$, setting

$$\sigma = \sigma_0 + (\hbar/i)\sigma_1 + (\hbar/i)^2\sigma_2 + \cdots . \tag{2.41}$$

At the leading (zeroth) order of the expansion, we can drop the first term in (2.40), leading to $(\partial_x\sigma_0)^2 = p^2(x)$. Defining $p(x) = +\sqrt{2m(E - V(x))}$, this equation permits the two solutions $\partial_x\sigma_0 = \pm p(x)$, from which we conclude

$$\sigma_0(x) = \pm\int^x p(x')\,\mathrm{d}x' . \tag{2.42}$$

From the form of the Schrödinger equation (2.40), it is evident that this approximate solution is only valid if we can ignore the first term. More precisely, we must have

$$\left|\frac{\hbar\partial_x^2\sigma(x)}{(\partial_x\sigma(x))^2}\right| \equiv |\partial_x(\hbar/\partial_x\sigma)| \ll 1. \tag{2.43}$$

But, in the leading approximation, $\partial_x\sigma(x) \simeq p(x)$ and $p(x) = 2\pi\hbar/\lambda(x)$, so the condition translates to the relation

$$\frac{1}{2\pi}|\partial_x\lambda(x)|/ll1. \tag{2.44}$$

This means that the change in wavelength over a distance of one wavelength must be small. This condition can not always be met: In particular, if the particle is confined by an attractive potential, at the edge of the classically allowed region, where $E = V(x)$, $p(x)$ must be zero and the corresponding wavelength infinite. The approximation is only valid well away from these **classical turning points**, a matter to which we will return shortly.

2.3.2 Next to Leading Order Correction

Let us now turn to the next term in the expansion in $\hbar$. Retaining terms from Eq. (2.40) which are of order $\hbar$, we have

$$-i\hbar\partial_x^2\sigma_0(x) + 2\partial_x\sigma_0(\hbar/i)\partial_x\sigma_1 = 0. \tag{2.45}$$

Rearranging this equation, and integrating, we find

$$\partial_x\sigma_1 = -\frac{\partial_x^2\sigma_0}{2\partial_x\sigma_0} = -\frac{\partial_x p}{2p}, \qquad \sigma_1(x) = -\frac{1}{2}\ln p(x) + \text{const.}. \tag{2.46}$$

So, to this order of approximation, the wavefunction takes the form,

$$\psi(x) = \frac{C_1}{\sqrt{p(x)}} e^{(i/\hbar)\int^x p\,\mathrm{d}x'} + \frac{C_2}{\sqrt{p(x)}} e^{(-i/\hbar)\int^x p\,\mathrm{d}x'}, \tag{2.47}$$

where C_1 and C_2 denote constants of integration.

To interpret the factors of $\sqrt{p(x)}$, consider the first term: a wave moving to the right. Since $p(x)$ is real (remember we are currently considering the classically allowed region where $E > V(x)$), the exponential has modulus unity, and the local probability density is proportional to $1/p(x)$, i.e. to $1/v(x)$, where $v(x)$ denotes the velocity of the particle. This dependence has a simple physical interpretation: The probability of finding the particle in any given small interval is proportional to the time it spends there. Hence it is inversely proportional to its speed.

We turn now to consider the wavefunction in the classically forbidden region where

$$\frac{p^2}{2m} = E - V(x) < 0. \tag{2.48}$$

Here $p(x)$ is of course pure imaginary, but the same formal phase solution of the Schrödinger equation applies provided, again, that the particle is remote from the classical turning points where $E = V(x)$. In this region, the wavefunction takes the general form,

$$\psi(x) = \frac{C_1'}{\sqrt{|p(x)|}} e^{-(i/\hbar)\int^x |p|\,\mathrm{d}x'} + \frac{C_2'}{\sqrt{|p(x)|}} e^{(i/\hbar)\int^x |p|\,\mathrm{d}x'}. \tag{2.49}$$

This completes our study of the wavefunction in the regions in which the semiclassical approach can be formally justified. However, to make use of this approximation, we have to understand how to deal with the regions close to the classical turning points. Remember that in our treatment of the Schrödinger equation the energy quantization derived from the implementation of boundary conditions.

2.3.3 Connection Formulae, Boundary Conditions and Quantization Rules

Let us assume that we are dealing with a one-dimensional confining potential where the classically allowed region is unique and spans the interval $b \leq x \leq a$. Clearly, in the classically forbidden region to the right, $x > a$, only the first term in Eq. (2.49) remains convergent and can contribute, while for $x < b$ it is only the second term that contributes. Moreover, in the classically allowed region, $b \leq x \leq a$, the wavefunction has the oscillating form (2.47).

But how do we connect the three regions together? To answer this question, it is necessary to make the assumption that the potential varies sufficiently smoothly that it is a good approximation to take it to be linear in the vicinity of the classical turning points. That is to say, we assume that a linear potential is a sufficiently good approximation out to the point where the short wavelength (or decay length for tunneling regions) description is adequate. Therefore, near the classical turning at $x = a$, we take the potential to be

$$E - V(x) \simeq F_0(x - a), \tag{2.50}$$

where F_0 denotes the (constant) force. For a strictly linear potential, the wavefunction can be determined analytically, and takes the form of an Airy function. In particular, it is known that the Airy function to the right of the classical turning point has the asymptotic form

$$\lim_{x \gg a} \psi(x) = \frac{C}{2\sqrt{|p(x)|}} e^{-(i/\hbar)\int^x |p|\, \mathrm{d}x'}, \tag{2.51}$$

translating to a decay into the classically forbidden region while, to the left, it has the asymptotic oscillatory solution,

$$\lim_{b \ll x < a} \psi(x) = \frac{C}{2\sqrt{|p(x)|}} \cos\left[\frac{1}{\hbar}\int_x^a p\, \mathrm{d}x' - \frac{\pi}{4}\right] \equiv \frac{C}{2\sqrt{|p(x)|}} \cos\left[\frac{\pi}{4} - \frac{1}{\hbar}\int_x^a p\, \mathrm{d}x'\right]. \tag{2.52}$$

At the second classical turning point at $x = b$, the same argument gives

$$\lim_{b < x \ll a} \psi(x) = \frac{C'}{2\sqrt{|p(x)|}} \cos\left[\frac{1}{\hbar}\int_b^x p\, \mathrm{d}x' - \frac{\pi}{4}\right]. \tag{2.53}$$

For these two expressions to be consistent, we must have $C' = \pm C$ and

$$\left(\frac{1}{\hbar}\int_b^x p(x')\, \mathrm{d}x' - \frac{\pi}{4}\right) - \left(\frac{\pi}{4} - \frac{1}{\hbar}\int_x^a p(x')\, \mathrm{d}x'\right) = n\pi, \tag{2.54}$$

where, for n even, $C' = C$ and for n odd, $C' = -C$. Therefore, we have the condition $\frac{1}{\hbar}\int_b^a p(x)\, \mathrm{d}x = (n + 1/2)\pi$, or when cast in terms of a complete periodic cycle of the classical motion,

$$\boxed{\oint p(x)\, \mathrm{d}x = 2\pi\hbar(n + 1/2).} \tag{2.55}$$

This is just the **Bohr-Sommerfeld quantisation condition**, and n can be interpreted as the number of nodes of the wavefunction.

Note that the integrated action, $\oint p\, \mathrm{d}x$, represents the area of the classical path in phase space. This shows that each state is associated with an element of phase space $2\pi\hbar$. From this, we can deduce the approximate energy splitting between levels in the semi-classical limit: The change in the integral with energy ΔE corresponding to one level must be $2\pi\hbar$ - one more state and one more node, i.e. $\Delta E\, \partial_E \oint p\, \mathrm{d}x = 2\pi\hbar$. Now $\partial_p E = v$, so $\oint \partial_E p\, \mathrm{d}x = \oint \mathrm{d}x / v = T$, the period of the orbit. Therefore, $\Delta E = 2\pi\hbar/T = \hbar\omega$: In the semi-classical limit, if a particle emits one photon and drops to the next level, the frequency of the photon emitted is just the orbital frequency of the particle.

For a particle strictly confined to one dimension, the connection formulae can be understood within a simple picture: The wavefunction "spills over" into the classically forbidden region, and its twisting there collects an $\pi/4$ of phase change. So, in the lowest state, the total phase change in the classically allowed region need only be $\pi/2$. For the radial equation, assuming that the potential is well behaved at the origin, the wavefunction goes to zero there. A bound state will still spill over beyond the classical turning point at r_0, say, but clearly there must be a total phase change of $3\pi/4$ in the allowed region for the lowest state, since there can be no spill over to negative r. In this case, the general quantization formula will be

$$\frac{1}{\hbar}\int_r^{r_0} p(r)\, \mathrm{d}r = (n + 3/4)\pi, \qquad n = 0, 1, 2, \cdots, \tag{2.56}$$

with the series terminating if and when the turning point reaches infinity. In fact, some potentials, including the Coulomb potential and the centrifugal barrier for $\ell \neq 0$, are in fact singular at $r = 0$. These cases require special treatment.

2.3.4 Example: Simple Harmonic Oscillator

For the quantum harmonic oscillator, $H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 = E$, the classical momentum is given by

$$p(x) = \sqrt{2m\Big(E - \frac{m\omega^2x^2}{2}\Big)}. \tag{2.57}$$

The classical turning points are set by $E = m\omega^2x_0^2/2$, i.e. $x_0 = \pm 2E/m\omega^2$. Over a periodic cycle, the classical action is given by

$$\oint p(x)\,\mathrm{d}x = 2\int_{-x_0}^{x_0}\mathrm{d}x\,\sqrt{2m\Big(E - \frac{m\omega^2x^2}{2}\Big)} = 2\pi\frac{E}{\omega}. \tag{2.58}$$

According to the WKB method, the latter must be equated to $2\pi\hbar(n+1/2)$, with the last term reflecting the two turning points. As a result, we find that the energy levels are as expected specified by $E_n = (n+1/2)\hbar\omega$.

In the WKB approximation, the corresponding wavefunctions are given by

$$\begin{aligned}\psi(x) &= \frac{C}{\sqrt{p(x)}}\cos\left(\frac{1}{\hbar}\int_{-x_0}^{x_0} p(x')\,\mathrm{d}x' - \frac{\pi}{4}\right) && (2.59)\\ &= \frac{C}{\sqrt{p(x)}}\cos\left(\frac{2\pi}{4}(n+1/2)\frac{1}{\hbar}\int_0^{x_0} p(x')\,\mathrm{d}x' - \frac{\pi}{4}\right) && (2.60)\\ &= \frac{C}{\sqrt{p(x)}}\cos\left(\frac{n\pi}{2} + \frac{E}{\hbar\omega}\left[\arcsin\left(\frac{x}{x_0}\right) + \frac{x}{x_0}\sqrt{1-\frac{x^2}{x_0^2}}\right]\right), && (2.61)\end{aligned}$$

for $0 < x < x_0$ and

$$\psi(x) = \frac{C}{2\sqrt{p(x)}}\exp\left(-\frac{E}{\hbar\omega}\left[\frac{x}{x_0}\sqrt{\frac{x^2}{x_0^2} - 1} - \operatorname{arcosh}\Big(\frac{x}{x_0}\Big)\right]\right) \tag{2.62}$$

for $x > a$. Note that the failure of the WKB approximation is reflected in the appearance of discontinuities in the wavefunction at the classical turning points. Nevertheless, the wavefunction at high energies provides a strikingly good approximation to the exact wavefunction.

2.3.5 Example: Quantum Tunneling

Consider the problem of quantum tunneling. Suppose that a beam of particles is incident upon a localised potential barrier, $V(x)$. Further, let us assume that, over a single continuous region of space, from b to a, the potential rises above the incident energy of the incoming particles so that, classically, all particles would be reflected. In the quantum system, the some particles incident from the left may tunnel through the barrier and continue propagating to the right. We are interested in finding the transmission probability.

From the WKB solution, to the left of the barrier (region 1), we expect a wavefunction of the form

$$\psi_1(x) = \frac{1}{\sqrt{p}}\exp\left[\frac{i}{\hbar}\int_b^x p\,\mathrm{d}x'\right] + r(E)\frac{1}{\sqrt{p}}\exp\left[-\frac{i}{\hbar}\int_b^x p\,\mathrm{d}x'\right], \tag{2.63}$$

with $p(x) = \sqrt{2m(E - V(x))}$, while, to the right of the barrier (region 3), the wavefunction is given by

$$\psi_3(x) = t(E)\frac{1}{\sqrt{p}} \exp\left[\frac{i}{\hbar}\int_a^x p \, \mathrm{d}x'\right]. \tag{2.64}$$

In the barrier region, the wavefunction is given by

$$\psi_2(x) = \frac{C_1}{\sqrt{|p(x)|}} \exp\left[-\frac{i}{\hbar}\int_a^x |p| \, \mathrm{d}x'\right] + \frac{C_2}{\sqrt{|p(x)|}} \exp\left[\frac{i}{\hbar}\int_a^x |p| \, \mathrm{d}x'\right]. \tag{2.65}$$

Applying the matching conditions on the wavefunction at the classical turning points, one obtains the transmissivity,

$$\boxed{T(E) \simeq \exp\left[-\frac{2}{\hbar}\int_a^b |p| \, \mathrm{d}x\right].} \tag{2.66}$$

Chapter 3

Operator Methods in Quantum Mechanics

While the wave mechanical formulation has proved successful in describing the quantum mechanics of bound and unbound particles, some properties can not be represented through a wave-like description. For example, the electron spin degree of freedom does not translate to the action of a gradient operator. It is therefore useful to reformulate quantum mechanics in a framework that involves only operators.

Before discussing properties of operators, it is helpful to introduce a further simplification of notation. One advantage of the operator algebra is that it does not rely upon a particular basis. For example, when one writes $\hat{H} = \frac{\hat{p}^2}{2m}$, where the hat denotes an operator, we can equally represent the momentum operator in the spatial coordinate basis, when it is described by the differential operator, $\hat{p} = -i\hbar\partial_x$, or in the momentum basis, when it is just a number $\hat{p} = p$. Similarly, it would be useful to work with a basis for the wavefunction which is coordinate independent. Such a representation was developed by Dirac early in the formulation of quantun mechanics.

In the parlons of mathematics, square integrable functions (such as wavefunctions) are said form a vector space, much like the familiar three-dimensional vector spaces. In the **Dirac notation**, a state vector or wavefunction, ψ, is represented as a "ket", $|\psi\rangle$. Just as we can express any three-dimensional vector in terms of the basis vectors, $\mathbf{r} = x\hat{\mathbf{e}}_1 + y\hat{\mathbf{e}}_2 + z\hat{\mathbf{e}}_3$, so we can expand any wavefunction as a superposition of basis state vectors,

$$|\psi\rangle = \lambda_1 |\psi_1\rangle + \lambda_2 |\psi_2\rangle + \cdots . \tag{3.1}$$

Alongside the ket, we can define the "bra", $\langle\psi|$. Together, the bra and ket define the **scalar product**

$$\langle\phi|\psi\rangle \equiv \int_{-\infty}^{\infty} \mathrm{d}x\, \phi^*(x)\psi(x), \tag{3.2}$$

from which follows the identity, $\langle\phi|\psi\rangle^* = \langle\psi|\phi\rangle$. In this formulation, the real space representation of the wavefunction is recovered from the inner product $\phi(x) = \langle x|\phi\rangle$ while the momentum space wavefunction is obtained from $\phi(p) = \langle p|\phi\rangle$. As with a three-dimensional vector space where $\mathbf{a} \cdot \mathbf{b} \leq |a||b|$, the magnitude of the scalar product is limited by the magnitude of the vectors,

$$\langle\psi|\phi\rangle \leq \sqrt{\langle\psi|\psi\rangle \langle\phi|\phi\rangle}, \tag{3.3}$$

a relation known as the **Schwarz inequality**.

3.1 Operators

An operator $\hat{A}$ is a mathematical object that maps one state vector, $|\psi\rangle$, into another, $|\phi\rangle$, i.e. $\hat{A}|\psi\rangle = |\phi\rangle$. If

$$\boxed{\hat{A}|\psi\rangle = a|\psi\rangle\,,} \tag{3.4}$$

then $|\phi\rangle$ is said to be an **eigenstate** (or **eigenfunction**) of $\hat{A}$ with eigenvalue a. For example, the plane wave state $\psi_x(x) = \langle x|\psi_p\rangle = Ae^{ipx/\hbar}$ is an eigenstate of the **momentum operator**, $\hat{p} = -i\hbar\partial_x$, with eigenvalue p. For a free particle, the plane wave is also an eigenstate of the Hamiltonian, $\hat{H} = \frac{\hat{p}^2}{2m}$ with eigenvalue $\frac{p^2}{2m}$.

In quantum mechanics, for any observable A, there is an operator $\hat{A}$ which acts on the wavefunction so that, if a system is in a state described by $|\psi\rangle$, the expectation value of A is

$$\boxed{\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\,\phi^*(x)\hat{A}\psi(x).} \tag{3.5}$$

Every operator corresponding to an observable is both linear and Hermitian: That is, for any two wavefunctions $|\phi\rangle$ and $|\phi\rangle$, and any two complex numbers α and β, **linearity** implies that

$$\hat{A}(\alpha|\psi\rangle + \beta|\phi\rangle) = \alpha\Big(\hat{A}|\psi\rangle\Big) + \beta\Big(\hat{A}|\phi\rangle\Big). \tag{3.6}$$

Moreover, for any linear operator $\hat{A}$, the **Hermitian conjugate** operator (also known as the adjoint) is defined by the relation

$$\boxed{\Big\langle\phi\Big|\hat{A}\psi\Big\rangle = \int \mathrm{d}x\,\phi^*\Big(\hat{A}\psi\Big) = \int \mathrm{d}x\,\psi\Big(\hat{A}^\dagger\phi\Big)^* = \Big\langle\hat{A}^\dagger\phi\Big|\psi\Big\rangle\,.} \tag{3.7}$$

From the definition, $\Big\langle\hat{A}^\dagger\phi\Big|\psi\Big\rangle = \Big\langle\phi\Big|\hat{A}\psi\Big\rangle$, we can prove some useful relations: Taking the complex conjugate, $\Big\langle\hat{A}^\dagger\phi\Big|\psi\Big\rangle^* = \Big\langle\psi\Big|\hat{A}^\dagger\phi\Big\rangle = \Big\langle\hat{A}\psi\Big|\phi\Big\rangle$, and then finding the Hermitian conjugate of $\hat{A}^\dagger$, we have

$$\Big\langle\psi\Big|\hat{A}^\dagger\phi\Big\rangle = \Big\langle\Big(\hat{A}^\dagger\Big)^\dagger\psi\Big|\phi\Big\rangle = \Big\langle\hat{A}\psi\Big|\phi\Big\rangle\,, \qquad \text{i.e. } \Big(\hat{A}^\dagger\Big)^\dagger = \hat{A}. \tag{3.8}$$

Therefore, if we take the Hermitian conjugate twice, we get back to the same operator. It's easy to show that $(\lambda\hat{A})^\dagger = \lambda^*\hat{A}^\dagger$ and $(\hat{A}+\hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger$ just from the properties of the dot product. We can also show that $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$ from the identity, $\Big\langle\phi\Big|\hat{A}\hat{B}\psi\Big\rangle = \Big\langle\hat{A}^\dagger\phi\Big|\hat{B}\psi\Big\rangle = \Big\langle\hat{B}^\dagger\hat{A}^\dagger\phi\Big|\psi\Big\rangle$. Note that operators are **associative** but not (in general) **commutative**,

$$\hat{A}\hat{B}|\psi\rangle = \hat{A}(\hat{B}|\psi\rangle) = (\hat{A}\hat{B})|\psi\rangle \neq \hat{B}\hat{A}|\psi\rangle\,. \tag{3.9}$$

It is helpful to define the **commutator** of two operators by

$$\boxed{\Big[\hat{A},\hat{B}\Big] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}.} \tag{3.10}$$

A physical variable must have real expectation values (and eigenvalues). This implies that the operators representing physical variables have some special properties. By computing the complex conjugate of the expectation value of a physical variable, we can easily show that physical operators are their own Hermitian conjugate,

$$\langle\psi|\hat{H}|\psi\rangle^* = \left[\int_{-\infty}^{\infty} \psi^*(x)\hat{H}\psi(x)\,\mathrm{d}x\right]^* = \int_{-\infty}^{\infty} \psi(x)(\hat{H}\psi(x))^*\,\mathrm{d}x = \left\langle \hat{H}\psi \middle| \psi \right\rangle. \tag{3.11}$$

i.e. $\left\langle \hat{H}\psi \middle| \psi \right\rangle = \left\langle \psi \middle| \hat{H}\psi \right\rangle = \left\langle \hat{H}^\dagger\psi \middle| \psi \right\rangle$, and $\hat{H}^\dagger = \hat{H}$. Operators that are their own Hermitian conjugate are called **Hermitian** (or self-adjoint).

3.1.1 Matrix representations of operators

Eigenfunctions of Hermitian operators $\hat{H}\,|i\rangle = E_i\,|i\rangle$ form an orthonormal (i.e. $\langle i|j\rangle = \delta_{ij}$) complete basis. For any complete basis $\{|i\rangle\}$, we can expand a state $|\psi\rangle$ as

$$|\psi\rangle = \sum_i \psi_i\,|i\rangle \tag{3.12}$$

This is a "representation" of $|\psi\rangle$ in this particular basis: e.g. if $\{|i\rangle\}$ are energy eigenstates, then we say that ψ_i is the "energy-representation" of $|\psi\rangle$.

To obtain an explicit form for ψ_i , we note that we can for any orthonormal complete set of states $\{|i\rangle\}$, we can always write

$$|\psi\rangle = \sum_i |i\rangle\,\langle i|\psi\rangle\,. \tag{3.13}$$

Thus, we see that the complex numbers $\langle i|\psi\rangle$ are the components of the state vector in the basis states $\{|i\rangle\}$, that is $\psi_i \equiv \langle i|\psi\rangle$.

A 'ket' state vector followed by a 'bra' state vector is an example of an operator. The **projection operator** onto a state $|j\rangle$ is given by $|j\rangle\langle j|$. First the bra vector dots into the state, giving the coefficient of $|j\rangle$ in the state, then it is multiplied by the unit vector $|j\rangle$, turning it back into a vector, with the right length to be a projection. An operator maps one vector into another vector, so this is an operator. If we sum over a complete orthonormal set of states, like the eigenstates of a Hermitian operator, we obtain the (useful) **resolution of the identity**

$$\boxed{\hat{\mathbb{I}} = \sum_i |i\rangle\langle i|\,.} \tag{3.14}$$

Using the resolution of the identity, it is possible to express any operator as

$$\hat{A} = \hat{\mathbb{I}}\hat{A}\hat{\mathbb{I}} = \sum_i\sum_j |j\rangle\ \langle j|\hat{A}|i\rangle\ \langle i|\,. \tag{3.15}$$

The complex numbers $A_{ji} = \langle j|A|i\rangle$ are the "matrix representation" of $\hat{A}$ in this basis,

$$\hat{A} = \sum_{ij} A_{ji}\,|j\rangle\langle i|\,. \tag{3.16}$$

Consider the action of $\hat{A}$ on a state $|\psi\rangle$

$$|\phi\rangle \equiv \hat{A}\,|\psi\rangle \tag{3.17}$$
$$= \sum_i \sum_j |j\rangle\,\langle j|\hat{A}|i\rangle\,\langle i|\psi\rangle = \sum_{i,j} |j\rangle\,A_{ji}\psi_i \tag{3.18}$$

The representation of $|\psi\rangle$ in this basis is

$$\phi_i \equiv \langle i|\phi\rangle = \langle i| \left(\sum_{k,j} |j\rangle\,A_{jk}\psi_k \right) = \sum_{k,j} \delta_{ij} A_{jk}\psi_k \tag{3.19}$$
$$= \sum_k A_{ik}\phi_k \tag{3.20}$$

Thus the action of the operator $\hat{A}$ is via matrix multiplication of A_{ik} on the components of the vector ψ_k. Any complete orthonormal set of vectors can be used as the basis. Each gives rise to a different (vector) representation of the states and (matrix) representation of the operators.

In the above discussion, we have assumed that the basis $\{|i\rangle\}$ is discrete (i.e. we can sum over the projectors $|i\rangle\langle i|$). How do we interpret these sums when the basis is described by a continuous variable? For example, we could consider the eigenstates $\{|x\rangle\}$ of the position operator $\hat{x}$, or the eigenstates $\{|p\rangle\}$ of the momentum operator $\hat{p}$.

For a continuous set of states, the resolution of the identity becomes

$$\boxed{\hat{\mathbb{I}} = \int \mathrm{d}x\,|x\rangle\langle x|\,.} \tag{3.21}$$

and the orthonormality condition becomes

$$\langle x'|x\rangle = \delta(x - x'), \tag{3.22}$$

where $\delta(x)$ is the **Dirac delta function**. Thus, for a state $|\psi\rangle$ we can write

$$|\psi\rangle = \int \mathrm{d}x\,|x\rangle\,\langle x|\psi\rangle = \int \mathrm{d}x\,\psi(x)\,|x\rangle \tag{3.23}$$

If $\{|x\rangle\}$ are the position eigenstates, then the complex function $\psi(x)$ the position representation of $|\psi\rangle$. This function $\psi(x)$ is nothing but the wavefunction of the Schrödinger equation. Eq. (3.23) shows how the Schrödinger wavefunction should be interpreted within the more abstract Dirac notation.

The basis states can be formed from any complete set of orthogonal states. In particular, they can be formed from the basis states of the position or the momentum operator, i.e. $\int_{-\infty}^{\infty} \mathrm{d}x\,|x\rangle\langle x| = \int_{-\infty}^{\infty} \mathrm{d}p\,|p\rangle\langle p| = \hat{\mathbb{I}}$. If we apply these definitions, we can then recover the familiar Fourier representation,

$$\psi(x) = \langle x|\psi\rangle = \int_{\infty}^{\infty} \mathrm{d}p\,\underbrace{\langle x|p\rangle}_{e^{ipx/\hbar}/\sqrt{2\pi\hbar}}\,\langle p|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int_{\infty}^{\infty} \mathrm{d}p\,e^{ipx/\hbar}\psi(x), \tag{3.24}$$

where $\langle x|p\rangle$ is the position representation of the momentum eigenstate $|p\rangle$.

3.1.2 Time-evolution operator

The ability to develop an eigenfunction expansion provides the means to explore the time evolution of a general wave packet, $|\psi\rangle$ under the action of a Hamiltonian. Formally, we can evolve a wavefunction forward in time by applying the time-evolution operator. For a Hamiltonian which is time independent, we have $|\psi(t)\rangle = \hat{U}\,|\psi(0)\rangle$, where

$$\boxed{\hat{U} = e^{-i\hat{H}t/\hbar},} \tag{3.25}$$

denotes the time-evolution operator.[1] By inserting the resolution of identity, $\mathbb{I} = \sum_i |i\rangle\langle i|$, where the states $|i\rangle$ are eigenstates of the Hamiltonian with eigenvalue E_i , we find that

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar} \sum_i \langle i|\,\langle i|\psi(0)\rangle = \sum_i \langle i|\,\langle i|\psi(0)\rangle\, e^{-iE_i t/\hbar}. \tag{3.26}$$

The time-evolution operator is an example of a **unitary operator**. The latter are defined as transformations which preserve the scalar product, $\langle\phi|\psi\rangle = \left\langle \hat{U}\phi \middle| \hat{U}\psi \right\rangle = \left\langle \phi \middle| \hat{U}^\dagger \hat{U}\psi \right\rangle \overset{!}{=} \langle\psi|\phi\rangle$, i.e.

$$\boxed{\hat{U}^\dagger \hat{U} = \hat{\mathbb{I}}} \tag{3.27}$$

3.1.2.1 Example: Evolution of Harmonic Oscillator

Consider the harmonic oscillator Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2$. Later in this chapter, we will see that the eigenstates, $|n\rangle$, have equally-spaced eigenvalues, $E_n = \hbar\omega(n+1/2)$, for $n = 0, 1, 2, \cdots$. Let us then consider the time-evolution of a general wavepacket, $|\psi(0)\rangle$, under the action of the Hamiltonian. From the equation above, we find that $|\psi(t)\rangle = \sum_n |n\rangle\,\langle n|\psi(0)\rangle\, e^{-iE_i t/\hbar}$. Since the eigenvalues are equally spaced, let us consider what happens when $t = t_r \equiv 2\pi r/\omega$, with r integer. In this case, since $e^{2\pi i n r} = 1$, we have

$$|\psi(t_r)\rangle = \sum_n |n\rangle\,\langle n|\psi(0)\rangle\, e^{-i\omega t_r/2} = (-1)^r\,|\psi(0)\rangle \tag{3.28}$$

From this result, we can see that, up to an overall phase, the wave packet is perfectly reconstructed at these times. This recurrence or "echo" is not generic, but is a manifestation of the equal separation of eigenvalues in the harmonic oscillator.

3.1.3 Uncertainty principle for non-commuting operators

For non-commuting Hermitian operators, $[\hat{A}, \hat{B}] \neq 0$, it is straightforward to establish a bound on the uncertainty in their expectation values. Given a state $|\psi\rangle$, the mean square uncertainty is defined as

$$(\Delta A)^2 = \langle\psi|\Big(\hat{A} - \left\langle\hat{A}\right\rangle\Big)^2|\psi\rangle = \langle\psi|\hat{U}^2|\psi\rangle\,, \tag{3.29}$$

$$(\Delta B)^2 = \langle\psi|\Big(\hat{B} - \left\langle\hat{B}\right\rangle\Big)^2|\psi\rangle = \langle\psi|\hat{V}^2|\psi\rangle\,, \tag{3.30}$$

[1]This equation follows from integrating the time-dependent Schrödinger equation, $\hat{H}\,|\psi\rangle = i\hbar\partial_t\,|\psi\rangle$.

where we have defined the operators $\hat{U} = \hat{A} - \left\langle \hat{A} \right\rangle$ and $\hat{V} = \hat{B} - \left\langle \hat{B} \right\rangle$. Since $\left\langle \hat{A} \right\rangle$ and $\left\langle \hat{B} \right\rangle$ are just constants, $[\hat{U}, \hat{V}] = [\hat{A}, \hat{B}]$. Now let us take the scalar product of $\hat{U} |\psi\rangle + i\lambda\hat{V} |\psi\rangle$ with itself to develop some information about the uncertainties. As a modulus, the scalar product must be greater than or equal to zero, i.e. expanding, we have $\langle\psi|\hat{U}^2|\psi\rangle + \lambda^2 \langle\psi|\hat{V}^2|\psi\rangle + i\lambda \left\langle \hat{U}\psi \middle| \hat{V}\psi \right\rangle - i\lambda \left\langle \hat{V}\psi \middle| \hat{U}\psi \right\rangle \geq 0$. Reorganising this equation in terms of the uncertainties, we thus find

$$(\Delta A)^2 + \lambda^2(\Delta B)^2 + i\lambda \left\langle [\hat{U}, \hat{V}] \right\rangle \geq 0. \tag{3.31}$$

If we minimise this expression with respect to λ, we can determine when the inequality becomes strongest. In doing so, we find

$$2\lambda(\Delta B)^2 + i \left\langle [\hat{U}, \hat{V}] \right\rangle = 0, \qquad \lambda = -\frac{i}{2} \frac{\left\langle [\hat{U}, \hat{V}] \right\rangle}{(\Delta B)^2}. \tag{3.32}$$

Substituting this value of λ back into the inequality, we then find,

$$(\Delta A)^2(\Delta B)^2 \geq -\frac{1}{4} \left\langle [\hat{U}, \hat{V}] \right\rangle^2. \tag{3.33}$$

We therefore find that, for non-commuting operators, the uncertainties obey the following inequality,

$$\boxed{\Delta A \Delta B \geq \left| \frac{1}{2} \left\langle [\hat{A}, \hat{B}] \right\rangle \right|.} \tag{3.34}$$

If the commutator is a constant, as in the case of the conjugate operators $[\hat{p}, \hat{x}] = -i\hbar$, the expectation values can be dropped, and we obtain the relation, $(\Delta A)(\Delta B) \geq \frac{i}{2}[\hat{A}, \hat{B}]$. For momentum and position, this result recovers **Heisenberg's uncertainty principle**,

$$\boxed{\Delta p \Delta x \geq \left| \frac{1}{2} \langle [\hat{p}, \hat{x}] \rangle \right| = \frac{\hbar}{2}.} \tag{3.35}$$

3.1.4 Time-evolution of expectation values

Finally, to close this section on operators, let us consider how their expectation values evolve. To do so, let us consider a general operator $\hat{A}$ which may itself involve time. The time derivative of a general expectation value has three terms.

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle\psi|\hat{A}|\psi\rangle = \partial_t(\langle\psi|)\hat{A} |\psi\rangle + \langle\psi|\partial_t\hat{A}|\psi\rangle + \langle\psi| \hat{A}(\partial_t |\psi\rangle). \tag{3.36}$$

If we then make use of the time-dependent Schrödinger equation, $i\hbar\partial_t |\psi\rangle = \hat{H} |\psi\rangle$, and the Hermiticity of the Hamiltonian, we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle\psi|\hat{A}|\psi\rangle = \underbrace{\frac{i}{\hbar}\Big(\langle\psi|\hat{H}\hat{A}|\psi\rangle - \langle\psi|\hat{A}\hat{H}|\psi\rangle \Big)} + \langle\psi|\partial_t\hat{A}|\psi\rangle. \tag{3.37}$$

$$\frac{i}{\hbar} \left\langle \left[\hat{H}, \hat{A}\right] \right\rangle \tag{3.38}$$

This is an important and general result for the time derivative of expectation values which becomes simple if the operator itself does not explicitly depend on time,

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t}\left\langle \hat{A}\right\rangle = \frac{i}{\hbar}\left\langle \left[\hat{H}, \hat{A}\right]\right\rangle .} \tag{3.39}$$

From this result, which is known as **Ehrenfest's theorem**, we see that expectation values of operators that commute with the Hamiltonian are constants of the motion

3.1.4.1 Example: Evolution of $\hat{x}$ and $\hat{p}$ Operators

From the non-relativistic Schrödinger operator for a single particle moving in a potential, $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$, we can derive the quantum mechanical counterparts of Hamilton's classical equations of motion.

Suppose we wanted to know the instantaneous change in the expectation of the momentum operator $\hat{p}$. Using Ehrenfest's theorem, we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{p}\rangle = \frac{i}{\hbar}\left\langle \left[\hat{H}, \hat{p}\right]\right\rangle + \left\langle \frac{\partial}{\partial t}\hat{p}\right\rangle = \frac{i}{\hbar}\left\langle [V(\hat{x}), \hat{p}]\right\rangle , \tag{3.40}$$

since the operator $\hat{p}$ commutes with itself and has no time dependence. By expanding the right hand side, using the identity $[F(\hat{x}), \hat{p}] = i\hbar\partial_{\hat{x}}F(\hat{x})$, we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{p}\rangle = -\left\langle \partial_{\hat{x}}V(\hat{x})\right\rangle = -\left\langle \partial_{\hat{x}}\hat{H}\right\rangle . \tag{3.41}$$

Similarly, we can obtain the instantaneous change in the position expectation value,

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{x}\rangle = \frac{i}{\hbar}\left\langle \left[\hat{H}, \hat{x}\right]\right\rangle + \left\langle \frac{\partial}{\partial t}\hat{x}\right\rangle = \frac{i}{2m\hbar}\left\langle \left[\hat{p}^2, \hat{x}\right]\right\rangle , \tag{3.42}$$

and thus from this we can evaluate the appropriate commutator, noting that $[\hat{p}, \hat{x}] = -i\hbar$, to give

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{x}\rangle = \frac{1}{m}\langle \hat{p}\rangle = \left\langle \partial_{\hat{p}}\hat{H}\right\rangle . \tag{3.43}$$

Although, at first glance, it might appear that the Ehrenfest theorem is saying that the quantum mechanical expectation values obey Newton's classical equations of motion, this is not actually the case. This result does not say that the pair $\{\langle \hat{x}\rangle , \langle \hat{p}\rangle\}$ satisfies Newton's second law, because the right-hand side of the formulae (3.41) and (3.43) are of the form $\langle F(\hat{x}, t)\rangle$ rather than $F(\langle \hat{x}\rangle , t)$. Nevertheless, for states that are highly localised in space, the expected position and momentum will approximately follow classical trajectories, which may be understood as an instance of the correspondence principle.

3.2 The Heisenberg picture

Until now, the time dependence of an evolving quantum system has been placed within the wavefunction while the operators have remained constant - this is the **Schrödinger picture** or **representation**. However, it is sometimes useful to transfer the time-dependence to the operators. To see how, let us consider the expectation value of some operator $\hat{B}$,

$$\langle\psi(t)|\hat{B}|\psi(t)\rangle = \left\langle e^{-i\hat{H}t/\hbar}\psi(0)\middle|\hat{B}\middle|e^{-i\hat{H}t/\hbar}\psi(0)\right\rangle = \langle\psi(0)|e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}|\psi(0)\rangle\,. \quad (3.44)$$

According to rules of associativity, we can multiply operators together before using them. If we define the operator $\hat{B}(t) = e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}$, the timedependence of the expectation values has been transferred from the wavefunction. This is called the **Heisenberg picture** or **representation** and in it, the operators evolve with time (even if, as in this case, they have no explicit time dependence) while the wavefunctions remain constant. In this representation, the time derivative of the operator is given by

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle\hat{B}\right\rangle = \frac{i\hat{H}}{\hbar}e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar} - e^{i\hat{H}t/\hbar}\hat{B}\frac{i\hat{H}}{\hbar}e^{-i\hat{H}t/\hbar} \quad (3.45)$$

$$= \frac{i}{\hbar}e^{i\hat{H}t/\hbar}\left[\hat{H},\hat{B}\right]e^{-i\hat{H}t/\hbar} \quad (3.46)$$

$$= \frac{i}{\hbar}\left[\hat{H},\hat{B}(t)\right]. \quad (3.47)$$

3.3 Quantum harmonic oscillator

As we will see time and again in this course, the harmonic oscillator assumes a privileged position in quantum mechanics and quantum field theory finding numerous and sometimes unexpected applications. It is useful to us now in that it provides a platform for us to implement some of the technology that has been developed in this chapter. In the one-dimensional case, the quantum harmonic oscillator Hamiltonian takes the form,

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2, \quad (3.48)$$

where $\hat{p} = -i\hbar\partial_x$. To find the eigenstates of the Hamiltonian, we could look for solutions of the linear second order differential equation corresponding to the time-independent Schrödinger equation, $\hat{H}\psi = E\psi$, where $\hat{H} = -\frac{\hbar^2}{2m}\partial_x^2 + \frac{1}{2}m\omega^2\hat{x}^2$. The integrability of the Schrödinger operator in this case allows the stationary states to be expressed in terms of a set of orthogonal functions known as Hermite polynomials. However, the complexity of the exact eigenstates obscure a number of special and useful features of the harmonic oscillator system. To identify these features, we will instead follow a method based on an operator formalism.

The form of the Hamiltonian as the sum of the squares of momenta and position suggests that it can be recast as the "square of an operator". To this end, let us introduce the operator

$$a = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + i\frac{\hat{p}}{m\omega}\right), \qquad a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - i\frac{\hat{p}}{m\omega}\right), \quad (3.49)$$

where, for notational convenience, we have not drawn hats on the operators a and its Hermitian conjugate $a^\dagger$. Making use of the identity,

$$a^\dagger a = \frac{m\omega}{2\hbar}\hat{x}^2 + \frac{\hat{p}^2}{2\hbar m\omega} + \frac{i}{2\hbar}[\hat{x},\hat{p}] = \frac{\hat{H}}{\hbar\omega} - \frac{1}{2} \quad (3.50)$$

and the parallel relation, $aa^\dagger = \frac{\hat{H}}{\hbar\omega} + \frac{1}{2}$, we see that the operators fulfil the commutation relations

$$\boxed{[a, a^\dagger] \equiv aa^\dagger - a^\dagger a = 1.} \tag{3.51}$$

Then, setting $\hat{n} = a^\dagger a$, the Hamiltonian can be cast in the form

$$\boxed{\hat{H} = \hbar\omega(n + 1/2).} \tag{3.52}$$

Since the operator $\hat{n} = a^\dagger a$ must lead to a positive definite result, we see that the eigenstates of the harmonic oscillator must have energies of $\hbar\omega/2$ or higher. Moreover, the ground state $|0\rangle$ can be identified by finding the state for which $a\,|0\rangle = 0$. Expressed in the coordinate basis, this translates to the equation, [2]

$$\left(x + \frac{\hbar}{m\omega}\partial_x\right)\psi_0(x) = 0, \qquad \psi_0(x) = \langle x|0\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar}. \tag{3.54}$$

Since $\hat{n}\,|0\rangle = a^\dagger a\,|0\rangle = 0$, this state is an eigenstate with energy $\hbar\omega/2$. The higher lying states can be found by acting upon this state with the operator $a^\dagger$. The proof runs as follows: If $\hat{n}\,|n\rangle = n\,|n\rangle$, we have

$$\hat{n}(a^\dagger\,|n\rangle) = a^\dagger \underbrace{aa^\dagger}_{a^\dagger a+1}\,|n\rangle = (a^\dagger \underbrace{a^\dagger a}_{\hat{n}} + a^\dagger)\,|n\rangle = (n+1)a^\dagger\,|n\rangle \tag{3.55}$$

or, equivalently, $[\hat{n}, a^\dagger] = a^\dagger$. In other words, if $|n\rangle$ is an eigenstate of $\hat{n}$ with eigenvalue n, then $a^\dagger\,|n\rangle$ is an eigenstate with eigenvalue $n+1$.

From this result, we can deduce that the eigenstates for a "tower" $|0\rangle\,,\ |1\rangle = C_1 a^\dagger\,|0\rangle\,,\ |2\rangle = C_2(a^\dagger)^2\,|0\rangle$, etc., where C_n denotes the normalisation. If $\langle n|n\rangle = 1$ we have

$$\langle n|aa^\dagger|n\rangle = \langle n|(\hat{n}+1)|n\rangle = (n+1). \tag{3.56}$$

Therefore, with $|n+1\rangle = \frac{1}{\sqrt{n+1}}a^\dagger\,|n\rangle$ the state $|n+1\rangle$ is also normalised, $\langle n+1|n+1\rangle = 11$. By induction, we can deduce the general normalisation,

$$\boxed{|n\rangle = \frac{1}{\sqrt{n!}}(a^\dagger)^n\,|0\rangle\,,} \tag{3.57}$$

with $\langle n|n'\rangle = \delta_{nn'}$, $\hat{H}\,|n\rangle\,\hbar\omega(n+1/2)\,|n\rangle$ and

$$\boxed{a^\dagger\,|n\rangle = \sqrt{n+1}\,|n+1\rangle\,, \qquad a\,|n\rangle = \sqrt{n}\,|n-1\rangle\,.} \tag{3.58}$$

The operators a and $a^\dagger$ represent **ladder operators** and have the effect of lowering or raising the energy of the state.

[2]Formally, in coordinate basis, we have $\langle x'|a|x\rangle = \delta(x'-x)(a+\frac{\hbar}{m\omega}\partial_x)$ and $\langle x|0\rangle = \psi_0(x)$. Then making use of the resolution of identity $\int dx\,|x\rangle\langle x| = \hat{\mathbb{I}}$, we have

$$\langle x|a|0\rangle = 0 = \int dx\,\langle x|a|x'\rangle\langle x'|0\rangle = \left(x + \frac{\hbar}{m\omega}\partial_x\right)\psi_0(x). \tag{3.53}$$

In fact, the operator representation achieves something quite remarkable and, as we will see, unexpectedly profound. The quantum harmonic oscillator describes the motion of a single particle in a one-dimensional potential well. Its eigenvalues turn out to be equally spaced - a ladder of eigenvalues, separated by a constant energy $\hbar\omega$. If we are energetic, we can of course translate our results into a coordinate representation $\psi_n(x) = \langle x|n\rangle$.[3] However, the operator representation affords a second interpretation, one that lends itself to further generalisation in quantum field theory. We can instead interpret the quantum harmonic oscillator as a simple system involving many fictitious particles, each of energy $\hbar\omega$. In this representation, known as the **Fock space**, the vacuum state $|0\rangle$ is one involving no particles, $|1\rangle$ involves a single particle, $|2\rangle$ has two and so on. These fictitious particles are created and annihilated by the action of the raising and lowering operators, $a^\dagger$ and a with canonical commutation relations, $[a, a^\dagger] = 1$. Later in the course, we will find that these commutation relations are the hallmark of **bosonic** quantum particles and this representation, known as the **second quantisation** underpins the quantum field theory of the electromagnetic field.

This completes our abridged survey of operator methods in quantum mechanics.

[3] Expressed in real space, the harmonic oscillator wavefunctions are in fact described by the Hermite polynomials,

$$\psi_n(x) = \langle x|n\rangle = \sqrt{\frac{1}{2^n n!}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) \exp\left[-\frac{m\omega x^2}{2\hbar}\right], \tag{3.59}$$

where $H_n(x) = (-1)^n e^{x^2} \frac{\mathrm{d}^n}{\mathrm{d}n^n} e^{-x^2}$.

Chapter 4

Quantum Mechanics in More Than One Dimension

Previously, we have explored the manifestations of quantum mechanics in one spatial dimension and discussed the properties of bound and unbound states. The concepts developed there apply equally to higher dimension. However, for a general two or three-dimensional potential, without any symmetry, the solutions of the Schr¨odinger equation are often inaccessible. In such situations, we may develop approximation methods to address the properties of the states (e.g. WKB method, and see chapter 7). However, in systems where there is a high degree of symmetry, the quantum mechanics of the system can often be reduced to a tractable low-dimensional theory.

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

Chapter 7

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

Chapter 8

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 Land´e 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+2ion

11.2 The H2 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

Chapter 14

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

$$i\hbar\frac{\partial}{\partial t}\int_{\mathcal{V}} P(\mathbf{r},t)\,\mathrm{d}V = i\hbar\frac{\partial}{\partial t}\int_{\mathcal{V}} \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t)\,\mathrm{d}V\,; \tag{A.1}$$

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