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

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

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

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

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

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

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

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,

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

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, $E^2 = (c\mathbf{p})^2 + (m_0 c^2)^2$. 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,

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

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,

$$\psi(x) = \left(\frac{1}{2\pi\alpha}\right)^{1/4} e^{ik_0x} e^{-\frac{x^2}{4\alpha}} \tag{2.11}$$

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

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

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

$$t = \frac{2k_1 k_2 e^{-ik_1 a}}{2k_1 k_2 \cos(k_2 a) - i\left(k_1^2 + k_2^2\right)^2 \sin(k_2 a)}, \tag{2.20}$$

translating to a transmissivity of

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

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 $k_2 a = n\pi$ 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,

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

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

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

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 $k = \frac{\sqrt{2mE}}{\hbar}$k =mpm2mE/ n2 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

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

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 wavefunction 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.

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

$$p(x)=\sqrt{2m\left(E-\frac{m\omega^2x^2}{2}\right)}. \tag{2.56}$$

The classical turning points are set by $E=m\omega^2x_0^2/2$, i.e. $x_0=\pm2E/m\omega^2$. Over a periodic cycle, the classical action is given by

$$\oint p(x)\,\mathrm{d}x=2\int_{-x_0}^{x_0}\mathrm{d}x\,\sqrt{2m\left(E-\frac{m\omega^2x^2}{2}\right)}=2\pi\frac{E}{\omega}. \tag{2.57}$$

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

$$\begin{aligned}\psi(x) &= \frac{C}{\sqrt{p(x)}}\cos\left(\frac{1}{\hbar}\int_{-x_0}^{x_0} p(x')\,\mathrm{d}x' - \frac{\pi}{4}\right)\\ &= \frac{C}{\sqrt{p(x)}}\cos\left(\frac{2\pi}{4}(n+1/2)\frac{1}{\hbar}\int_0^{x_0} p(x')\,\mathrm{d}x' - \frac{\pi}{4}\right)\\ &= \frac{C}{\sqrt{p(x)}}\cos\left(\frac{n\pi}{2} + \frac{E}{\hbar\omega}\left[\arcsin\left(\frac{x}{x_0}\right) + \frac{x}{x_0}\sqrt{1-\frac{x^2}{x_0^2}}\right]\right),\end{aligned} \tag{2.58}$$

for $0 < x < x_0$ and

$$\psi(x) = \frac{C}{2\sqrt{p(x)}}\exp\left(-\frac{E}{\hbar\omega}\left[\frac{x}{x_0}\sqrt{\frac{x^2}{x_0^2}-1} - \mathrm{arcosh}\left(\frac{x}{x_0}\right)\right]\right) \tag{2.59}$$

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 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

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3.1.2 Time-evolution operator

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3.2 The Heisenberg picture

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11.3 From molecules to solids

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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):