

Chapter 1

Wave mechanics and the Schrödinger equation

Although this lecture course will assume a familiarity with the basic concepts of wave mechanics, to introduce more advanced topics in quantum theory, it makes sense to begin with a concise review of the foundations of the subject. In particular, in the first chapter of the course, we will begin with a brief discussion of the historical challenges that led to the development of quantum theory almost a century ago.

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

1.1 Historical foundations of quantum physics

1.1.1 Black-body radiation

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

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

where, as usual, c is the speed of light.¹

¹If we take the cavity to have dimension L^3 , the modes of the cavity involve wave numbers $\mathbf{k} = \pi\mathbf{n}/L$ where $\mathbf{n} = (n_x, n_y, n_z)$ denote the vector of integers $n_x = 0, 1, 2, \dots \infty$, etc. The corresponding frequency of each mode is given by $\nu = c|\mathbf{k}|/2\pi$, where c is the velocity of light. The number of modes (per unit volume) having frequencies between ν and $\nu + d\nu$ is

William Thomson, 1st Baron Kelvin 1824–1907

Kelvin was educated at Glasgow and Cambridge. He became professor of natural philosophy at Glasgow in 1846. From 1846 to 1851 Kelvin edited the “Cambridge and Dublin Mathematical Journal,” to which he contributed several important papers. Some of his chief discoveries are announced in the “Secular Coating of the Earth,” and the Bakerian lecture, the “Electrodynamic Qualities of Metals.” He invented the quadrant, portable, and absolute electrometers, and other scientific instruments. In January 1892, he was raised to the peerage as Lord Kelvin.



Gustav Robert Kirchhoff 1824–1887

A German physicist who contributed to the fundamental understanding of electrical circuits, spectroscopy, and the emission of black-body radiation by heated objects. He coined the term “black body” radiation in 1862, and two sets of independent concepts in both circuit theory and thermal emission are named “Kirchhoff’s laws” after him.



John William Strutt, 3rd Baron Rayleigh OM (1842–1919)

An English physicist who, with William Ramsay, discovered the element argon, an achievement for which he earned the Nobel Prize in 1904. He also discovered the phenomenon of Rayleigh scattering, explaining why the sky is blue, and predicted the existence of surface waves known as Rayleigh waves.



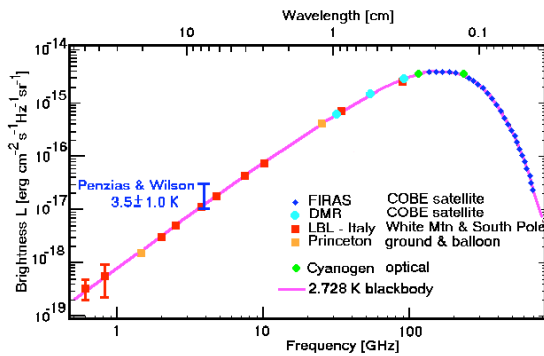


Figure 1.1: The COBE (Cosmic Background Explorer) satellite made careful measurements of the shape of the spectrum of the emission from the cosmic microwave background. As one can see, the behaviour at low-frequencies (long-wavelengths) conforms well with the predicted Rayleigh-Jeans law translating to a temperature of 2.728K. However, at high frequencies, there is a departure from the predicted ν^2 dependence.

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 have an equal chance of being excited, and the average energy in each mode is $k_B T$ (equipartition), where k_B is the Boltzmann constant. The corresponding energy density is therefore given by the **Rayleigh-Jeans law**,

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

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 short-wavelength dependence was quite benign (see, e.g., Fig. 1.1).

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 by²

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

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

$$\rho(\nu, T) = \frac{8\pi\nu^2}{c^3} \langle \varepsilon(\nu) \rangle = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1}. \tag{1.1}$$

This result conforms with experiment (Fig. 1.1), and converges on the Rayleigh-Jeans law at low frequencies, $h\nu/k_B T \rightarrow 0$.

Planck’s result suggests that electromagnetic energy is quantized: 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

therefore given by $N(\nu)d\nu = \frac{1}{L^3} \times 2 \times \frac{1}{8} \times \frac{(4\pi k^2)dk}{(\pi/L)^3}$, where the factor of 2 accounts for the two polarizations, the factor $(4\pi k^2)dk$ is the volume of the shell from k to $k + dk$ in reciprocal space, the factor of $1/8$ accounts for the fact that only positive wavenumbers are involved in the closed cavity, and the factor of $(\pi/L)^3$ denotes the volume of phase space occupied by each mode. Rearranging the equation, and noting that $dk = 2\pi d\nu/c$, we obtain the relation in the text.

²If we define the partition function, $\mathcal{Z} = \sum_{n=0}^{\infty} e^{-\beta nh\nu}$, where $\beta = 1/k_B T$, $\langle E \rangle = -\partial_{\beta} \ln \mathcal{Z}$. Making use of the formula for the sum of a geometric progression, $\sum_{n=0}^{\infty} r^n = 1/(1-r)$, we obtain the relation.

Max Karl Ernst Ludwig Planck 1858-1947

German physicist whose work provided the bridge between classical and modern physics. Around 1900 Planck developed a theory explain the nature of



black-body radiation. He proposed that energy is emitted and absorbed in discrete packets or “quanta,” and that these had a definite size — Planck’s constant. Planck’s finding didn’t get much attention until the idea was furthered by Albert Einstein in 1905 and Niels Bohr in 1913. Planck won the Nobel Prize in 1918, and, together with Einstein’s theory of relativity, his quantum theory changed the field of physics.

Albert Einstein 1879-1955

was a German-born theoretical physicist. He is best known for his theory of relativity and specifically mass-energy equivalence, expressed by the equation $E =$



mc^2 . Einstein received the 1921 Nobel Prize in Physics “for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect.”

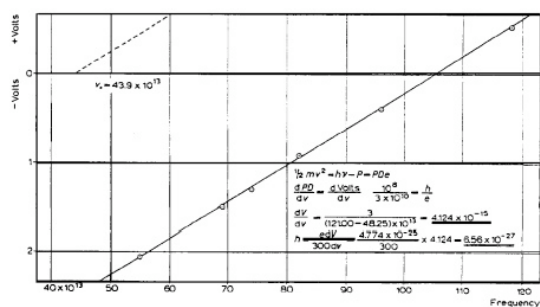


Fig. 4.

Figure 1.2: Measurements of the photoelectric effect taken by Robert Millikan showing the variation of the stopping voltage, eV, with variation of the frequency of incident light. Figure reproduced from Robert A. Millikan's Nobel Lecture, *The Electron and the Light-Quanta from the Experimental Point of View*, The Nobel Foundation, 1923.

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.

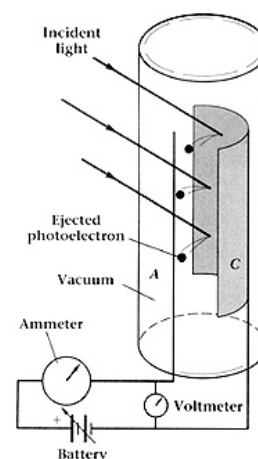
In 1905, Einstein resolved this paradox by describing light as composed of discrete quanta (photons), rather than continuous waves. Based upon Planck's theory of black-body radiation, Einstein theorized that the energy in each quantum of light was proportional to the frequency. A photon above a threshold 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

$$k.e._{\max} = h\nu - W.$$

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 were 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 (see Fig. 1.2), 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



Robert Andrews Millikan 1868-1953

He received his doctorate from Columbia University and taught physics at the University of Chicago (1896-1921) and the California Institute of Technology (from 1921). To measure electric charge, he devised the Millikan oil-drop experiment. He verified Albert Einstein's photoelectric equation and obtained a precise value for the Planck constant. He was awarded the 1923 Nobel Prize in physics.



Arthur Holly Compton 1892-1962:

An American physicist, he shared the 1927 Nobel Prize in Physics with C. T. R. Wilson for his discovery of the Compton effect. In addition to his work on X rays he made valuable studies of cosmic rays and contributed to the development of the atomic bomb.



particle – Thomson scattering – the wavelength of a low-intensity beam should remain unchanged.³

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,⁴

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

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

1.1.4 Atomic spectra

The discovery by Rutherford that the atom was comprised of a small positively charged nucleus surrounded by a diffuse cloud of electrons lead naturally to the consideration of a planetary model of the atom. However, a classical theory of electrodynamics would predict that an accelerating charge would radiate energy leading to the eventual collapse of the electron into the nucleus. Moreover, as the electron spirals inwards, the emission would gradually increase in frequency leading to a broad continuous spectra. Yet, detailed studies of electrical discharges in low-pressure gases revealed that atoms emit light at discrete frequencies.

The clue to resolving these puzzling observations lay in the discrete nature of atomic spectra. For the hydrogen atom, light emitted when the atom is thermally excited has a particular pattern: Balmer had discovered in 1885 that the emitted wavelengths follow the empirical law, $\lambda = \lambda_0(1/4 - 1/n^2)$ where $n = 3, 4, 5, \dots$ and $\lambda_0 = 3645.6 \text{ \AA}$ (see Fig. 1.4). 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 quantized and varying as $E_n = -\frac{hcR_H}{n^2}$, where $R_H = 109678 \text{ cm}^{-1}$ denotes the Rydberg constant.

³Classically, light of sufficient intensity for the electric field to accelerate a charged particle to a relativistic speed will cause radiation-pressure recoil and an associated Doppler shift of the scattered light. But the effect would become arbitrarily small at sufficiently low light intensities regardless of wavelength.

⁴If we assume that the total energy and momentum are conserved in the scattering of a photon (γ) from an initially stationary target electron (e), we have $E_\gamma + E_e = E_{\gamma'} + E_{e'}$ and $\mathbf{p}_\gamma = \mathbf{p}_{\gamma'} + \mathbf{p}_{e'}$. Here $E_\gamma = h\nu$ and $E_e = m_e c^2$ denote the energy of the photon and electron before the collision, while $E_{\gamma'} = h\nu'$ and $E_{e'} = \sqrt{(p_{e'}c)^2 + (m_e c^2)^2}$ denote the energies after. From the equation for energy conservation, one obtains $(p_{e'}c)^2 = (h(\nu - \nu') + m_e c^2)^2 - (m_e c^2)^2$. From the equation for momentum conservation, one obtains $p_{e'}^2 = p_\gamma^2 + p_{\gamma'}^2 - 2|p_\gamma||p_{\gamma'}|\cos\theta$. Then, noting that $E_\gamma = p_\gamma c$, a rearrangement of these equations obtains the Compton scattering formula.

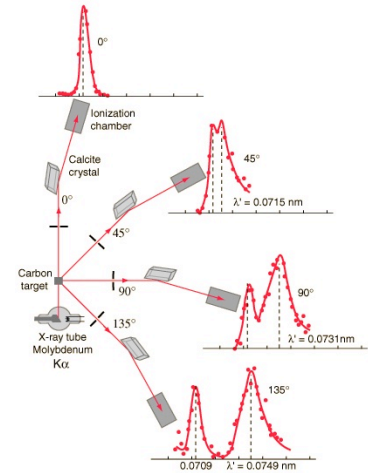
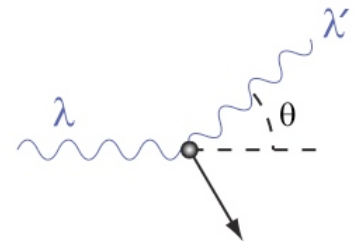


Figure 1.3: Variation of the wavelength of X rays scattered from a Carbon target. A. H. Compton, Phys. Rev. **21**, 483; **22**, 409 (1923)



Ernest Rutherford, 1st Baron Rutherford of Nelson, 1871-1937

was a New Zealand born British chemist and Physicist who became known as the father of nuclear physics. He discovered that atoms have a small charged nucleus, and thereby pioneered the Rutherford model (or planetary model of the atom, through his discovery of Rutherford scattering. He was awarded the Nobel Prize in Chemistry in 1908. He is widely credited as splitting the atom in 1917 and leading the first experiment to "split the nucleus" in a controlled manner by two students under his direction, John Cockcroft and Ernest Walton in 1932.



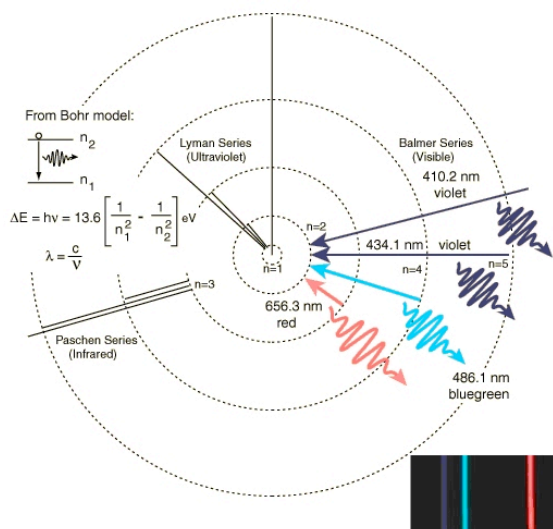


Figure 1.4: Schematic describing various transitions (and an image with the corresponding visible spectral lines) of atomic hydrogen.

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 was quantized in units of Planck's constant,

$$L = m_e v r = n\hbar, \quad \hbar = \frac{h}{2\pi}. \quad (1.2)$$

As a result, one finds that $R_H = \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{2\pi^2 m}{ch^3}$.

▷ EXERCISE. Starting with the Bohr's planetary model for atomic hydrogen, find how the quantization condition (1.2) restricts the radius of the allowed (circular) orbits. Determine the allowed energy levels and obtain the expression for the Rydberg constant above.

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

$$\lambda = \frac{h}{p}, \quad \text{i.e. } p = \hbar k, \quad (1.3)$$

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 (Fig. 1.5) confirmed that the diffraction angles depend on the incident energy (and therefore momentum).

This completes the summary of the pivotal conceptual insights that paved the way towards the development of quantum mechanics.

Niels Henrik David Bohr 1885-1962

A Danish physicist who made fundamental contributions to the understanding of atomic structure and quantum mechanics, for which he received the Nobel Prize in Physics in 1922. Bohr mentored and collaborated with many of the top physicists of the century at his institute in Copenhagen. He was also part of the team of physicists working on the Manhattan Project. Bohr married Margrethe Norlund in 1912, and one of their sons, Aage Niels Bohr, grew up to be an important physicist who, like his father, received the Nobel prize, in 1975.



Louis Victor Pierre Raymond, 7th duc de Broglie 1892-1987

A French physicist, de Broglie had a mind of a theoretician rather than one of an experimenter or engineer. de Broglie's 1924 doctoral thesis *Recherches sur la théorie des quanta* introduced his theory of electron waves. This included the particle-wave property duality theory of matter, based on the work of Einstein and Planck. He won the Nobel Prize in Physics in 1929 for his discovery of the wave nature of electrons, known as the de Broglie hypothesis or *mécanique ondulatoire*.



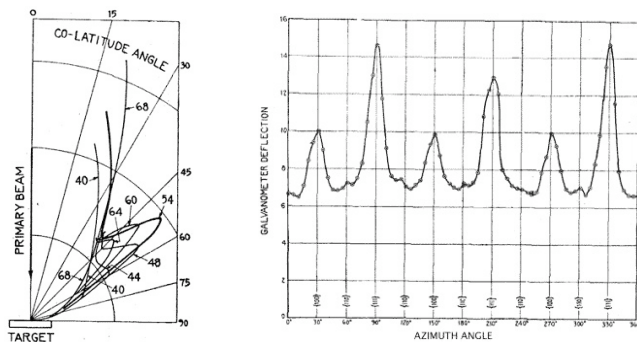


Figure 1.5: In 1927, Davisson and Germer bombarded a single crystal of nickel with a beam of electrons, and observed several beams of scattered electrons that were almost as well defined as the incident beam. The phenomenological similarities with X-ray diffraction were striking, and showed that a wavelength could indeed be associated with the electrons. The first figure shows the intensity of electron scattering against co-latitude angle for various bombarding voltages. The second figure shows the intensity of electron scattering vs. azimuth angle - 54V, co-latitude 50. Figures taken from C. Davisson and L. H. Germer, *Reflection of electrons by a crystal of nickel*, Nature **119**, 558 (1927).

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.

There is no rigorous derivation of Schrödinger's equation from previously established theory, but it can be made very plausible by thinking about the connection between light waves and photons, and constructing an analogous structure for de Broglie's waves and electrons (and, of course, other particles).


1.2.1 Maxwell's wave equation

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

$$\nabla^2 \mathbf{E} - \frac{1}{c^2} \ddot{\mathbf{E}} = 0, \quad (1.4)$$

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, $\ddot{\mathbf{E}} \equiv \partial_t^2 \mathbf{E}$. 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

James Clerk Maxwell 1831-1879
 was a Scottish theoretical physicist and mathematician. His greatest achievement was the development of classical electromagnetic theory, synthesizing all previous unrelated observations of electricity, magnetism and optics into a consistent theory. Maxwell's equations demonstrated that electricity, magnetism and light are all manifestations of electromagnetic field.



particle as $\mathbf{E}_0 e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}$. Then, one may see that the wave equation applied to the plane wave describing particle propagation yields the familiar energy-momentum 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, $E^2 = (c\mathbf{p})^2 + m_0^2 c^4$. Writing the plane wave function $\phi(\mathbf{r}, t) = A e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}$, where A is a constant, we can recover the energy-momentum invariant by adding a constant mass term to the wave operator,

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

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 seems 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 $\Psi(x, t) = A e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}$. We need to construct an operator which, when applied to this wave function, just gives us the ordinary non-relativistic energy-momentum relation, $E = \frac{\mathbf{p}^2}{2m}$. The factor of \mathbf{p}^2 can obviously 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.

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

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 effect 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 Kepler-like 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**

Arnold Johannes Wilhelm Sommerfeld 1868-1951

A German theoretical physicist who pioneered developments in atomic and quantum physics, and also educated and groomed a large number of students for the new era of theoretical physics. He introduced the fine-structure constant into quantum mechanics.



quantization condition

$$\oint p dq = nh, \quad (1.5)$$

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.

▷ EXERCISE. As a challenging exercise, try to prove Sommerfeld's result for the elliptical orbit.

1.2.2 Schrödinger's equation

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

$$i\hbar\partial_t\Psi(x,t) = -\frac{\hbar^2\partial_x^2}{2m}\Psi(x,t) + V(x)\Psi(x,t), \quad (1.6)$$

with the generalization to three-dimensions leading to the Laplacian operator 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, $e^{-iEt/\hbar}$; 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.

1.2.3 Time-independent Schrödinger equation

As with all second order linear differential equations, if the potential $V(x, t) = V(x)$ is time-independent, the time-dependence of the wavefunction can be

Erwin Rudolf Josef Alexander Schrödinger 1887-1961

was an Austrian theoretical physicist who achieved fame for his contributions to quantum mechanics, especially the Schrödinger equation, for which he received the Nobel Prize in 1933. In 1935, after extensive correspondence with personal friend Albert Einstein, he proposed the Schrödinger's cat thought experiment.



separated from the spatial dependence. Setting $\Psi(x, t) = T(t)\psi(x)$, and separating the variables, the Schrödinger equation takes the form,

$$\frac{\left(-\frac{\hbar^2 \partial_x^2}{2m} \psi(x) + V(x)\psi(x)\right)}{\psi(x)} = \frac{i\hbar \partial_t T(t)}{T(t)} = \text{const.} = E.$$

Since we have a function of only x 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 x is then given by the stationary, or **time-independent Schrödinger equation**,

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

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

$$\boxed{\hat{H} = -\frac{\hbar^2 \partial_x^2}{2m} + V(x)}$$

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

1.2.4 Particle flux and conservation of probability

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

$$j(x, t) = -\frac{i\hbar}{2m} [\psi^* \partial_x \psi - \psi \partial_x \psi^*]. \quad (1.7)$$

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

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

$$\boxed{\mathbf{j}(\mathbf{r}, t) = -\frac{i\hbar}{2m} [\psi^*(\mathbf{r}, t) \nabla \psi(\mathbf{r}, t) - \psi(\mathbf{r}, t) \nabla \psi^*(\mathbf{r}, t)]}. \quad (1.8)$$

This completes a survey of the foundations and development of quantum theory. In due course, it will be necessary to develop some more formal mathematical aspects of the quantum theory. However, before doing, it is useful to acquire some intuition for the properties of the Schrödinger equation. Therefore, in the next chapter, we will explore the quantum mechanics of bound and unbound particles in a one-dimensional system turning to discuss more theoretical aspects of the quantum formulation in the following chapter.