

Chapter 2

The Early History of Quantum Mechanics

IN the early years of the twentieth century, Max Planck, Albert Einstein, Louis de Broglie, Neils Bohr, Werner Heisenberg, Erwin Schrödinger, Max Born, Paul Dirac and others created the theory now known as quantum mechanics. The theory was not developed in a strictly logical way – rather, a series of guesses inspired by profound physical insight and a thorough command of new mathematical methods was sewn together to create a theoretical edifice whose predictive power is such that quantum mechanics is considered the most successful theoretical physics construct of the human mind. Roughly speaking the history is as follows:

Planck’s Black Body Theory (1900) One of the major challenges of theoretical physics towards the end of the nineteenth century was to derive an expression for the spectrum of the electromagnetic energy emitted by an object in thermal equilibrium at some temperature T . Such an object is known as a *black body*, so named because it absorbs light of any frequency falling on it. A black body also emits electromagnetic radiation, this being known as black body radiation, and it was a formula for the spectrum of this radiation that was being sort for. One popular candidate for the formula was Wein’s law:

$$S(f, T) = \alpha f^3 e^{-\beta f/T} \quad (2.1)$$

The quantity $S(f, T)$, otherwise known as the *spectral distribution function*, is such that $S(f, T)df$ is the energy contained in unit volume of electromagnetic radiation in thermal equilibrium at an absolute temperature T due to waves of frequency between f and $f + df$. The above expression for S was not so much derived from a more fundamental theory as quite simply guessed. It was a formula that worked well at high frequencies, but was found to fail when improved experimental techniques made it possible to measure S at lower (infrared) frequencies. There was another candidate for S which was derived using arguments from classical physics which lead to a formula for $S(f, T)$ known as the Rayleigh-Jeans formula:

$$S(f, T) = \frac{8\pi f^2}{c^3} k_B T \quad (2.2)$$

where k_B is a constant known as Boltzmann’s constant. This formula worked well at low frequencies, but suffered from a serious problem – it clearly increases without limit with increasing frequency – there is more and more energy in the electromagnetic field at higher and higher frequencies. This amounts to saying that an object at *any* temperature would radiate an infinite

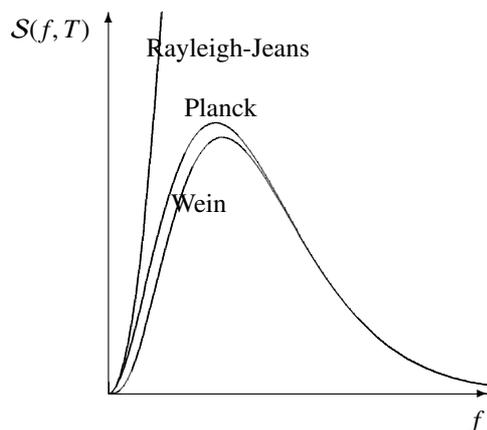


Figure 2.1: Rayleigh-Jeans (classical), Wein, and Planck spectral distributions.

amount of energy at infinitely high frequencies. This result, ultimately to become known as the ‘ultra-violet catastrophe’, is obviously incorrect, and indicates a deep flaw in classical physics.

In an attempt to understand the form of the spectrum of the electromagnetic radiation emitted by a black body, Planck proposed a formula which he obtained by looking for a formula that fitted Wein’s law at high frequencies, and also fitted the new low frequency experimental results (which happen to be given by the Rayleigh-Jeans formula, though Planck was not aware of this). It was when he tried to provide a deeper explanation for the origin of this formula that he made an important discovery whose significance even he did not fully appreciate.

In this derivation, Planck proposed that the atoms making up the black body object absorbed and emitted light of frequency f in multiples of a fundamental unit of energy, or quantum of energy, $E = hf$. On the basis of this assumption, he was able to rederive the formula he had earlier guessed:

$$S(f, T) = \frac{8\pi hf^3}{c^3} \frac{1}{\exp(hf/kT) - 1}. \quad (2.3)$$

This curve did not diverge at high frequencies – there was no ultraviolet catastrophe. Moreover, by fitting this formula to experimental results, he was able to determine the value of the constant h , that is, $h = 6.6218 \times 10^{-34}$ Joule-sec. This constant was soon recognized as a new fundamental constant of nature, and is now known as Planck’s constant.

In later years, as quantum mechanics evolved, it was found that the ratio $h/2\pi$ arose time and again. As a consequence, Dirac introduced a new quantity $\hbar = h/2\pi$, pronounced ‘h-bar’, which is now the constant most commonly encountered. In terms of \hbar , Planck’s formula for the quantum of energy becomes

$$E = hf = (h/2\pi) 2\pi f = \hbar\omega \quad (2.4)$$

where ω is the angular frequency of the light wave.

Einstein’s Light Quanta (1905) Although Planck believed that the rule for the absorption and emission of light in quanta applied only to black body radiation, and was a property of the atoms, rather than the radiation, Einstein saw it as a property of electromagnetic radiation, whether it was black body radiation or of any other origin. In particular, in his work on the photoelectric effect, he proposed that light of frequency ω was made up of quanta or ‘packets’ of energy $\hbar\omega$ which could be only absorbed or emitted in their entirety.

Bohr’s Model of the Hydrogen Atom (1913) Bohr then made use of Einstein’s ideas in an attempt to understand why hydrogen atoms do not self destruct, as they should according to the laws of classical electromagnetic theory. As implied by the Rutherford scattering experiments, a hydrogen atom consists of a positively charged nucleus (a proton) around which circulates a very light (relative to the proton mass) negatively charged particle, an electron. Classical electromagnetism says that as the electron is accelerating in its circular path, it should be radiating away energy in the form of electromagnetic waves, and do so on a time scale of $\sim 10^{-12}$ seconds, during which time the electron would spiral into the proton and the hydrogen atom would cease to exist. This obviously does not occur.

Bohr’s solution was to propose that provided the electron circulates in orbits whose radii r satisfy an ad hoc rule, now known as a quantization condition, applied to the angular momentum L of the electron

$$L = mvr = n\hbar \quad (2.5)$$

where v is the speed of the electron and m its mass, and n a positive integer (now referred to as a *quantum number*), then these orbits would be *stable* – the hydrogen atom was said to be in a stationary state. He could give no physical reason why this should be the case, but on the basis of

this proposal he was able to show that the hydrogen atom could only have energies given by the formula

$$E_n = -\frac{ke^2}{2a_0} \frac{1}{n^2} \quad (2.6)$$

where $k = 1/4\pi\epsilon_0$ and

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.0529 \text{ nm} \quad (2.7)$$

is known as the Bohr radius, and roughly speaking gives an indication of the size of an atom as determined by the rules of quantum mechanics. Later we shall see how an argument based on the uncertainty principle gives a similar result.

The tie-in with Einstein's work came with the further proposal that the hydrogen atom emits or absorbs light quanta by 'jumping' between the energy levels, such that the frequency f of the photon emitted in a downward transition from the stationary state with quantum number n_i to another of lower energy with quantum number n_f would be

$$f = \frac{E_{n_i} - E_{n_f}}{h} = \frac{ke^2}{2a_0h} \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \quad (2.8)$$

Einstein used these ideas of Bohr to rederive the black body spectrum result of Planck. In doing so, he set up the theory of emission and absorption of light quanta, including spontaneous (i.e. 'uncaused' emission) – the first intimation that there were processes occurring at the atomic level that were intrinsically probabilistic. This work also led him to the conclusion that the light quanta were more than packets of energy, but carried momentum in a particular direction – the light quanta were, in fact, particles, subsequently named photons by the chemist Gilbert Lewis.

There was some success in extracting a general method, now known as the 'old' quantum theory, from Bohr's model of the hydrogen atom. But this theory, while quite successful for the hydrogen atom, was an utter failure when applied to even the next most complex atom, the helium atom. The ad hoc character of the assumptions on which it was based gave little clue to the nature of the underlying physics, nor was it a theory that could describe a dynamical system, i.e. one that was evolving in time. Its role seems to have been one of 'breaking the ice', freeing up the attitudes of researchers at that time to old paradigms, and opening up new ways of looking at the physics of the atomic world.

De Broglie's Hypothesis (1924) Inspired by Einstein's picture of light, a form of wave motion, as also behaving in some circumstances as if it was made up of particles, and inspired also by the success of the Bohr model of the hydrogen atom, de Broglie was led, by purely aesthetic arguments to make a radical proposal: if light waves can behave under some circumstances like particles, then by symmetry it is reasonable to suppose that particles such as an electron (or a planet?) can behave like waves. More precisely, if light waves of frequency ω can behave like a collection of particles of energy $E = \hbar\omega$, then by symmetry, a massive particle of energy E , an electron say, should behave under some circumstances like a wave of frequency $\omega = E/\hbar$. But assigning a frequency to these waves is not the end of the story. A wave is also characterised by its wavelength, so it is also necessary to assign a wavelength to these 'matter waves'. For a particle of light, a photon, the wavelength of the associated wave is $\lambda = c/f$ where $f = \omega/2\pi$. So what is it for a massive particle? A possible formula for this wavelength can be obtained by looking a little further at the case of the photon. In Einstein's theory of relativity, a photon is recognized as a particle of zero rest mass, and as such the energy of a photon (moving freely in empty space) is related to its momentum p by $E = pc$. From this it follows that

$$E = \hbar\omega = \hbar 2\pi c/\lambda = pc \quad (2.9)$$

so that, since $\hbar = h/2\pi$

$$p = h/\lambda. \quad (2.10)$$

This equation then gave the wavelength of the photon in terms of its momentum, but it is also an expression that contains nothing that is specific to a photon. So de Broglie assumed that this relationship applied to all *free* particles, whether they were photons or electrons or anything else, and so arrived at the pair of equations

$$f = E/h \quad \lambda = h/p \quad (2.11)$$

which gave the frequency and wavelength of the waves that were to be associated with a free particle of kinetic energy E and momentum p . Strictly speaking, the relativistic expressions for the momentum and energy of a particle of non-zero rest mass ought to be used in these formulae, as these above formulae were derived by making use of results of special relativity. However, here we will be concerned solely with the non-relativistic limit, and so the non-relativistic expressions, $E = \frac{1}{2}mv^2$ and $p = mv$ will suffice¹.

This work constituted de Broglie's PhD thesis. It was a pretty thin affair, a few pages long, and while it was looked upon with some scepticism by the thesis examiners, the power and elegance of his ideas and his results were immediately appreciated by Einstein, more reluctantly by others, and lead ultimately to the discovery of the wave equation by Schrödinger, and the development of wave mechanics as a theory describing the atomic world.

Experimentally, the first evidence of the wave nature of massive particles was seen by Davisson and Germer in 1926 when they fired a beam of electrons of known energy at a nickel crystal in which the nickel atoms are arranged in a regular array. Much to the surprise of the experimenters (who were not looking for any evidence of wave properties of electrons), the electrons reflected off the surface of the crystal to form an interference pattern. The characteristics of this pattern were entirely consistent with the electrons behaving as waves, with a wavelength given by the de Broglie formula, that were reflected by the periodic array of atoms in the crystal (which acted much like slits in a diffraction grating).

An immediate success of de Broglie's hypothesis was that it gave an explanation, of sorts, of the quantization condition $L = n\hbar$. If the electron circulating around the nucleus is associated with a wave of wavelength λ , then for the wave not to destructively interfere with itself, there must be a whole number of waves (see Fig. (2.2)) fitting into one circumference of the orbit, i.e.

$$n\lambda = 2\pi r. \quad (2.12)$$

Using the de Broglie relation $\lambda = h/p$ then gives $L = pr = n\hbar$ which is just Bohr's quantization condition. But now, given that particles can exhibit wave like properties, the natural question that arises is: what is doing the 'waving'? Further, as wave motion is usually describable in terms of some kind of wave equation, it is then also natural to ask what the wave equation is for these de Broglie waves. The latter question turned out to be much easier to answer than the first – these waves satisfy the famous Schrödinger wave equation. But what these waves are is still, largely speaking, an incompletely answered question: are they 'real' waves, as Schrödinger believed, in the sense that they represent some kind of physical vibration in the same way as water or sound or light waves, or are

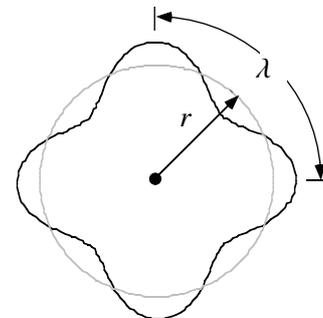


Figure 2.2: De Broglie wave for which four wavelengths λ fit into a circle of radius r .

¹For a particle moving in the presence of a spatially varying potential, momentum is not constant so the wavelength of the waves will also be spatially dependent – much like the way the wavelength of light waves varies as the wave moves through a medium with a spatially dependent refractive index. In that case, the de Broglie recipe is insufficient, and a more general approach is needed – Schrödinger's equation.

they something more abstract, waves carrying information, as Einstein seemed to be the first to intimate. The latter is an interpretation that has been gaining in favour in recent times, a perspective that we can support somewhat by looking at what we can learn about a particle by studying the properties of these waves. It is this topic to which we now turn.