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 failings of classical physics was its inability to correctly predict the spectrum of the electromagnetic radiation emitted by an object in thermal equilibrium at some temperature T, (a black body). Classically this spectrum $\mathcal{S}(f, T)$ could be shown to be given by the formula (the Rayleigh-Jeans formula):

$$\mathcal{S}(f, T) = \frac{8\pi f^2}{c^3} kT. \tag{2.1}$$

This quantity $\mathcal{S}(f, T)df$, otherwise known as the *spectral distribution function* 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 constant k is known as Boltzmann's constant. It clearly increases without limit with increasing frequency – there is more and more energy in the elctromagnetic field at higher and higher frequencies. This amounts to saying that an object at any temperature would radiate an infinite amount of energy at infinitely high frequencies. This result, known as the 'ultra-violet catastrophe', is obviously incorrect, and indicates a deep flaw in classical physics.

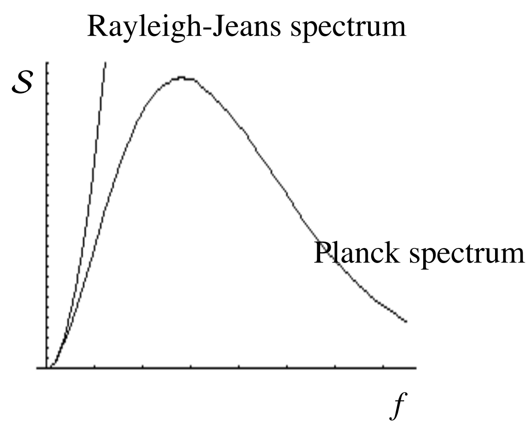

Figure 2.1: Rayleigh-Jeans (classical) and Planck spectral distributions.

In an attempt to understand the form of the spectrum of the electromagnetic radiation emitted by a black body, Planck proposed that the atoms making up the 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 show that the spectral distribution function took the form

$$S(f,T) = \frac{8\pi hf^3}{c^3}\frac{1}{\exp(hf/kT) - 1}. \tag{2.2}$$

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, now known as Planck's constant, was soon recognized as a new fundamental constant of nature.

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

$$E = hf = (h/2\pi)\,2\pi f = \hbar\omega \tag{2.3}$$

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 particles of energy $\hbar\omega$, now known as photons, which could be only absorbed or emitted in their entirety. So light, a form of wave motion, had been given a particle character. Much later, in 1922, the particle nature of light was quite explicitly confirmed in the light scattering experiments of Compton.

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

$$L = mvr = n\hbar \tag{2.4}$$

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

$$E_n = -\frac{ke^2}{2a_0}\frac{1}{n^2} \tag{2.5}$$

where $k = 1/4\pi\epsilon_0$ and $a_0 = \hbar^2/mke^2 = 0.0529$ nm 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, or photons, 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

$$f = \frac{E_{n_i} - E_{n_f}}{h} = \frac{ke^2}{2a_0 h}\Big[\frac{1}{n_f^2} - \frac{1}{n_i^2}\Big]. \tag{2.6}$$

Einstein used these ideas of Bohr to rederive the black body spectrum result of Planck, and set up the theory of photon emission and absorption, including spontaneous (i.e. 'uncaused' emission) – the first intimation that there were processes occurring at the atomic level that were intrinsically probabilistic.

While there was some success in extracting from Bohr's model of the hydrogen atom a general method, now known as the 'old' quantum theory, his 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 lead, by purely aesthetic arguments to make a radical proposal. If light waves of frequency ω can behave under some circumstances 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 a defining characteristic of a wave is its wavelength. For 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? From Einstein's theory of relativity, which showed that the energy of a photon (moving freely in empty space) is related to its momentum p by $E = pc$, it follows that

$$E = \hbar\omega = \hbar\, 2\pi c/\lambda = pc \tag{2.7}$$

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

$$p = h/\lambda. \tag{2.8}$$

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

$$f = E/h \qquad \lambda = h/p \tag{2.9}$$

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 [1].

This work constituted de Broglie's PhD thesis – a pretty thin affair, a few pages long, and Einstein was one of the examiners of the thesis. But 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 a beam of electrons of known energy was fired through a nickel crystal in which the nickel atoms are arranged in a regular array. The result was a diffraction pattern whose characteristics were entirely consistent with the electrons behaving as waves, with a wavelength given by the de Broglie formula, being diffracted by the periodic array of atoms in the crystal (which acted much like a slit 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.

$$n\lambda = 2\pi r. \tag{2.10}$$

Using the de Broglie relation $\lambda = h/p$ then gives $L = pr = n\hbar$ which is just Bohr's quantization condition.

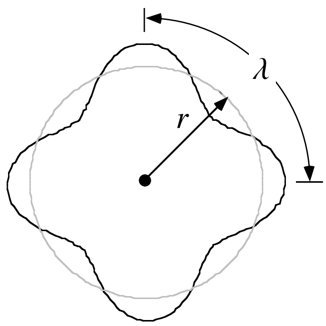

Figure 2.2: De Broglie wave for which four wavelengths λ fit into a circle of radius r.

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'

[1]For 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.

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 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.