PART I

BASICS
Quantum mechanics emerged as a natural extension of classical mechanics. As physics probed into the microscopic realm, it could be argued it would be almost impossible not to discover quantum mechanics. The spectra of atoms, the blackbody spectra, the photoelectric effect and the behaviour of particles through an array of slits had characteristically non-classical features. These phenomena were waiting their time for a theory to explain them. That does not diminish from the huge scientific insights of the founders of the subject. In physics, the great accomplishments come more often than not from insight rather than foresight. Knowing what will be the right physics 50 years into the future is a game of speculation. Recognising what is the important physics in the present and being able to explain it is the work of scientific insight. Thus, whereas we might say Democritus had great foresight millennia ago to envision the discrete nature of particles, it was Albert Einstein, Max Planck, Niels Bohr, Erwin Schrödinger, Werner Heisenberg, Paul Dirac, Max Born and Wolfgang Pauli who had the insights to develop quantum mechanics. And since their foundational work, our understanding of the physical world grew dramatically like never before.

The ideas leading to quantum mechanics started with the realisation that phenomena which up to then were considered wave-like in nature, could also have particle properties and vice versa. In the classical picture, particle properties mean the phenomena have energy and momentum that are localised in space, whereas wave properties mean the energy and momentum are coherently distributed over space. Radiation, which classically was considered to be wave-like, was the first phenomenon to be found to also have a particle nature. This was first noticed in blackbody radiation. In the classical theory, based on a wave description of radiation, the theoretical expectation near the end of the nineteenth century was that at low wavelength, the power per unit area radiated by a blackbody became infinite, the Rayleigh–Jeans law. This was in contradiction to experiment, which found the power spectrum to go to zero. In what might be the most significant curve fit in the history of physics, in 1900 Planck observed that he could arrive at a function that explained the observed blackbody spectrum, but it required the energy of the radiation to take discrete values. In particular, at a given wavelength $\lambda$, the energy needed to take values $E_\lambda = 0, 2\epsilon, \ldots, n\epsilon, \ldots$, where $\epsilon = h c / \lambda$. Planck introduced the proportionality constant $\hbar$ between energy $\epsilon$ and wavelength $\lambda$, thus necessarily the dimensions of angular momentum, which is now known as Planck’s constant. The value of Planck’s constant, $\hbar = 6.626196 \times 10^{-27}$ erg s,
sets the typical scale of quantum phenomena. The rationalised Planck’s constant is defined as

\[ \hbar = h/(2\pi). \]

Planck attempted to reconcile this strange functional form that he had obtained with classical physics but achieved limited success.

The full realisation that light possesses a dual particle-like property came in 1905 by Einstein. It was known from experiments by then that when light strikes a clean metal surface, electrons get emitted. Increasing the intensity of the light increased in proportion the number of electrons emitted, but the kinetic energy of the electrons would remain the same, contrary to classical expectation. Einstein applied the Planck blackbody results to assert that quantisation of light was an inherent property. His picture was that light was made up of discrete quanta of energy, using Planck’s expression, \[ E = \frac{hc}{\lambda}. \] The idea that radiation was composed of particles was further confirmed in 1923 by Arthur Compton in studies of electrons scattered by radiation, where he concluded that the scattering process could easily be explained as a scattering between the electron with another particle of energy \( h\nu \), where \( \nu \) is the frequency of the radiation. In other words, as if the radiation has particles of this quanta of energy.

The classical picture of radiation also posed a problem for atoms. By 1913, experiments by Ernest Rutherford had established the structure of atoms as having a very tiny nucleus of positively charged particles. Niels Bohr, who had been working in the Rutherford laboratory at the time of his exciting discoveries, suggested the picture of the electrons as orbiting around this nucleus, bound to it by electrostatic attraction. In this classical picture, as the electrons are orbiting, as such accelerating, they are radiating energy. In such a picture the electron orbit should diminish as its energy goes into radiation, and within a fraction of a second the electron should spiral into the nucleus. Bohr showed in 1913 how this dilemma could be resolved by postulating that electrons only move in certain stable orbits of certain energy where they don’t radiate, and in jumping between orbits they radiate energy equal to the difference between the energies of the two levels. Within this classical picture for an electron moving in a circular orbit at distance \( r \) from the nucleus

\[ E = -\frac{Ze^2}{2r}. \]  

Thus the energy radiated by the atom as the electron moves from an orbit \( r_i \) to an orbit \( r_f \) under Bohr’s assumption is

\[ E_{\text{radiated}} = E_i - E_f = -\frac{Ze^2}{2} \left( \frac{1}{r_i} - \frac{1}{r_f} \right). \]

Bohr argued his quantisation ideas in a few different ways, but perhaps the most far-reaching was his postulate that the angular momentum of the electron in the atom is quantised:

\[ mvr = \frac{nh}{2\pi}. \]
where \( n \) is an integer and \( h \) is Planck’s constant. From this expression was implied

\[
E_{\text{radiated}} = \frac{2\pi^2 Z^2 m e^4}{c h^3} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right). \tag{1.4}
\]

A few years later, in 1916, Sommerfeld and Wilson developed a generalised quantisation rule that the integral of a dynamical variable over its conjugate variable around a cycle had to be equal to an integer of the Planck constant. This could be applied for example to angular momentum as the dynamical variable, leading to angular momentum quantisation or momentum and position, leading to energy quantisation. The work on radiation and the Bohr atom constituted what has come to be called the old quantum mechanics. This was an attempt at patching up experimental results within what was still believed to be an underlying classical picture of nature.

With the idea of radiation, which classically had been pictured as wave-like, successfully demonstrating particle-like properties, in 1924 Louis de Broglie suggested that perhaps matter, in particular electrons, which classically were pictured as particles, possess dual wave-like properties. He postulated that an electron of energy \( E \) and momentum \( p \) has a wavelength associated with it of

\[
\lambda = \frac{h}{p} \tag{1.5}
\]

and frequency

\[
f = \frac{E}{h}. \tag{1.6}
\]

A cursory examination of de Broglie’s idea might suggest that it was a simple-minded guess and he just happened to be lucky enough to be right. This view might be further supported by the fact that de Broglie had completed his university studies in history with plans for a career in the civil service, to then go back and study science. This interpretation of de Broglie’s work is in fact misleading. What is less well remembered is that Louis de Broglie had a physicist older brother, Maurice de Broglie, who was an experimental physicist studying X-rays, a research area at the cutting edge of the then developing quantum mechanics. Maurice helped initiate his brother’s interest in physics, including sharing certain prevailing views advocated by W. H. Bragg, that X-rays display characteristics that are both wave- and particle-like. Louis had considerable knowledge of Maurice’s views and had an in-depth understanding of the developments underway in physics at the time. Louis was by no means just an outsider who made a good guess. He had studied deeply the issues and views of his time, and it was more than a decade after he entered his studies in science that he came forth with his ideas on the wave nature of particles.

Verification of these properties was confirmed in 1927 in experiments on diffraction of electrons in crystals by Davisson and Germer and thin films by G. P. Thomson (Davisson and Thomson shared the 1937 Nobel Prize for discovering these wave properties of electrons). This was 31 years after J. J. Thomson, G. P.’s father, was awarded the Nobel Prize for discovering the electron as a particle. (An example from physics why children should not always listen to their parents!) This timeline may suggest a tidy picture of theoretical insight followed by experimental verification, but reality in physics is seldom
so clean. In fact, experiments on electron beams through material had been done for many years previously, displaying evidence of their wave-like property. In particular, Davisson’s experiments on electron scattering dated back before 1920, with results indicating patterns akin to diffraction. But these results needed proper interpretation, which seemed only to come once a compelling theoretical perspective was put forth.

De Broglie’s ideas that a wave is associated with a particle led to the expectation that there must be an equation that governs the wave. It was Schrödinger who arrived at the equation for such waves, which now is called the Schrödinger equation. There were other attempts at obtaining such a wave equation, notably by Peter Debye and separately Erwin Madelung, but they all failed in one way or another and are forgotten to the mainstream history on physics. Schrödinger was motivated by de Broglie’s interpretation of the Sommerfeld quantisation condition that this can be viewed as the number of wavelengths which cover the exact orbit of the electron around the nucleus. To Schrödinger, this looked like an eigenvalue problem, which he was familiar with from his early work in continuous media. Schrödinger’s key step was to replace in the Hamilton equation for classical mechanics

$$H \left( \psi, \frac{\partial S}{\partial q} \right) = E \quad (1.7)$$

by $k \ln \psi$, with $\psi$ the wave function. He imposed the conditions on this wave function that it must be real, single-valued and twice continuously differentiable. The reality condition he subsequently relinquished in deriving what now is called the time-dependent Schrödinger equation.

The question that perplexed physicists initially was what exactly does this wave function $\psi$ represent. In particular, did this wave function represent a single particle or a beam of particles? If it were representing a beam of particles, then the resulting diffraction patterns that were observed could be argued as some kind of collective effect.

When just a single particle goes through a diffraction apparatus, such as an array of slits, and deposits its signature on the observation screen, in any single case the individual particle appears to leave the diffractive apparatus in a random fashion. However, when carried out many times, each time with a single particle through the diffraction apparatus, the result from all those cases is the screen showing an interference pattern. Such an experiment implies that the wave property attached to the particle applies to a single particle and that it has a probabilistic meaning. It was Max Born who, in 1926 (he was at Göttingen at the time but later became part of the faculty at Edinburgh), first put forth the probabilistic interpretation of the wave function. At that time, experiments to this level of sophistication were not available. In fact, even the wave nature of matter was not entirely on an experimental footing. Born was guided by his work on applying Schrödinger’s wave function to the scattering of particles. He was trying to find an interpretation for his quantum scattering ideas. He liked the particle interpretation of scattering. The only way he could see to adhere to this picture and reconcile it with the Schrödinger wave function was to assert a probability interpretation of the wave function. Thus, he arrived at the conclusion that when particles scatter at the quantum level, one cannot ascribe a definite prediction where the particle will go but simply predict probabilities for the different occurrences.
The Schrödinger approach to quantum mechanics is now the one most commonly used. But in fact a year before Schrödinger discovered his equation, it was Heisenberg who had formulated his matrix approach to quantum mechanics. It was from this line of development that the formal underlying mathematical structure of quantum mechanics started to be understood. Heisenberg’s work led in 1926 to the paper by Born and Pascual Jordan and then the famous paper by Born, Heisenberg and Jordan, which were the first to set out a logical mathematical foundation for quantum mechanics based on the matrix approach. Subsequently Schrödinger, and separately Pauli, showed that the wave and matrix approaches were in fact equivalent. The final phase in the development of quantum mechanics was the formalisation of ideas. Up to even the end of the 1920s quantum mechanics was a collection of ideas with different equations seeming to work for different physical situations. What was missing was a formal understanding of the mathematical structure of the theory. It is in fact this work at the final phases that has since been the main point explained and studied in the many textbooks of quantum mechanics written from then to now. Several people were involved in this step of formalising the theory, including of course Schrödinger and Heisenberg but also Born, Pauli and Paul Dirac and most notably Jordan, David Hilbert and John von Neumann. The culmination of this work by the end of the 1920s was the formulation of quantum mechanics in Hilbert space with the concepts of representation and transformation.

Further Reading
