18.2: Brief summary of the origins of quantum theory

The last decade of the 19^{th} century saw the culmination of classical physics. By 1900 scientists thought that the basic laws of mechanics, electromagnetism, and statistical mechanics were understood and worried that future physics would be reduced to confirming theories to the fifth decimal place, with few major new discoveries to be made. However, technical developments such as photography, vacuum pumps, induction coil, etc., led to important discoveries that revolutionized physics and toppled classical mechanics from its throne at the beginning of the 20^{th} century. Table $18.2.1$ summarizes some of the major milestones leading up to the development of quantum mechanics.

Max Planck searched for an explanation of the spectral shape of the black-body electromagnetic radiation. He found an interpolation between two conflicting theories, one that reproduced the short wavelength behavior, and the other the long wavelength behavior. Planck's interpolation required assuming that electromagnetic radiation was not emitted with a continuous range of energies, but that electromagnetic radiation is emitted in discrete bundles of energy called quanta. In December 1900 he presented his theory which reproduced precisely the measured black body spectral distribution by assuming that the energy carried by a single quantum must be an integer multiple of $h\nu$:

$$E = h\nu = \frac{hc}{\lambda} \tag{18.2.1}$$

where ν is the frequency of the electromagnetic radiation and Planck's constant, $h = 6.62610^{-34}\ \ J \cdot s$ was the best fit parameter of the interpolation. That is, Planck assumed that energy comes in discrete bundles of energy equal to $h\nu$ which are called quanta. By making this extreme assumption, in an act of desperation, Planck was able to reproduce the experimental black body radiation spectrum. The assumption that energy was exchanged in bundles hinted that the classical laws of physics were inadequate in the microscopic domain. The older generation physicists initially refused to believe Planck's hypothesis which underlies quantum theory. It was the new generation physicists, like Einstein, Bohr, Heisenberg, Born, Schrödinger, and Dirac, who developed Planck's hypothesis leading to the revolutionary quantum theory.

In 1905, Einstein predicted the existence of the photon, derived the theory of specific heat, as well as deriving the Theory of Special Relativity. It is remarkable to realize that he developed these three revolutionary theories in one year, when he was only 26 years old. Einstein uncovered an inconsistency in Planck's derivation of the black body spectral distribution in that it assumed the statistical part of the energy is quantized, whereas the electromagnetic radiation assumed Maxwell's equations with oscillator energies being continuous. Planck demanded that light of frequency ν be packaged in quanta whose energies were multiples of $h\nu$, but Planck never thought that light would have particle-like behavior. Newton believed that light involved corpuscles, and Hamilton developed the Hamilton-Jacobi theory seeking to describe light in terms of the corpuscle theory. However, Maxwell had convinced physicists that light was a wave phenomena; interference plus diffraction effects were convincing manifestations of the wave-like properties of light. In order to reproduce Planck's prediction, Einstein had to treat black-body radiation as if it consisted of a gas of photons, each photon having energy $E = h\nu$. This was a revolutionary concept that returned to Newton's corpuscle theory of light. Einstein realized that there were direct tests of his photon hypothesis, one of which is the photo-electric effect. According to Einstein, each photon has an energy $E = h\nu$, in contrast to the classical case where the energy of the photoelectron depends on the intensity of the light. Einstein predicted that the ejected electron will have a kinetic energy

$$KE = h\nu - W \tag{18.2.2}$$

where W is the work function which is the energy needed to remove an electron from a solid.

Many older scientists, including Planck, accepted Einstein's theory of relativity but were skeptical of the photon concept, even after Einstein's photon concept was vindicated in 1915 by Millikan who showed that, as predicted, the energy of the ejected photoelectron depended on the frequency, and not intensity, of the light. In 1923 Compton's demonstrated that electromagnetic radiation scattered by free electrons obeyed simple two-body scattering laws which finally convinced the many skeptics of the existence of the photon.

Table 18.2.1: Chronology of the development of quantum mechanics

Date	Author	Development
1887	Hertz	Discovered the photo-electric effect
1895	Röntgen	Discovered x-rays

Date	Author	Development
1896	Becquerel	Discovered radioactivity
1897	J.J. Thomson	Discovered the first fundamental particle, the electron
1898	Pierre & Marie Curie	Showed that thorium is radioactive which founded nuclear physics
1900	Planck	Quantization $E = h\nu$ explained the black-body spectrum
1905	Einstein	Theory of special relativity
1905	Einstein	Predicted the existence of the photon
1906	Einstein	Used Planck's constant to explain specific heats of solids
1909	Millikan	The oil drop experiment measured the charge on the electron
1911	Rutherford	Discovered the atomic nucleus with radius $10^{-15}\ m$
1912	Bohr	Bohr model of the atom explained the quantized states of hydrogen
1914	Moseley	X-ray spectra determined the atomic number of the elements.
1915	Millikan	Used the photo-electric effect to confirm the photon hypothesis.
1915	Wilson-Sommerfeld	Proposed quantization of the action-angle integral
1921	Stern-Gerlach	Observed space quantization in non-uniform magnetic field
1923	Compton	Compton scattering of x-rays confirmed the photon hypothesis
1924	de Broglie	Postulated wave-particle duality for matter and EM waves
1924	Bohr	Explicit statement of the correspondence principle
1925	Pauli	Postulated the exclusion principle
1925	Goudsmit-Uhlenbeck	Postulated the spin of the electron of $s = \frac{1}{2}\hbar$
1925	Heisenberg	Matrix mechanics representation of quantum theory
1925	Dirac	Related Poisson brackets and commutation relations
1926	Schrödinger	Wave mechanics
1927	G.P. Thomson/Davisson	Electron diffraction proved wave nature of electron

Date	Author	Development
1928	Dirac	Developed the Dirac relativistic wave equation

Bohr model of the atom

The Rutherford scattering experiment, performed at Manchester in 1911, discovered that the Au atom comprised a positively charge nucleus of radius $\approx 10^{-14}\ m$ which is much smaller than the $1.35\times 10^{-10}\ m$ radius of the Au atom. Stimulated by this discovery, Niels Bohr joined Rutherford at Manchester in 1912 where he developed the Bohr model of the atom. This theory was remarkably successful in spite of having serious inconsistencies and deficiencies. Bohr's model assumptions were:

1. Electromagnetic radiation is quantized with $E = h\nu$.
2. Electromagnetic radiation exhibits behavior characteristic of the emission of photons with energy $E = h\nu$ and momentum $p = \frac{h\nu}{c}$. That is, it exhibits both wave-like and particle-like behavior.
3. Electrons are in stationary orbits that do not radiate, which contradicts the predictions of classical electromagnetism.
4. The orbits are quantized such that the electron angular momentum is an integer multiple of $\frac{h}{2\pi} = \hbar$.
5. Atomic electromagnetic radiation is emitted with photon energy equal to the difference in binding energy between the two atomic levels involved. $h\nu = E_1 - E_2$

The first two assumptions are due to Planck and Einstein, while the last three were made by Niels Bohr.

The deficiencies of the Bohr model were the philosophical problems of violating the tenets of classical physics in explaining hydrogen-like atoms, that is, the theory was prescriptive, not deductive. The Bohr model was based implicitly on the assumption that quantum theory contains classical mechanics as a limiting case. Bohr explicitly stated this assumption which he called the **correspondence principle**, and which played a pivotal role in the development of the older quantum theory. In 1924 Bohr justified the inconsistencies of the old quantum theory by writing "As frequently emphasized, these principles, although they are formulated by the help of classical conceptions, are to be regarded purely as laws of quantum theory, which give us, not withstanding the formal nature of quantum theory, a hope in the future of a consistent theory, which at the same time reproduces the characteristic features of quantum theory, important for its applicability, and, nevertheless, can be regarded as a rational generalization of classical electrodynamics."

The old quantum theory was remarkably successful in reproducing the black-body spectrum, specific heats of solids, the hydrogen atom, and the periodic table of the elements. Unfortunately, from a methodological point of view, the theory was a hodgepodge of hypotheses, principles, theorems, and computational recipes, rather than a logical consistent theory. Every problem was first solved in terms of classical mechanics, and then would pass through a mysterious quantization procedure involving the correspondence principle. Although built on the foundation of classical mechanics, it required Bohr's hypotheses which violated the laws of classical mechanics and predictions of Maxwell's equations.

Quantization

By 1912 Planck, and others, had abandoned the concept that quantum theory was a branch of classical mechanics, and were searching to see if classical mechanics was a special case of a more general quantum physics, or quantum physics was a science altogether outside of classical mechanics. Also they were trying to find a consistent and rational reason for quantization to replace the ad hoc assumption of Bohr.

In 1912 Sommerfeld proposed that, in every elementary process, the atom gains or loses a definite amount of action between times t_0 and t of

$$S = \int_{t_0}^{t} L(t')dt' \tag{18.2.3}$$

where S is the quantal analogue of the classical action function. It has been shown that the classical principle of least action states that the action function is stationary for small variations of the trajectory. In 1915 Wilson and Sommerfeld recognized that the quantization of angular momentum could be expressed in terms of the action-angle integral, that is equation $(15.5.1)$. They postulated that, for every coordinate, the action-angle variable is quantized

$$\oint p_k dq_k = nh \tag{18.2.4}$$

where the action-angle variable integral is over one complete period of the motion. That is, they postulated that Hamilton's phase space is quantized, but the microscopic granularity is such that the quantization is only manifest for atomic-sized domains. That is, n is a small integer for atomic systems in contrast to $n \approx 10^{64}$ for the Earth-Sun two-body system.

Sommerfeld recognized that quantization of more than one degree of freedom is needed to obtain a more accurate description of the hydrogen atom. Sommerfeld reproduced the experimental data by assuming quantization of the three degrees of freedom,

$$\oint p_r dr = n_1 h \quad \oint p_\theta d\theta = n_2 h \quad \oint p_\phi d\phi = n_3 h \tag{18.2.5}$$

and solving Hamilton-Jacobi theory by separation of variables. In 1916 the Bohr-Sommerfeld model solved the classical orbits for the hydrogen atom, including relativistic corrections as described in example $17.7.1$. This reproduced fine structure observed in the optical spectra of hydrogen. The use of the canonical transformation to action-angle variables proved to be the ideal approach for solving many such problems in quantum mechanics. In 1921, Stern and Gerlach demonstrated space quantization by observing the splitting of atomic beams deflected by non-uniform magnetic fields. This result was a major triumph for quantum theory. Sommerfeld declared that "With their bold experimental method, Stern and Gerlach demonstrated not only the existence of space quantization, they also proved the atomic nature of the magnetic moment, its quantum-theoretic origin, and its relation to the atomic structure of electricity."

In 1925, Pauli's Exclusion Principle proposed that no more than one electron can have identical quantum numbers and that the atomic electronic state is specified by four quantum numbers. Two students, Goudsmit and Uhlenbeck suggested that a fourth two-valued quantum number was the electron spin of $\pm\frac{\hbar}{2}$. This provided a plausible explanation for the structure of multi-electron atoms.

Wave-particle duality

In his 1924 doctoral thesis, Prince Louis de Broglie proposed the hypothesis of wave-particle duality which was a pivotal development in quantum theory. de Broglie used the classical concept of a matter wavepacket, analogous to classical wave packets discussed in chapter 3.11. He assumed that both the group and signal velocities of a matter wave packet must equal the velocity of the corresponding particle. By analogy with Einstein's relation for the photon, and using the Theory of Special Relativity, de Broglie assumed that

$$\hbar\omega = E = \frac{mc^2}{\sqrt{\left(1-\frac{v^2}{c^2}\right)}} \tag{18.2.6}$$

The group velocity is required to equal the velocity of the mass

$$v_{group} = \left(\frac{d\omega}{dk}\right) = \left(\frac{d\omega}{dv}\right)\left(\frac{dv}{dk}\right) = v \tag{18.2.7}$$

This gives

$$\frac{dk}{dv} = \frac{1}{v}\left(\frac{d\omega}{dv}\right) = \left(\frac{m}{\hbar}\right)\left(1-\frac{v^2}{c^2}\right)^{-\frac{3}{2}} \tag{18.2.8}$$

Integration of this equation assuming that $k=0$ when $v=0$, then gives

$$\hbar\mathbf{k} = \frac{m\mathbf{v}}{\sqrt{\left(1-\frac{\mathbf{v}\cdot\mathbf{v}}{c^2}\right)}} = \mathbf{p} \tag{18.2.9}$$

This relation, derived by de Broglie, is required to ensure that the particle travels at the group velocity of the wave packet characterizing the particle. Note that although the relations used to characterize the matter waves are purely classical, the physical content of such waves is beyond classical physics. In 1927 C. Davisson and G.P. Thomson independently observed electron diffraction confirming wave/particle duality for the electron. Ironically, J.J. Thomson discovered that the electron was a particle, whereas his son attributed it to an electron wave.

Heisenberg developed the modern matrix formulation of quantum theory in 1925; he was 24 years old at the time. A few months later Schrödinger's developed wave mechanics based on de Broglie's concept of wave-particle duality. The matrix mechanics, and wave mechanics, quantum theories are radically different. Heisenberg's algebraic approach employs non-commuting quantities and unfamiliar mathematical techniques that emphasized the discreteness characteristic of the corpuscle aspect. In contrast, Schrödinger used the familiar analytical approach that is an extension of classical laws of motion and waves which stressed the element of continuity.