Chapter 16

QUANTUM MECHANICS

"Those who are not shocked when they first come across quantum theory cannot possibly have understood it."

Niels Bohr

"I think I can safely say that nobody understands quantum mechanics."

Richard Feynman

Empirical Refinements of Bohr's model

Bohr's achievement in 1913 was remarkable, but his theory was by no means complete. It did not account, for instance, for the fact that some spectral lines are brighter than others; nor could it be applied to more complex atoms.

Bohr tried for many years to develop a mathematical theory for helium, which has the second simplest atom (a nucleus and two electrons). When more than one electron is involved, the situation becomes much more complicated because, in addition to the attractive forces between the positive nucleus and the electrons, one must consider the repulsive forces among the negative electrons.

In the years that followed Bohr's discovery, physicists extended his theory, in order to account for various features of atomic spectra. Defining the "state" of an electron became more complicated than specifying one of a number of concentric circular orbits, all on the same plane.

Whereas a single "quantum number" had sufficed for Bohr's theory, four quantum numbers, eventually, had to be used. Three were associated with the size, shape and orientation of the allowed electronic orbits, which could be circular or elliptical. The fourth quantum number was associated with a spinning motion of the electron about its axis.

Quantum numbers were assigned to the electron using rules that were discovered empirically. What was lacking was a sound mathematical foundation.

Einstein's Statistics of Electron Excitation

In 1916, after he completed his General Theory of Relativity, Einstein turned his attention again to quantum theory. He used statistical techniques and Bohr's model of the atom to study the behavior of huge numbers of atoms. According to Bohr, in a hot gas, as countless atoms constantly collide with one another, electrons are excited to higher energy levels; later, they fall back to lower levels and emit radiation (photons).

Einstein's statistical approach could explain why some spectral lines are brighter than others, the reason being that some transitions between energy states are more likely to happen than others.

After Maxwell, reality seemed to consist of empty space populated by two totally different kinds of "things": particles and waves. Particles were thought of as being point-like and having such properties as energy, momentum, mass and, possibly, an electrical charge. Waves, on the other hand, were thought of as being spread out in space, and having such properties as energy, amplitude, frequency, wavelength and speed of propagation.

In 1905, Einstein upset this sharp distinction. As we saw, he proposed that light - whose wave-like nature had been accepted after Young's 2-slit experiment - could be emitted or absorbed only as discrete quanta of energy. In 1909, he started talking of "point-like" quanta or massless particles, later called photons.

Einstein's statistical calculations of how matter absorbs or emits radiation explained how momentum could be transferred from a photon to an electron. It was necessary, however, to assume that each photon carried with it a momentum which was proportional to frequency.

Momentum had been considered before to be a particle-like property, normally expressed as mass x velocity. The massless photon was seen now as something that had both a particle-like property (momentum) and a wave-like property (frequency).

Prince de Broglie

In 1924, while still a graduate student in physics, a French nobleman, Louis de Broglie (pronounced de Broy), proposed a brilliantly bold conjecture. If light waves can behave like particles, why shouldn't particles, such as electrons, behave like waves? Why couldn't an electron be a wave?

Prince de Broglie was born in 1892 in one of Europe's most aristocratic families. For centuries, his family had contributed diplomats, cabinet ministers and generals. After he entered the University of Paris in 1910, inspired by his brother, who was a physicist, he developed an interest in physics and in Einstein's work. His idea of a wave/particle duality became the basis of the doctoral thesis he submitted in 1924.

De Broglie proposed that electrons as well as photons have associated with them both a momentum and a wavelength[6]. He could not say what was the physical significance of an electron's wavelength, but he could show an interesting connection between it and Bohr's orbits. The circular orbits that were allowed in Bohr's theory turned out to be those that could contain exactly a whole number of wavelengths.

Even for a doctoral thesis, de Broglie's proposal was too original to be comfortably accepted by the examiners without any experimental support. A copy of the thesis was sent to Einstein, who commented "It may look crazy, but it really is sound". (Years later, shortly before his death, commenting about some controversial new theory, Bohr remarked that the theory was certainly crazy, but wondered whether it was crazy enough to have merit.)

In 1927, confirmation of de Broglie's electron wave was provided by experiments performed by Clinton Davisson at Bell Telephone Laboratories in New York. In 1929, de Broglie became the first to receive a Nobel Prize for a doctoral thesis.

In 1937, Davisson shared the Nobel Prize with George Thomson, who independently had found confirmation for the electron wave. Interestingly, in 1906, J.J. Thomson had received the Nobel Prize for proving that electrons are particles; 31 years later, his son received the Nobel Prize for proving that electrons are waves! The reader may be totally mystified by the idea of a "particle" behaving like a "wave", but so was de Broglie who proposed the idea, and so were the physicists of his day.

QUANTUM MECHANICS

At the beginning of 1925, the quantum theory that started with Bohr in 1913 was still a hodgepodge of hypotheses and cookbook rules. In the 12 months following June 1925, quantum theory finally gained a firm mathematical footing.

Not one but two theories emerged, independently of one another. Although their approaches seemed at first sharply different, the two theories were later proved to be equivalent aspects of a single theory. Now called "quantum mechanics", this combined theory was the creation of a new generation of physicists, mostly born since Planck's discovery of the quantum. Their youth made them scientific revolutionaries willing to break away from classical physics. Bohr was the undisputed guiding spirit of this extraordinary development, and Copenhagen became its center.

The Gottingen Trio

The first of the two mathematical theories was developed by three German

[6] For light or, more generally, electromagnetic waves, we can talk in terms of either frequency or wavelength because the product wavelength x frequency is a constant, the speed of light c.

physicists at the University of Gottingen: Werner Heisenberg (1901-1976), Max Born (1882-1970), and Pascual Jordan (1902-1980).

Heisenberg, who was at the time a research assistant to Max Born, proposed a radical reinterpretation of the basic concepts of mechanics with regard to atomic particles. The new approach was guided by the principle that a physical theory is obligated to consider only those things that can actually be observed. There is no way of observing directly an electron orbiting around the nucleus of an atom. What can be observed are spectral lines, which are interpreted in terms of electrons jumping from one energy level to another.

The notion of tiny balls in orbits is a convenient mental image that is superimposed on the actual observations, because that is how we see things moving in our everyday world. In developing his theory, Heisenberg was willing to abandon convenient analogies and mental images, and to follow a totally abstract approach.

The breakthrough came in June of 1925 while he was recovering from a severe attack of hay fever on a North Sea island. There, away from distractions, he was able to concentrate on the new ideas that were forming in his mind. Within three months, the collaboration of Heisenberg, Born and Jordan resulted in the publication of a comprehensive paper.

Schrodinger's Equation

Only months later, Erwin Schrodinger (Austrian, 1887-1961) published a different mathematical theory he had developed independently of the Gottingen group. He had been inspired by Einstein's support of de Broglie's theory. Unlike the Gottingen group, he was guided by mental images of atoms with electrons as waves.

Before long, the two theories were proved to be fully equivalent. Being much simpler to use, Schrodinger's equation became the preferred mathematical tool of quantum mechanics to solve atomic problems. The equation gave a very good account of the spectrum of the hydrogen atom in a way that was mathematically consistent. But even for the very simple case of hydrogen, the mathematics involved is very difficult. To convey just a flavor of this complex theory, it will suffice to summarize the results as follows.

Each allowed "state" of the electron is some configuration identified by a particular set of values for three "quantum numbers" n, l (the letter l) and m. These are whole numbers related by simple rules, which stem directly from the equation.

For the hydrogen atom, Schrodinger obtained energy levels that are the same as Bohr's and depend only on the quantum number n. Except for n=1, however, more than one state is associated with the same energy level, see **Figure 16.1**.

For each state (i.e., for each set of values for the three quantum numbers n, l and m), instead of a circular orbit, Schrodinger's equation yields a so-called "orbital", a mathematical expression that is unique to that state. There is a single orbital for the lowest energy level (n=1). As Figure 16.1 shows, the number of orbitals increases with the energy level.

Usually called a "wave function," [7] an orbital describes a standing wave of some particular shape. What is the significance of this "wave"? In Schrodinger's view, the electron was not a particle but a wave. Instead of having its entire mass and charge concentrated at some point, the electron would have that same mass and charge smeared over some region of space. The density of mass or the density of charge at any point would be proportional to the square of the amplitude of the wave at that point.

This interpretation, however, is not consistent with the fact that, whenever an electron is observed, it always comes as a whole lump with a fixed charge and a fixed mass.

Born's Probability Interpretation

To Schrodinger's wave amplitude, Max Born gave a radically different interpretation, which has become one of the cornerstones of quantum mechanics.

He proposed that the square of the "wave function" at some point is a measure, not of a mass density or charge density, but of the *probability* of detecting the electron, if we were looking for it at that point. In this interpretation, nothing will be found at that point most of the time, but when something is detected there, it will be a whole electron.

Schrodinger's wave function does not tell us where the electron is at any given moment, only what is the probability of its being at various places, depending on its energy level. The electron could be anywhere: it is extremely likely to be in some places, and very unlikely to be in others.

The probability is highest in the immediate vicinity of the nucleus; it becomes inconsequentially small even at moderate distances. For instance, the probability of the electron being farther than about 5 hundredmillionths of a centimeter from the nucleus is 1 in 30,000. The more energy the electron has, the higher the probability that it will be found at greater distances from the nucleus. Each orbital is a particular pattern of how the probability of detecting the electron varies from point to point.

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[7]. In mathematics, the term "function" is used to refer to a mathematical formula, which states how some variable quantity depends on one or more other variables, such as time or position.

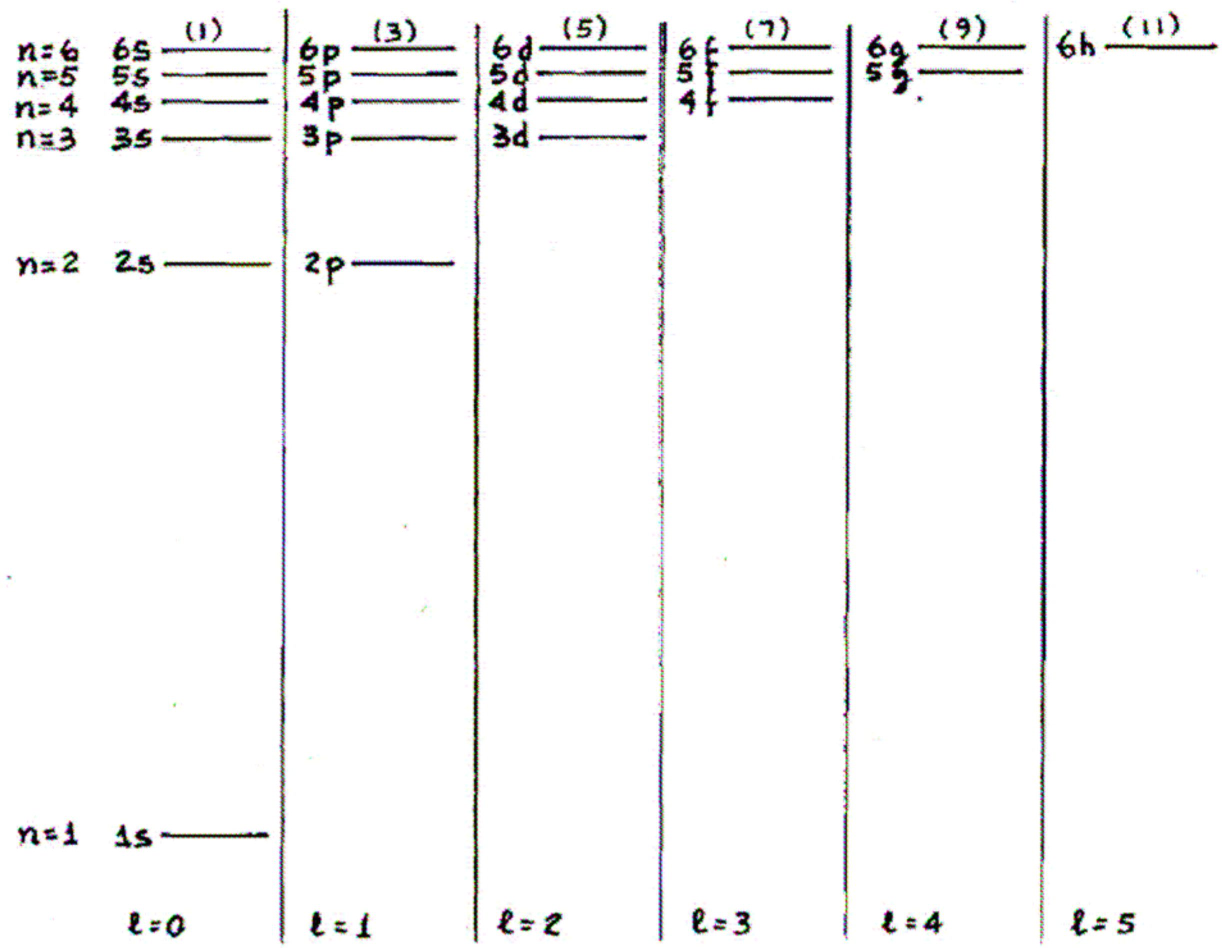

Figure 16.1 - Energy level diagram for hydrogen in Schrodinger's model

As shown above, for n=1, we have a single state possible, called the "1s" state.

For n=2, we have a single "2s" state, and three "2p" states; the latter are represented by the single line labeled "2p".

As a final example, for n=3, we have a single "3s" state, three "3p" states, and five "3d" states, for a total of 9 states.

Note that the interpretation of atomic behavior is still based on a ladder of energy levels, although the ladder is no longer as simple as the one we first saw for Bohr's model of the hydrogen atom. Electrons climbing up or down the ladder still account for the absorption or emission of radiation at discrete frequencies.

Schrodinger's equation can be applied not only to an electron bound within an atom, but, more generally, to a free electron, a photon, a proton, or any of the many “quantum entities” (particles) that have been discovered. A particular "wave function" is associated with a quantum entity. This mathematical expression describes a so-called "psi" wave, which may be a standing or traveling wave. It is not, however, an ordinary wave because it does not carry any energy. The square of its amplitude at some point in space represents the probability that the quantum entity will be detected, if we look for it there.

Except for not carrying energy, "psi" waves behave like ordinary waves. In particular, they can interfere with one another. When two or more waves are involved, they are first combined in the usual interference fashion, and then the square of the resulting amplitude is computed. The peculiar, but very important, result is that combining "psi" waves may result in diminished or even canceled probabilities.

The role of probability is the great divide that separates quantum mechanics from all preceding theories of physics. Newtonian mechanics was deterministic: given the position and velocity of a particle at some point in time, and given the forces acting on the particle, its path for all past and future times can be completely determined, at least in principle. The motion of the planets around the Sun provides a classical example.

Quantum mechanics, on the other hand, asserts that it is possible to predict only the probabilities of events. Instead of predicting a specific path for a particle, it gives a distribution of probabilities of where the particle might be.

Heisenberg's Uncertainty Principle

Another major blow to classical physics was delivered by Heisenberg in 1927 with his famous *Uncertainty Principle*, which he derived from the fundamental equations of quantum mechanics.

He was the first to point out that the laws of quantum mechanics imply a fundamental limitation to the accuracy of experimental measurements. This limitation has nothing to do with any flaw in the design of the experiment one might perform, or of the instruments one might use. It reflects a fundamental aspect of reality itself.

Heisenberg's uncertainty principle states that it is not possible to measure simultaneously the momentum (mass x velocity) and the position of a particle with whatever accuracy we might wish.

There is always some error or uncertainty associated with any measurement of position, and also some uncertainty associated with any measurement of momentum. What Heisenberg discovered is that these two uncertainties are unavoidably linked together. The more accurately we try to measure the position of an electron, the more uncertain becomes our knowledge of its momentum, and vice versa. In standard centimeter-gram-second units, Heisenberg's principle states that

(uncertainty in position) x (uncertainty in momentum)
must be larger than, or equal to about one billion-billion-billionth.

Note that, if one uncertainty is very small, the other must be large enough for the product of the two uncertainties to be larger than, or equal to, the very small number above.

Because of this very small value, the uncertainty principle affects only the submicroscopic world. When masses and distances have ordinary values, the quantum theory and the classical theory give results that are essentially identical. It is only with masses in the order of the electron mass, and distances in the order of atomic distances that we cannot neglect quantum effects.

Heisenberg illustrated the uncertainty principle by analyzing how we might go about to determine the position of an electron. To do so very accurately, it is necessary to use light with a very short wavelength. But a very short wavelength means a very high frequency, which in turn, by Planck's law, means a very large energy quantum.

Shining a light of very high frequency on a particle amounts to bombarding the particle with high-energy photons, which are going to deliver a very large kick, changing the particle's momentum by an indeterminate amount. Unavoidably, we have disrupted the very conditions we were trying to measure.

Conversely, if we want to know the momentum very accurately, we must use light that will deliver a very small kick, which means low frequency, long wavelength and, consequently, a large uncertainty in the measurement of position.

Dirac

In 1928, the most complete mathematical formulation of quantum mechanics was developed by the English theoretical physicist Paul Dirac (1902-1984), who shared in 1933 the Nobel Prize with Schrodinger.

Shy and withdrawn since childhood, Dirac became notoriously reserved as an adult. He seldom spoke and, when he did, chose his words with utmost care. He preferred to work alone. His favorite pastime was solitary walks. At the age of 30, he was appointed to the chair of mathematics at Cambridge, which had been occupied by Newton. His achievements are considered comparable to those of Newton, Maxwell and Einstein.

To arrive at his equation, Schrodinger had not taken into account Einstein's Special Theory of Relativity, which comes into play because of the very high speed of particles. Later, he and others tried to take relativity into account, but with meaningless results. Dirac succeeded using a very ingenious method. His mathematical solution showed that, in addition to the three quantum numbers n, l and m of Schrodinger's equation, an electron requires a fourth quantum number, which had been introduced earlier, but only on empirical grounds. This fourth quantum number is associated with a spinning motion of the electron about its axis, in either direction. It has only two values, which are called at times "spin up" and "spin down".

Quantum Mechanics and the Periodic Table

One of the many achievements of quantum mechanics was its ability to account, at least qualitatively, for many features of the periodic table of chemical elements. It can account, for instance, for how the number of elements varies from one row of the periodic table to another. (As shown at the end of Chapter 5, the numbers of elements in the 7 rows are: 2, 8, 8, 18, 18, 32 and 20). That these numbers differ has to do with how the number of energy states increases with the quantum number n.

The theory can also explain why elements in the same column of the periodic table have similar properties. Such elements have the same number of electrons outside an outermost "shell" in the atom, even though they have different numbers of electrons inside this "shell". It is the equal number of outlying electrons that is mainly responsible for the similarity of properties for elements in the same column.

With its ability to explain the chemical behavior of atoms, quantum mechanics achieved the unification of the previously distinct fields of physics and chemistry.