Chapter 5
The Electron and Atomic Structure

Particles attract one another by some force, which in immediate contact is exceedingly strong, at small distances performs the chemical operations, and reaches not far from the particles with any sensible effect.
(Isaac Newton, Query 31, Opticks)

5.1 Birth of the Electron

In the nineteenth century, chemists and physicists had a completely different image of electricity. The chemists, in contact with a discontinuous and discrete world made of atoms and molecules that they handled and combined together at will in their laboratories, conceived electricity as made of charges indissolubly bound to matter and responsible for the affinities binding together the atoms in the molecules. Volta's pile, which at first appeared to be just an instrument to break molecules into pieces, soon led to a new theoretical paradigm. The Arrhenius theory of electrolytic dissociation had in fact clearly proved that even the electrical charges of ions occurred in a discrete and discontinuous form, and in 1873 Maxwell had shown that the cations all carried a positive electrical charge, always a multiple of the same quantity, and that the same situation occurred for anions but with negative charges. The fact that ions carried a "definite quantity" of electrical charge had been reinforced by von Helmholtz in a famous *Faraday Lecture* held on 5 April 1881 at the Chemical Society in London (Helmholtz 1881):

> Thus established, Faraday's law tells us that through each section of an electrolytic conductor we have always equivalent electrical and chemical motion. The same definite quantity of either positive or negative electricity moves always with each univalent ion, or with each unit of affinity of a multivalent ion, and accompanies it during all its motions through the interior of the electrolytic fluid. This quantity we may call the electric charge of the atom.

However, the proposition that electricity could consist of particles looked like heresy to the physicists, used to discussing the phenomena of electrical conduction

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in terms of a continuous fluid and to master abstract concepts as waves, fields, and potentials. At the end of the century, the idea of the corpuscular nature of electricity had, however, already entered the physics world through the study of electrical discharges in rarefied gases at low pressure, a phenomenon known for some time and normally presented to show the properties of electricity in elegant soirées to ladies and gentlemen. This physical effect was discovered in 1838 by Michael Faraday who found that a flux of electrical current is observed by applying a potential difference of thousands of volts to the metallic electrodes of a void glass tube.

In 1855, Heinrich Geissler (1814–1879), a glass blower who possessed a private building laboratory for physical instruments in Bonn, invented the mercury displacement pump able to achieve sufficiently high vacuum in glass tubes. In 1858 Julius Plucker (1801–1868), professor of physics at Bonn, used Geissler's pump to produce the vacuum in a glass tube equipped with electrodes at each end. He noticed that when sufficient potential was applied to the electrodes, a greenish luminescence occurred at the cathode extending in the tube as the pressure decreased and observed that it could be shifted along the tube by means of a magnet (Plucker 1858). In 1869, Johann Wilhelm Hittorf (1824–1914), a pupil of Plucker who contributed from 1853 to 1859 to the study of electrolytic conduction, concluded that during the electrical discharge in rarefied gases some rays of unknown nature, that he named cathode rays, were emitted from the cathode and proceeded along a straight line toward the anode, giving rise to an intense fluorescence on the glass in the anodic region (Hittorf 1869).

For several years the nature of the cathode rays remained unknown. Several physicists continued to believe that they were of a wave nature until in 1879 the English chemist and spectroscopist William Crookes (1832–1919) performed a series of experiments with magnetic fields, concluding that they were made of negatively charged particles that he called "molecules" (Crookes 1879a, b).

If the cathode rays were charged particles, they should feel the effect of an electric field. New experiments made by the German physicist Heinrich Hertz (1857–1894) did not, however, confirm this hypothesis. By letting the cathode rays go through an electric field created by two metallic plates inserted in the tube, he noticed that these were not deflected as expected for charged particles. Furthermore, Hertz (Hertz 1892) proved in 1892 that one could not stop the fluorescence in the anodic region by inserting a thin metallic foil in the beam's path inside the tube, a fact that seemed incomprehensible if the beams were made of particles. Hertz's research was continued (Lénárd 1893) by his assistant Philipp Eduard Anton von Lénárd (1862–1947), a fervent Nazi and a violent anti-Semite, who in 1905 obtained the Nobel Prize in physics for his research on the cathode beams. Lénárd constructed a glass tube with a thin metallic foil soldered at one end and showed that not only did it hold the vacuum well but also that the cathode rays went easily through, a fact inconceivable for a physicist of the time if these were solid objects such as particles (Lénárd 1894). Even Eugen Goldstein, who in 1886 performed a series of experiments on cathode rays, was convinced that they were of a wave nature.

The particle-wave nature of cathode rays was also the object of the research of the Italian physicist Augusto Righi (1850–1920), professor of physics at the University of Bologna, who studied the trajectories followed by the cathode rays (Righi 1890) using an electrometer to measure their negative charge (Righi 1896). The fact that the cathode rays were made of particles with a negative charge was, however, definitively proved by the French physicist Jean-Baptiste Perrin (1870–1942), Nobel Prize in physics in 1926, who used a cathode tube in which the rays, crossing a metallic cylinder with a thin slit, charged an electroscope (Perrin 1897).

In 1897, Joseph John Thomson (1856–1940), professor of physics at the Cavendish Laboratory of Cambridge, took up the study of the mysterious cathode rays. At the beginning of his experiments, Thomson was convinced that the cathode rays were corpuscles made of fragments of atoms. Later, however, he considered the cathode rays as vortices of ether, the support that the electromagnetic theory envisaged at that time for wave propagation.

Thomson devoted himself for some times to the theoretical treatment of the dynamics of vortices (Thomson 1883, 1885), influenced by an old hypothesis of Helmholtz on atomic structure. The possibility that the atoms were vortices of ether was also maintained by his friend and roommate at Cambridge, Joseph Larmor (1857–1942).

If the cathode rays consisted of charged particles they should necessarily feel the presence of a magnetic field. The argument in favor of the particle hypothesis was, however, in contrast with the Hertz-Lénárd experiments that seemed to support the opposite idea, namely, that cathode rays were not deflected by electric fields.

Since a moving charged particle is not affected by the presence of an electric field only when located inside a metallic conductor, the only possible explanation for the Hertz experiment was that the residual gas molecules left in the tube, once ionized by the cathode rays, formed an electric shield. Pushing to the maximum the vacuum inside the tube, Thomson succeeded in proving that this hypothesis was correct and that at very high vacuum, when the shielding effect due to the residual molecules was reduced and eventually vanished, deviation of the cathode rays from the straight path occurred regularly.

By studying their deviation in both electric and magnetic fields, Thomson finally succeeded in computing the ratio e/m between the charge and the mass of the cathode rays, particles that he continued to call "corpuscles." He proved that the mass was about 1/1,000 the mass of the hydrogen atom. On 30 April 1897, at the Royal Institution theater in London, J.J. Thomson told a selected audience of ladies and gentlemen that he had discovered a particle 1,000 times smaller than an atom. As Thomson wrote (Thomson 1897):

> Could anything at first sight seem more impractical than a body which is so small that its mass is an insignificant fraction of the mass of an atom of hydrogen?

In 1881, George Johnstone Stoney (1826–1911) suggested the name *electron* for these negatively charged particles and that was soon accepted (Stoney 1881). From that moment, the electron entered the scientific world as the first-known elementary particle and as a basic constituent of matter.

At that point it was evident that if electrical discharges were able to extract negative particles from the atoms of a gas, an equivalent number of positive particles had to be produced. The existence of these particles was discovered in 1886 by Eugen Goldstein (1850–1931), pupil of Von Helmholtz at the Potsdam Observatory in Berlin. Goldstein presented his experiments on these strange rays, that he named *Kanalstrahlen* (canal rays), in several papers published in the Monatsberichte of the Berliner Academy of Sciences (Goldstein 1876, 1880, 1886). It was, however, Wilhelm Wien (1864–1928) who in 1898 proved that the canal rays were made of positively charged particles with a mass of the same dimension as that of the hydrogen atom (Wien 1898). The instrument devised by Wien to study these particles was the origin of the mass spectrograph, an instrument that later became one of the most powerful for the study of the composition of molecules.

In 1907, J.J. Thomson returned to the Wien experiments, improving the instrument, and measuring the ratio e/m for the particles H^+ and H_2^+ (Thomson 1907b). Finally, Lord Rutherford in 1919 continued with his pupil Aston the experiments of Wien and Thomson, proving that the mass of these particles was a thousand times larger than that of the electron.

5.2 Models of the Atom

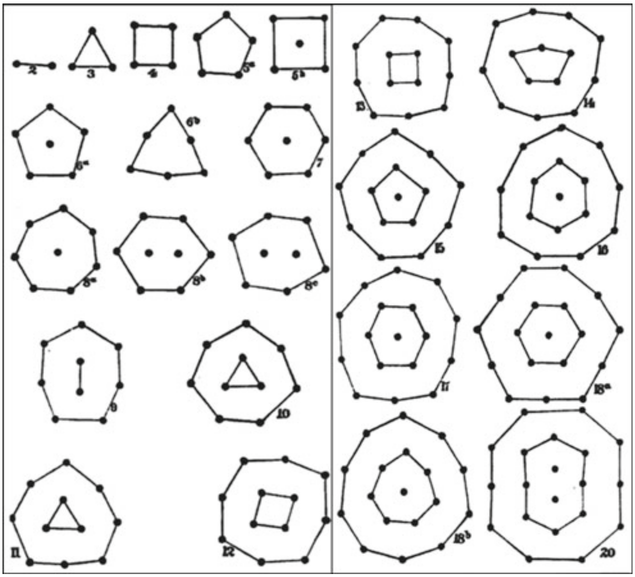
The discovery of the electron represented a fundamental step in the development of the structure of matter. The indivisible atom of the Greek philosophers, whose existence had given rise to so many discussions and controversies during the nineteenth century, was now known to be made of particles of dimension smaller than that of the atom and, in addition, they were electrically charged. Electricity, long considered as a continuous fluid, now acquired a particle structure and the interaction between opposite charges became the basic interaction in the interpretation of atomic structure. Soon, models of the atom started to flourish, filling the scientific literature. A model of the atom had been already proposed in 1867, before the discovery of the electron, by Lord Kelvin (William Thomson) taking up an old paper of Helmholtz on the dynamics of vortices (Helmholtz 1858). Helmholtz's idea was that filaments of an ideal incompressible and nonviscous fluid, rolled up in the form of rings in vortex motion, would be stable and last to infinity. Of course in air and water, which are nonideal fluids, the vortices are rapidly dissolved. Ether, however, was considered a true ideal fluid and therefore vortices in the ether could possess an infinite life – nothing better for resuming the old Prout's theory on primordial matter.

Lord Kelvin started to become interested in vortices after having assisted to a lecture by his friend Peter Tait. Peter Guthrie Tait (1831–1901), professor of physics at the University of Edinburgh, was a mathematical physicist who, in addition to developing quaternion physics, had worked for long time on the vortex theory (Tait 1877, 1884, 1885). In order to prove experimentally the validity of Helmholtz's vortex theory, he even built a machine made of two receivers, each equipped with a rubber diaphragm that once compressed produced beautiful smoke rings in vortex rotation in air. These rings behaved as if made of rubber: colliding with one another they would bounce without breaking and if one tried to break them with a knife they would simply roll up around the blade. Lord Kelvin was enthused with the idea of the vortices and in the period 1867–1900 published a series of papers on the matter. Since he had always been an adversary of atoms as material objects, he ventured with great enthusiasm to represent them as vortices in the ether (Thomson 1869, 1875).

The vortices theory of the atom had a short life but the fact that a scientist of the stature of Lord Kelvin had adopted it and also that Maxwell, even without believing it without doubt, had considered it as "a marvelous example of creative interaction between mathematics and physics" excited the interest of several mathematicians especially in England, leading to important developments in hydrodynamic theory. In 1902, however, Lord Kelvin completely abandoned the idea of the vortices and proposed a new model that regarded the atom as made of a positive charge balanced by a negative one. In this model, Lord Kelvin took up again the ideas developed more than a century before by Franz Maria Ulrich Theodosius Aepinus (1724–1802), a German physicist and astronomer at the court of Catherine the Great in Russia, who in a treatise of 1759 had been the first to connect electricity and magnetism, developing a theory of the electrical fluid made of very small immaterial particles filling the space. According to him, matter was made of particles permeated by the electric fluid and of particles free of it (Aepinus 1759). Particles filled with electric fluid would repel each other but would be attracted by those free of fluid with which they would easily associate (Thomson 1901, 1902):

> According to the well-known doctrine of Aepinus, commonly referred to as the one-fluid theory of electricity, positive and negative electrifications consist in excess above, and deficiency below, a natural quantum of a fluid, called the electric fluid, permeating among the atoms of ponderable matter. Portions of matter void of the electric fluid repel one another; portions of the electric fluid repel one another; portions of the electric fluid and of void matter attract one another. My suggestion is that the Aepinus' fluid consists of exceedingly minute equal and similar atoms, which I call electrions, much smaller than the atoms of ponderable matter; and that they permeate freely through the spaces occupied by these greater atoms and also freely through space not occupied by them.

Lord Kelvin's idea of atoms balancing positive and negative charges was accepted by J.J. Thomson (Thomson 1904). Thomson's model was made of a sphere of uniform positive charge of the dimension of the atom in which the electrons were inserted as seeds in a watermelon or as raisins in a *plum-pudding*, the typical English Christmas cake. The electrons occupied equilibrium positions stabilized by the balance between their repulsion and by the attractive interaction with that part of positive charge internal to their position. Up to a given number, the electrons were disposed on a plane and for greater numbers on ring structures. In this pudding of positive charge, the electrons would oscillate with fixed frequencies around their equilibrium positions, emitting or absorbing the spectral lines characteristic of the atoms. Thomson concluded on the basis of complex calculations that few electrons would form triangular, tetrahedral, etc., structures, whereas after eight electrons concentric structures would be formed. In 1878, the American Alfred Marshall Mayer (1836–1897) of the University of Maryland, in the attempt to prove how atoms were organized in the molecules, had the idea of immersing in a water container a series of magnetized needles mounted upon corks, with their south poles upward. Hanging at the center of the receiver a powerful steel magnet with its north pole oriented toward them (Mayer 1878), he discovered that the needles were arranged in concentric circles forming regular structures. Three magnets would form a triangle and four would arrange themselves at the corners of a square. Five either formed a square with one magnet in the center, or arranged themselves into a pentagon. Six would form a pentagon with one in the center, or arrange themselves three on a side in the form of an equilateral triangle. Seven magnets would form a hexagon with a magnet at the centre and eight magnets would be arranged either in the form of a hexagon with two magnets at the center or alternatively of a heptagon with a center magnet. For higher combinations of nine or more needles, represented in the figure below, Mayer discovered that the configurations of the floating magnets may be divided into primary, secondary, tertiary, etc., classes, and that the stable configurations of a lower class form the basis of the succeeding ones. When there are two or more forms of arrangement, some are more stable than others, and only the most stable would survive in higher classes.



Mayer's picture of the arrangement of the magnetized needles

From 9 to 18 magnets the stable configuration had 2 central magnets and 2 concentric rings. From 19 magnets on, 3 concentric rings were formed and for a larger numbers 4, 5, and so on rings would be formed. In 1897, J.J. Thomson had considered the Mayer picture very appealing, pointing out the close resemblance with the periodic table of the elements and using Mayer's organization of magnets to build his atomic model in the framework of the Mendeleev periodic system (Thomson 1897).

In the same year, 1904, the Japanese Hantaro Nagaoka (1865–1961), professor of physics at the University of Tokyo, developed a planetary model of the atom of the type of the planet Saturn, namely, a structure made of a heavy central nucleus of positive charge surrounded by a ring of electrons orbiting around it.

The model predicted that the electron ring should be stabilized by the relatively large mass of the nucleus (Nagaoka 1904):

> The system, which I am going to discuss, consists of a large number of particles of equal mass arranged in a circle at equal angular intervals and repelling each other with forces inversely proportional to the square of distance; at the centre of the circle, place a particle of large mass attracting the other particles according to the same law of force. If these repelling particles be revolving with nearly the same velocity about the attracting centre, the system will generally remain stable for small disturbances, provided the attracting force is sufficiently great. The system differs from the Saturnian system considered by Maxwell in having repelling particles instead of attracting satellites.

This prediction, although supported by Lord Rutherford, was soon recognized to be physically incorrect since a ring of negative charges would be very unstable due to the disruptive repulsion of the electrons and was in fact abandoned by Nagaoka himself in 1908.

Thomson's atomic model also had a short life. It was not well thought of by the chemistry community of the time, which could not easily accept the idea that such a huge dissymmetry could occur between the negative charge condensed in very small particles, the electron, and the positive charge uniformly spread in a volume many orders of magnitude larger. However, even after the speech of Helmholtz at the London Chemical Society, the physicists were now convinced of this kind of corpuscular structure of electricity.

In that period of time the most important center of atomic physics was the Cavendish Laboratory of Cambridge where two great physicists, John William Strutt (Lord Rayleigh) (1842–1919) and Joseph John Thomson, had created the basis of the new atomic physics. It was a pupil of Thomson, Ernest Rutherford, who invented the crucial experiment that marked the end of the *plum-pudding* model and paved the way to the modern theory of the atom. Ernest Rutherford (1871–1937), from a Scottish family and educated in New Zealand, having obtained his degree, went in 1894, thanks to a fellowship, to work in Thomson's laboratory at Cambridge and started research on the electric discharge in rarefied gases. He soon showed great experimental ability coupled with an uncommon imagination, developing clever instruments to study the mechanism by which strong electric fields or intense electromagnetic radiation such as x-rays could ionize the gas molecules in a discharge tube.

With the discovery of Becquerel rays in 1896, his research oriented toward the study of radioactivity. Rutherford's activity in this field is extensively discussed in the following chapter, whereas here we shall concentrate on his contribution to the field of atomic structure. In 1909, he proved that the Becquerel's radiation emitted by radioactive materials was made of two types of particles, α rays that are ionized helium nuclei and β rays that are very fast electrons (Rutherford and Royds 1909):

> These experiments show that the uranium radiation is complex, and that there are present at least two distinct types of radiation – one that is very readily absorbed, which will be termed for convenience the α radiation, and the other of a more penetrative character, which will be termed the ß radiation.

At the end of the century, Rutherford's research was already recognized to be of a very high level, in particular by his master Thomson who wanted to keep him in Cambridge. The rules at Cambridge were, however, very strict and offered little hope that a stable university position could be found in the available time. An interesting opportunity was, however, offered to him when a position of full professor was made available at the McDonald Laboratory of the McGill University of Montreal in Canada. Rutherford decided to accept this offer and in 1898 left for the new position. He stayed in Canada until 1907 when he returned to England to become professor of physics at the University of Manchester. There he remained until 1919, when he took over from Sir Joseph Thomson as *Cavendish Professor* of physics at Cambridge.

When in 1907 Rutherford moved to Manchester, a young German physicist, Johannes Wilhelm (Hans) Geiger (1882–1945) went to work with him, starting a collaboration that lasted until 1912 and gave rise in 1908 to the identification of the α particles as ionized helium atoms and in 1911 to the development of the first instrument to count their number. This instrument, that later became the famous Geiger counter, used in its earlier version a screen covered by zinc sulfide that sparkled when hit by a particle.

In 1909, Rutherford asked Geiger to investigate a phenomenon that he had noticed when working at the McGill University in Canada (Rutherford and Royds 1909), namely, that a beam of α particles was broadened by traversing a thin mica foil and suggested to Geiger that he count the number of α particles diffused by metallic foils as a function of the diffusion angle.

Geiger, who was in charge of orienting young students toward research, told Rutherford that a new student, Ernest Marsden (1889–1970) was, according to him, ready to start research and Rutherford asked him to study just the problem of the diffusion of the α particles. Geiger and Marsden started to work together using thin foils of aluminum, iron, gold, and lead of different thicknesses and even very thin overlapping foils of gold. The result of their experiments was that, while the majority of the α particles easily crossed the metallic foils with slight deviation from the straight path, once in a while one of them would come back as having bumped against a solid wall. This result seemed absolutely inconceivable within the framework of Thomson's model: it was like a cannon ball shot against paper foil coming back!

Geiger and Marsden published in 1909 the result of their experiment without even attempting to supply an explanation for this strange behavior (Geiger and Marsden 1909). Rutherford, thought it through for 2 years, until he grasped the right solution that he presented at the March 7 1911 meeting of the *Literary and*

Philosophical Society of Manchester in the form of a short note in which he concluded that the only possible explanation for the Geiger and Marsden results was to assume that both the positive charge and the atomic mass were localized in a volume much smaller than the total volume of the atom, a volume that he named atomic nucleus.

On the basis of this new hypothesis, the majority of α particles was able to cross the metallic foils without encountering obstacles of dimensions such as to disturb their path. Only a very small fraction of them would, however, follow a path sufficiently close to a nucleus to feel its repulsion and to be deflected by a small angle. Finally, a very small number of α particles, of the order of about 1 every 8,000, would follow a path leading to a collision with a nucleus and thus to a deflection of 90° or more, in very few cases even close to about 180°. By measuring the fraction of α particles deflected by large angles, Rutherford was able to estimate the nuclear dimension, obtaining a value for the nuclear radius about 1,000 times smaller than that of the atom, i.e., of the order of 10^{-13} cm. Rutherford's atom was then essentially empty and the real dimensions of the atom were determined only by the orbits of the electrons distributed around the nucleus. The new model of the atomic structure which definitively eliminated Thomson's model was published the same year in a paper that is today considered as one of the classics of the scientific literature (Rutherford 1911):

> In comparing the theory outlined in this paper with the experimental results, it has been supposed that the atom consists of a central charge supposed concentrated at a point, and that the large single deflexions of the α and ß particles are mainly due to their passage through the strong central field.

In this paper, Rutherford developed in detail the theory of the diffusion of the α particles by collision with a metallic sheet, obtaining the result that the number of particles diffused at a given angle depend on the thickness of the metallic sheet, on the square of the nuclear charge, and on the inverse fourth power of the particles' speed. Geiger and Marsden verified experimentally (Geiger and Marsden 1913) Rutherford's conclusions in 1913. In the same period of time Charles Galton Darwin (1887–1962), a student of Rutherford, highly gifted as theoretician and mathematician, of noble academic origin as the son of the mathematician George Howard Darwin and grandson of the great Charles Darwin, also worked on the theory of the diffusion of the α particles (Darwin 1914a) contributing in particular to evaluate their slowing down due to the shielding effect of the external electrons of the atoms and proving that the gradual energy loss of an α particle travelling through a metallic foil depended on the number of electrons that it encountered on its path (Darwin 1914b).

5.3 The Old Quantum Theory

During the autumn of 1911, the Danish physicist Niels Bohr (1885–1962), thanks to a fellowship of the Carlsberg foundation, reached Cambridge from Copenhagen, where he had obtained his degree with a thesis on the electronic theory of metals.

He wanted to visit the laboratory directed by J.J. Thomson, intending, among other things, to discuss with him some errors that he had noticed reading Thomson's treatise *Conduction of Electricity through Gases*. Thomson, who not only was very effervescent as director of the laboratory, but had no enthusiasm for discussing his own errors, did his best to avoid the discussion and limited his intervention to assigning him an experiment on canal rays. Bohr found this of very limited interest so he spent most of his time writing a paper on the electrons in metals and playing football.

In December, Rutherford visited Cambridge to attend the ritual dinner of the end of the year and met Bohr with whom he enjoyed a pleasant evening. They met again in Manchester and after a short while Bohr decided to join Rutherford's group at Manchester. There Bohr had long discussions with Darwin concerning the role of the external electrons in slowing down and reducing the energy of α particles, a problem of considerable interest to him since he was just working on the distribution of electrons in atoms. Bohr made several suggestions to Darwin and helped him correct and improve the paper on the argument that he later published.

In July 1912, Bohr returned to Copenhagen where he started teaching, in the meantime writing down what he had seen and done at Manchester. He soon realized that the interpretation in terms of classical mechanics of Rutherford's atomic model, using a structure of electricity made of charged particles, corresponded to a planetary model of the atom in which the electrons orbited around the nucleus as the planets orbited around the sun. For a physicist, an atomic model with a positive central nucleus around which the electrons rotated was undoubtedly fascinating and presented a nice parallelism between the infinitely big and the infinitely small worlds, between electrons and planets, both forced to move in fixed orbits by the deterministic laws of classical dynamics. This model, although highly appealing, presented, however, an insurmountable difficulty, being in strong contrast with Maxwell's electromagnetic theory that dictates that an electric charge in motion in an orbit, being subjected to an acceleration, must continuously radiate energy. The atom then, losing energy, would be unstable and after an extremely short time the electron would fall in on the nucleus.

Rutherford, who was aware of the limits of the planetary model for electrically charged particles, had actually avoided in his 1911 paper to speak of orbits, specifying that in his model the atom consisted of a positively charged nucleus surrounded by a uniform distribution of negative charges.

The problem of assigning the electron to specific orbits was instead tackled by Niels Bohr in a famous series of three papers (Bohr 1913a, b, c), which soon become the basis of the whole of modern spectroscopy.

The first paper was limited to the simplest case of the hydrogen atom, one proton and one electron, whereas the two following ones extended the treatment to many electron atoms.

In these papers, Niels Bohr made a brilliant attempt to save the determinism of classical mechanics, bound to the concept of orbit, by conciliating electron dynamics with electromagnetism on the basis of a hypothesis made by Max Planck in 1900. Planck had supposed, to explain blackbody radiation, that the radiation could not be emitted or absorbed in a continuous process but only by discrete amounts that he named light quanta, thus giving rise to the theory known today as the old quantum theory. Using this quantum hypothesis he developed a new atomic model in which the electrons preserved their classical motion in circular orbits but their energy possessed only discrete values, defined by two conditions known as the quantization conditions.

The first of these conditions radically changed the mechanism of classical electromagnetism at the microscopic level, dictating that the energy difference between two orbits was equal to a multiple of the quantity hν, where *h* is a constant introduced by Planck and ν is the frequency of the radiation emitted or absorbed in the transition between two discrete orbits. Bohr defined this first quantization condition on the basis of a discussion with his friend and former classmate, the spectroscopist Hans Marius Hansen (1886–1956), who told him of the existence of the Balmer equation that Bohr had ignored.

The Swiss Johann Jacob Balmer (1825–1898), teacher of mathematics in a girls' school in Basel and passionate about numerology, belonged to the large group of atomic spectroscopists interested in that period in finding simple relationships between the spectral lines of the elements (Balmer 1885a, b). Balmer succeeded in representing the frequency *ν* of the hydrogen atom spectral lines (in units of cm^{-1}) with the empirical formula

$$\nu = R_H\left(\frac{1}{4} - \frac{1}{n^2}\right)$$

where $n = 3, 4, 5$, etc. and $\mathrm{R_H}$ is the so-called Rydberg constant ($R_H = 109{,}737\ \mathrm{cm}^{-1}$).

To the same group of atomic spectroscopists belonged the Swedish physicist Johannes Robert Rydberg (1854–1919), professor of physics at the University of Lund. He was convinced that the order of the elements in the periodic table was connected to the atomic structure and should be reflected in the atomic spectra. On this basis, he generalized Balmer's empirical formula in order to classify the spectral lines of the elements (Rydberg 1886, 1890) with the expression

$$\nu = \mathrm{R_H}\left(\frac{1}{\mathrm{n_f}} - \frac{1}{\mathrm{n_i}}\right)$$

where $\mathrm{n_i}$ and $\mathrm{n_f}$ are integers, 1, 2, 3, … up to infinity, with $\mathrm{n_i} > \mathrm{n_f}$. The Balmer series for the hydrogen atom corresponds to $\mathrm{n_i} = 2$. Other series for the hydrogen atom are a set of ultraviolet lines (the Lyman series) that fit the above relationship with $\mathrm{n_i} = 1$. A series in the infrared region is the Paschen series that corresponds to $\mathrm{n_i} = 3$. Other series are the Brackett and Pfund series corresponding to $\mathrm{n_i} = 4$ and $\mathrm{n_i} = 5$, respectively

Bohr examining Balmer's formula realized that the frequencies emitted or absorbed by the hydrogen atom were all obtained as the difference between two numbers and he concluded that only the difference between the energy of two electronic states would explain the atomic spectra.

The second condition “quantized” the angular momentum of the electron, stating that it should be a multiple of $h\nu/c$ where c is the speed of light. This condition was suggested to Bohr by the papers of John William Nicholson (1881–1955), a mathematical physicist of Cambridge, who had attempted to interpret the complex emission spectrum of the solar corona with an atomic model in which rings of electrons orbited around the nucleus (Nicholson 1912). According to Nicholson, the electron oscillations in these rings gave rise to the spectrum. Even if incorrect, this theory involved an important idea that was included in Bohr’s theory. Nicholson wanted to incorporate Planck’s ideas in his model and, knowing that the Planck h constant had the right dimension, he decided to use it as a unit of angular momentum, stating that the atom could lose or gain angular momentum only in definite amounts, multiples of h. According to him, the angular momentum quantization was more correct and important than the energy quantization.

Bohr’s genial ideas were, on the one hand to couple the energy and the angular momentum quantization, reducing in this way the number of possible circular electron orbits only to the stationary ones, and on the other to understand the importance of introducing a “foreign” quantity such as Planck’s constant in the laws governing the old quantum theory:

> Whatever the alteration in the laws of motion of the electrons may be, it seems necessary to introduce in the laws in question a quantity foreign to the classical electrodynamics, i.e. Planck’s constant, or as it often is called the elementary quantum of action. By the introduction of this quantity the question of the stable configuration of the electrons in the atoms is essentially changed as this constant is of such dimensions and magnitude that it, together with the mass and charge of the particles, can determine a length of the order of magnitude required.

In reality, Nicholson and Bohr did not realize that their idea to quantize the angular momentum corresponded to considering the electron not only as a particle but also as a wave, anticipating by 10 years the Louis de Broglie principle. In fact, an orbit that in order to be stable satisfies the de Broglie principle, corresponds to a stationary wave and therefore the circumference of the orbit must necessarily be an integer multiple of the wavelength. As a consequence, only special values of the circumference radius are allowed.

Bohr succeeded in this way in obtaining a stupefying agreement between his theory and the empirical relationships found by several authors, in particular by Balmer and Rydberg, for the visible frequencies of the hydrogen atom. A further significant success of his theory was the direct calculation of Rydberg’s constant as a function only of the mass and charge of the electron and of Planck’s constant.

The quantization of the electronic orbits had already been proposed in 1910 by the Viennese physicist Arthur Erich Haas (1884–1941), who anticipated Bohr’s papers by 3 years (Haas 1910), but was never seriously considered and instead largely ignored or even ridiculed by the scientific community.

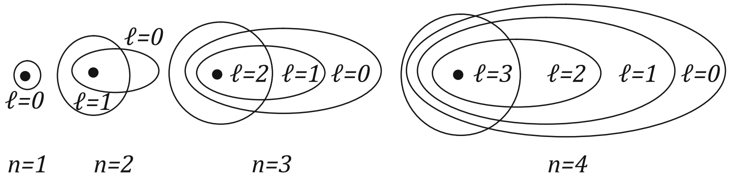
The extension of Bohr’s theory to many electron systems, presented in the second and third papers of 1913, was not very satisfactory for the interpretation of their emission spectra and turned out worse as the number of electrons increased. An important improvement of the theory was developed by Arnold Sommerfeld

(1868–1951), professor at the University of Munich, and one of the founders of the great school of theoretical physics in Germany. The role played by Sommerfeld in the development of the golden period of German physics is immense and is testified by the large number of Nobel laureates that studied with him and by the fact that he reached a record of 81 nominations for the Nobel Prize in physics.

Sommerfeld introduced elliptical orbits in addition to circular ones in Bohr's theory (Sommerfeld 1916) and defined more general quantization conditions than those of Bohr. The addition of elliptical orbits turned out to be very useful for the interpretation of the periodic system of the elements in terms of electron orbits. A further correction due to Sommerfeld was to assume that both the nucleus and the electrons orbited around the atomic center of mass, not coinciding with the nucleus as in Bohr's version of the theory. This modification led to a small correction of the numerical value of the Rydberg constant and to a reasonable explanation of the difference observed between the spectrum of hydrogen and deuterium, which in the old version of Bohr were identical.

Sommerfeld also introduced a relativistic correction of the electronic motion that led to a splitting in multiplets of fine structure of the single spectral lines predicted by Bohr's version of the theory. Finally, Sommerfeld, taking into account the fact that Bohr's orbits represented electrical currents in closed loops, thus giving rise to a magnetic moment perpendicular to the plane of the orbit, introduced into the theory a further quantization condition that allowed the orbits not necessarily to be all in the same plane and to assume different orientations in a magnetic field.

Sommerfeld published a detailed presentation of the theory in his famous 1924 book *Atombau und Spektrallinien*. For him, to quantize a physical entity corresponded to isolating in his continuum of classical values only some discrete multiple of a quantum unit of measure.



Electronic orbits according to the Bohr-Sommerfeld model

In the quantum theory that includes Sommerfeld contributions, known as the Bohr–Sommerfeld theory, the three quantization conditions of energy, angular momentum, and magnetic moment orientation were specified by three quantum numbers labeled with the letters n, ℓ, and m. The theory also specified the relations between their possible values. The principal quantum number n could assume only integer value with $n = 1, 2, 3$, etc., corresponding to energies $E = -R_H(1/n^2)$. The orbital quantum number ℓ could instead assume all values from $\ell = 0$ up to $\ell = n - 1$. Finally, the magnetic quantum m could vary from $-\ell$ up to $+\ell$.

With these quantum conditions, the Bohr–Sommerfeld theory explained relatively well the spectra of the hydrogen atom and of the hydrogenoid atoms, i.e., of atoms with Z protons but only one electron such as a singly ionized helium He^+, a twice ionized lithium Li^{++}, etc. This form of the theory deviated, however, more and more from the experimental data as the number of electrons increased. Despite several attempts to adjust the theory to more complex cases it became evident that the theory had insurmountable limits and soon it was forced to leave the way clear for the development of quantum mechanics.

5.4 The Electronic Theories of the Chemical Bond

The Bohr–Sommerfeld theory, even if far from supplying a correct description of the structure of matter at the microscopic level, still allowed one to establish a convenient basis for a description in electronic terms of a useful theory of the chemical bonds. At the beginning of the twentieth century, the concept of chemical bond, although of central interest for the chemical community, was still unclear until two German physicists, Richard Abegg and Walther Kossel, thanks to their imaginative research, succeeded in clarifying its nature, contributing to its understanding in terms of electronic theory.

The German physicist Richard Wilhelm Heinrich Abegg (1869–1910), student of Nernst at Göttingen, was one of the pioneers of the chemical valence theory, a term coined by the former student of Kekulé, Carl Hermann Wichelhaus in 1867 (Wichelhaus 1867). In collaboration with Guido Bodländer (1855–1904), professor at the University of Braunschweig, Abegg developed an electronic theory of chemical affinity to describe the valence in terms of interactions of electrons (Abegg et al. 1899). In 1904, he realized that the noble gases, showing a particular chemical inertia to react, possess a complete external electron shell of eight electrons and defined the concept of normal valence and of positive and negative contra-valence for the atoms, maintaining that every element always had eight available "valence places." The positive valence corresponded to the number of valence places occupied by electrons and the contra- or negative valence to the number of free valence places in the atom. Every element therefore possesses a maximum positive and a maximum negative valence such that their difference was always equal to eight (Abegg's rule) (Abegg 1904). For example, sulfur has valence +6 in H_2SO_4 and valence −2 in H_2S. In the same way, nitrogen has valence +5 in HNO_3 and valence −3 in NH_3 while chlorine has valence −1 in HCl and +7 in $HClO_4$.

Abegg and his wife Line were both avid enthusiasts of hot-air-balloon trips. He was the founder and chairperson of the Silesian club for aeronautics in Breslau. This hobby ultimately caused his death at the age of 41 when he flew his balloon together with an engineer and female relative. When the balloon encountered strong winds, they decided to descend. The balloon reached the ground safely and the other two were able to exit the basket. Abegg hesitated to exit and was caught by a gust of wind and crushed by the basket.

In 1913, in the period in which Bohr elaborated his theory, the young German physicist Walther Kossel (1888–1956), son of the Nobel Prize winner for medicine Albrecht Kossel (1888–1956) and assistant of Lénárd at the University of Berlin, went to work with Sommerfeld at Munich, where he dedicated himself to the theoretical study of the emission and absorption of x-rays with atoms. On the basis of Abegg's ideas, Kossel developed the famous octet theory (Kossel 1916), independently proposed in the same year by Gilbert Lewis in the USA, and succeeded in explaining the formation of positive and negative ions such as those encountered in electrochemical processes (Kossel 1920). According to Kossel, the electrons of all element atoms, except hydrogen and helium, were divided into internal and external shells. The internal shells possessed a number of electrons equal to that of the closest noble gas. The start of any new period in the periodic system of Mendeleev corresponded to the formation of a new electron shell. The electrons located in the external shells were those determining the reactivity of the elements. If the element had an incomplete external shell it had the tendency to acquire electrons up to a number that would fill it to reach the electronic structure of the following noble gas in the periodic table. If instead the element had an excess of electrons with respect to the noble gas situated before in the periodic system, it would prefer to lose them to reach a stable structure. External electrons could be therefore lost or gained, giving rise to positive and negative ions, respectively. The affinity of the chemist of the nineteenth century was finally interpreted on a theoretical basis as the tendency to fill the external electron shells.

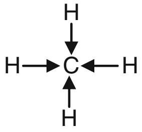
The ideas of Abegg and Kossel explained perfectly the formation of ions in the framework of Bohr's theory, but could not justify the stability of the majority of molecules which are neutral and do not contain ions, in particular the existence of diatomic molecules formed by two identical atoms such as Cl_2, N_2, O_2, etc.

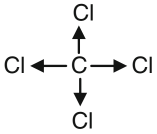
After the discovery of the electron, J.J. Thomson, who undoubtedly possessed a very creative mind, tried to explain the existence of neutral molecules developing a valence theory of electrical "force tubes" binding the atoms through a polarization mechanism consisting in the transfer of a "corpuscle," the electron, from one donor to an acceptor atom (Thomson 1907a, pp. 138–139):

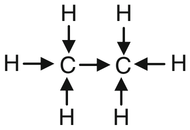
> For each valency bond established between two atoms the transference of one corpuscle from the one atom to the other has taken place, the atom receiving the corpuscle acquiring a unit charge of negative electricity, the other by the loss of a corpuscle acquiring a unit charge of positive.

In his book *The Corpuscular Theory of Matter* of 1907, Thomson represented this electron transfer process in molecules by means of arrow from the donor to the acceptor atom (Thomson 1907a). For example, in the H–C bond, the electron of the hydrogen atom migrated toward the carbon atom whereas in the case of the Cl–C bond, a carbon electron migrated toward the chlorine atom.

In this way he represented methane, carbon tetrachloride, and ethane with the formulas







Thomson's idea was resumed taken up again in 1910 by Kaufman George Falk (1880–1953), professor at the MIT and by John Maurice Nelson (1876–1965) professor at the Columbia University in New York, who improved Thomson's electronic valence theory (Falk and Nelson 1910) assuming that the electrons shifted between two atoms in chemical bonds as a function of their relative position in the periodic system. Falk and Nelson also extended the arrow symbolism to represent double and triple bonds:

$$CH_2 \rightrightarrows CH_2 \qquad CH_2 \rightleftarrows CH_2 \qquad CH_2 \overset{\longleftarrow}{\rightrightarrows} CH_2$$

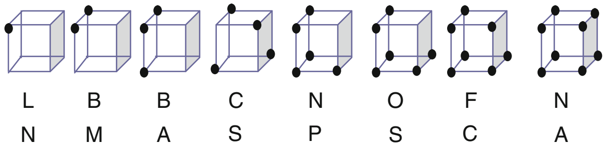
hinting even at the possibility of the existence of isomers.

This theory of polar bonds, although purely heuristic in nature, had some success among organic chemists interested in the effect of substituents in organic reactions and was later used by the English school in the theory of reaction mechanisms.

An important step toward the understanding of the basic nature of the chemical bond was made in 1916 by the American chemist Gilbert Lewis who, with his research, brought America to the forefront in chemistry. Son of a Bostonian lawyer, Gilbert Newton Lewis (1875–1946) had joined the University of Nebraska before moving at the age of 17 to Harvard, where in 1899 he obtained a Ph.D. in chemistry. After the Ph.D. he stayed for 1 year at Harvard before leaving, thanks to a fellowship, for Europe where he studied under the supervision of Ostwald at Leipzig and Nernst at Göttingen. Lewis did not get along too well with Nernst to the point where they developed a true and lifelong enmity which later retarded Lewis's nomination for the Nobel Prize in chemistry. Back in the USA, he worked for 3 years at Harvard as chemistry instructor under the direction of Theodor Richards who had studied also at Leipzig with Ostwald.

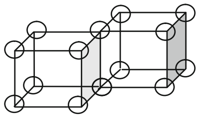
Owing to his strong character, Lewis's stay at Harvard did not last for long. Richards had adopted the same skeptical position of his former master Ostwald toward the concept of the atom, even if his scrupulous determinations of atomic weights would have provided him in 1914 with the Nobel Prize in chemistry. Lewis, who could not stand his very authoritative behavior toward his coworkers and his scorn for any form of theory of the chemical bond as interaction between the atoms, decided to leave Cambridge in 1904, accepting a position of Superintendent of Weights and Measures for the Bureau of Science of the Philippine Islands in Manila. Next year, however, he returned to the USA with a research position at the Massachusetts Institute of Technology (MIT) where he had the chance to work with a group of excellent physical chemists interested in the study of strong electrolytes directed by Arthur Amos Noyes, also a former pupil of Ostwald. In 1907 he became assistant, in 1908 associate, and in 1911 full professor. During this period his scientific activity was essentially devoted to the theory of relativity, a field in which he published a series of papers on the relationship between mass and energy, derived in a different fashion compared to Einstein. At the same time, he also published a physicochemical paper on osmotic pressure (Lewis 1908). In 1912, he moved to California where he later became professor of chemical physics and director of the College of Chemistry at Berkeley. The research activity of Noyes's research group pushed the young Lewis to get interested in thermodynamics (Lewis 1907), a field in which he would became known worldwide for his famous textbook *Thermodynamics and the Free Energy of Chemical Substances*, written in collaboration with Merle Randall (Lewis and Randall 1923). Even more influential was the stimulating MIT atmosphere that extended his interest to the study of the chemical bond both through the reading of Werner's papers on coordination complexes and through the study of the new theories of atomic structure such as that of J.J. Thomson in which the atom resembled a watermelon with electrons immersed at the side of the seeds in a pulp of positive electricity.

At the beginning of the century in the lectures that he used to give to first year chemistry students, Lewis used to represent the electrons in an atom with points or small circles at the vertex of a cube. At that time there started to circulate in the chemical community the idea that the stability of the rare gas elements depended upon the fact that they possessed eight electrons in the external Thomson's shell, as described by Abegg in 1904 and later reinforced by Kossel in 1916. Having realized that a cube possesses eight vertices, Lewis had the idea to represent, for purely teaching purposes, the atom as a cube with eight positions available to arrange the external electrons.



Lewis cubic atoms

By formally representing the atoms as cubes, Lewis arranged at the vertices a number of external electrons equal to the position of the elements in the eight columns of the periodic table. Starting from these formal structures he proposed the octet rule that bears his name. This strange theory of the cubic atom had clearly only didactical finality, but in 1916 he recovered it to formulate his theory of the chemical bond (Lewis 1916). In 1913, Lewis had the opportunity to read the manuscript of an English Ph.D. student, Alfred Lauck Parson (1889–1970), visiting Berkeley for a year, who suggested that the electron was not simply an electrical charge but also a magnet and that a bond could be formed between two atoms if two electrons were shared between the two atoms. Lewis represented this situation with two cubes with a side in common as shown in the figure. On this basis (Lewis 1916), Lewis introduced the concept of the covalent bond, a term actually coined only a few years later by his friend and coworker Irvin Langmuir. In the same way, ionic bonds were formed by transferral of one electron from one cube to another without sides in common. The main difference with previous theories was that in his formulation of the shared electron pair, Lewis allowed for partial transfers of electrons from one atom to another, in contrast with the positive–negative theory. He describes the partial transfer of two electrons, one from each of the two bonding atoms, so that there is a shared pair of electrons between them. This eliminates the need for the formation of oppositely charged atoms when there was no indication of individually charged atoms (ions) in a compound. This was the first true description of covalent bonding. Lewis theorized that electrons in an atom pair up around the nucleus, usually forming a tetrahedral arrangement. Although he never actually used the term "octet" for four pairs of electrons, the octet rule is often associated with his name. His main concern was with individual bonds between atoms rather than with all the electron pairs around each nucleus. Lewis's book *Valence and the Structure of Atoms and Molecules* is a classic, one of the greatest contributions to modern bonding theory (Lewis 1923).

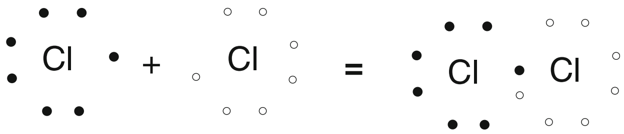


Two cubic atoms with one side in common

Lewis theory found in the industrial chemist Irvin Langmuir (1881–1957) the ideal person to popularize it and make it known in all basic aspects necessary to understand the chemical bond.

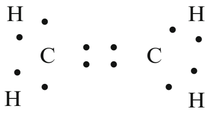
Langmuir, who obtained his Ph.D. at the Columbia University, started his scientific career in 1906 with a Ph.D. thesis entitled *Über partielle Wiedervereinigung dissociierter Gase im Verlauf einer Abkühlung*, developed in Göttingen under the supervision of Nernst (Langmuir 1906), who had just discovered his filament lamp. Langmuir, who was employed at the General Electric Company, soon became internationally known for his brilliant industrial applications of the kinetic theories and of surface adsorption as well as for the study of thermal effects in gases that led him to develop a filament lamp which was much more efficient than that of his master (Langmuir and Orange 1913). Impressed by Lewis's papers and by the importance that Lewis assigned to electrons as responsible for the "chemical forces" between atoms, Langmuir dedicated himself in the period 1916–1921 to the development, with great efficacy and ability, of the octet theory and to diffusion in the chemical milieu, thanks also to the creation of well-selected words such as *octet* and *covalent bond*, easily introduced into everyday slang in the laboratory. Starting from the Lewis theory he divided the electronic shells in cells, each able to host two electrons. In filling, the external shell around the nucleus could not host electrons until the internal ones were completely filled. An innovative aspect of his formulation of the octet theory was that two electrons could fill the same cell only if all others possessed at least one electron, a condition that anticipated the Hund rule.

According to the octet theory, enlarged and completed by Irving Langmuir, two atoms were held together by covalent bonds when each of the two atoms shared with the other one or more electrons to complete its external octet of electrons (Langmuir 1919b, c). For example, the chlorine atom possesses seven electrons in its external shell L. If two chlorine atoms share one electron each, both atoms complete their L shell with eight electrons, giving rise to a stable Cl_2 molecule as schematically shown in the figure below, where the electrons are represented by black and white dots.

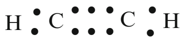


. Formation of a chlorine molecule from the separated atoms

The ethylene molecule $CH_2 = CH_2$ is made of two carbon atoms each with four electrons in the L shell and of four hydrogen atoms each with an electron in the K shell. By shearing the electrons as shown in the figure, the hydrogen atoms complete their K shell with two electrons whereas the two carbon atoms complete their L shells, with eight electrons. The four shared electrons between the two carbon atoms form a double bond. In the case of acetylene the two carbon atoms share six electrons forming a triple bond.



The Lewis ethylene molecule



The *Lewis* acethylene molecule

Langmuir also invented in 1919 the concept of *isosterism* (Langmuir 1919a) to associate molecules like nitrogen N_2 and carbon oxide CO with the same number of electrons to which he attributed similar chemical properties (Langmuir 1920). The concept was later extended to biological systems by Friedrich Erlenmeyer in 1932.

The Lewis–Langmuir theory was soon found to be a simple but extremely effective structure that clarified the importance of the electrons in chemistry. More than that, it transformed the chemistry of the elements into the chemistry of the electrons. The valence electrons became in fact the true protagonists of the molecular structure and of chemical reactions, whereas the nuclei and the inner electrons remained passive bystanders in this new world of chemistry that replaced that invented a century before by Dumas. The theory that possessed enormous didactic power was largely used by the synthetic chemists since it provided not only a convenient instrument to represent the molecular structures correctly, but also a practical formalism to explain many reaction mechanisms and to predict substitution of chemical groups.

Its static nature, the absence of any connection with first principles, and the disconnection from physical theories, in particular the Bohr–Sommerfeld one, made it, rather than a theory, a simplifying model endowed with, however, an enormous heuristic power and of a very strong predictive capacity. It represented the concrete performance of practical laboratory chemists with respect to the abstraction of theoretical physicists. It was, however, just this abstractness that, by assigning physical consistence to abstruse mathematical operators, finally succeeded, giving origin to that great revolution of physics at the microscopic level, quantum mechanics, that in few years would completely change our vision of the world.

Langmuir's theory was taken up in 1921 by Charles R. Bury (1890–1968), who replaced Langmuir's postulate of cells with two electrons with a different one directly connected to the Bohr–Sommerfeld theory (Bury 1921). Bury's new postulate was that the maximum number of electrons in each shell was proportional to the area of its surface. From this idea it directly followed that successive shells contained 2, 8, 18, and 32 electrons, respectively.

5.5 The Aufbau Principle

With Sommerfeld's help, and taking into account Abegg's and Kossel's ideas, Bohr developed in a series of papers from 1921 to 1923 the *Aufbau* (building) principle that established how the electrons are distributed in the atomic orbits of the elements of the periodic table (Bohr 1921). The Aufbau principle started from the hypothetical possibility of constructing the electronic structure of an atom of the periodic table adding one electron to the electronic distribution of the previous atom and applying the concept of quantization of the orbits. Starting from the hydrogen atom with only one electron, the energy levels of the following atoms were, one at a time, filled with electrons starting from the lowest energy levels up on the basis of essentially empirical rules.

The electronic orbits were thus distributed in the atoms in shells or "barks" that contained the nucleus like onion layers (Bohr 1922). The original form of the Aufbau principle, developed in the period 1921–1923, soon showed its limitations when Bohr tried to extend his idea to filling the electronic orbits of many-electron atoms. In 1924, a new and more efficient version was proposed separately by two English scientists, the chemist John David Main Smith of the University of Birmingham and the physicist Edmund Clifton Stoner who worked at the Cavendish Laboratory of Cambridge. In 1924, Main Smith published four short letters (Main Smith 1924a, 1925) and a book entitled *Chemistry and Atomic structure* (Main Smith 1924b) in which he corrected, on purely chemical grounds, the condition by which Bohr assumed that the second electronic shell included eight electrons distributed in two subgroups each with four electrons. Main Smith stated instead that each group necessarily had to include a subgroup with two electrons and that in each subgroup there could be located a maximum $2(2\ell + 1)$ electrons.

At the same time, Edmund Stoner (1899–1968) published in the Philosophical Magazine a paper (Stoner 1924) that reached the same results on the basis of magnetic and spectroscopic data and in addition established that the maximum number of electrons in each shell was equal to $2n^2$. Stoner's paper was much better known than that of Main Smith in the physicist community that almost completely ignored the existence of a journal of industrial chemistry. Wolfgang Pauli who by chance read Stoner's paper quickly succeeded in giving an axiomatic form to his conclusions, establishing the famous exclusion principle (Pauli 1925). The Aufbau principle was definitively completed in 1926 with the discovery of electron spin by Uhlenbeck and Goudsmit and with the introduction in the theory of the fourth spin quantum number. During a meeting at Leyden, after a discussion with Einstein, and after even longer discussions with Pauli, Bohr accepted – with some hesitation – the concept of spin, of which he later became a strong supporter.

In the final formulation of the Aufbau principle realized in the framework of the Bohr–Sommerfeld theory, each shell, indicated by a letter (K, L, M, N, etc.), was characterized by the principal quantum number n that could assume all integer values 1, 2, 3, etc. In each shell a maximum of $2n^2$ electrons were allocated. The K ($n = 1$) shell therefore included at maximum 2 electrons, the L ($n = 2$) shell at maximum 8, the M ($n = 3$) shell 18, and so on. Each shell was further divided into subshells (s, p, d, f, ...), characterized by the orbital quantum number ℓ which assumed all integer values from 0 up to $n - 1$. In each subshell a maximum of $2(2\ell + 1)$ electrons were positioned. The magnetic quantum number m assumed all integer values from $-\ell$ to $+\ell$, including the value 0. In this way, in the s subshell were located two electrons, in the p six, in the d ten electrons, etc., as summarized in the table for the first four values of n.

Bohr–Sommerfeld quantum numbers

Quantum numbers			Number of states	
n	ℓ	m	Subshell	Total
1	0	0	2	2
2	0 (s)	0	2	8
	1 (p)	−1, 0, +1	6	
3	0 (s)	0	2	18
	1 (p)	−1, 0, +1	6	
	2 (d)	−2, −1, 0, +1, +2	10	
4	0 (s)	0	2	32
	1 (p)	−1, 0, +1	6	
	2 (d)	−2, −1, 0, +1, +2	10	
	3 (f)	−3, −2, −1, 0, +1, +2, +3	14	

5.6 Electron Spin

The discovery of the Pauli exclusion principle is intimately entangled with that of electron spin and the complexity of their history reflects the difficulties that nineteenth-century physics had to face in the transition from classical to quantum physics. The first to suggest that a fourth quantum number could be connected with a spinning motion of the electron was a young American student of physics, Ralph de Laer Kronig (1904–1995), born and educated at Dresden in Germany, but then transferred to the Columbia University in New York where he obtained his Ph.D. in 1925. Kronig, upon the suggestion of Paul Ehrenfest who visited Columbia while he was studying there, moved to Europe at the end of 1924 to visit the most important centers of theoretical physics of the old continent. In particular he went to Leyden, where he collaborated with Samuel Goudsmit to compute the band intensity in the Zeeman effect (Goudsmit and Kronig 1925). At the Tubingen University, Kronig had the opportunity to listen to a lecture by Wolfgang Pauli on the need to introduce a new quantum number in the Sommerfeld quantum mechanical formalism. Back in America, the young Kronig proposed in 1925 the existence of a spin quantum number, assuming that the electron could whirl round on itself giving rise to a spinning angular momentum.

The idea that the electron could spin like a whipping top did not please Heisenberg or Pauli who suggested he give up insisting on this funny idea that he qualified as lacking any physical reality. Kronig, discouraged by these criticisms, gave up and decided not to publish his ideas. Unfortunately for him the same idea was published next year by Goudsmit. Kronig did not bear any grudge for Pauli, however; on the contrary, the two became excellent friends and Kronig had a brilliant career. In 1927, he found, in collaboration with Isidor Isaac Rabi (1898–1988), the exact solution for the Schrödinger equation in the case of the symmetric rotor (Kronig et al. 1927).

In reality, the need for a fourth quantum number had already been put forward by Sommerfeld who in 1920 proposed the existence of an internal quantum number associated with a “hidden” rotation (Sommerfeld 1920) to describe the anomalous reaction of many electron atoms to an external magnetic field (anomalous Zeeman effect).

In 1925, Pauli published his *Ausschliessungsprinzip* exclusion principle (Pauli 1925) that proposed the existence of a fourth quantum number. The Viennese Wolfgang Pauli (1900–1958) arrived at the exclusion principle starting from the impossibility of explaining with only three quantum numbers the anomalous Zeeman effect. While in the spectra of atoms like hydrogen, triplets of equidistant lines were observed (normal Zeeman effect) in the presence of a magnetic field, perfectly explained with three quantum numbers, in some atoms the spectral lines were split into four, five, and even more components, with a separation larger than predicted by theory (anomalous Zeeman effect). This anomalous effect remained unexplained for several years and only with the introduction of a fourth quantum number was it possible to create a reasonable interpretative scheme for atomic spectra.

Another factor that pushed Pauli to look for a new quantum number was Stoner's paper, previously discussed, further supported by the fact that the Swede Rydberg had noticed that the number series 2, 8, 18, 32, . . ., defining the length of the periods of the periodic system, was the series $2n^2$. Pauli realized that this factor 2 recurring in Rydberg's formula, as well as in Bohr's and in Langmuir's theory, had no theoretical justification and arose from an as yet undiscovered condition.

The Pauli exclusion principle dictates that two electrons cannot have the same set of four quantum numbers. When an electron occupies an energy state defined by four values of the quantum numbers, that state is filled and cannot host another electron. This rule is actually valid only for particles like the electrons obeying the Fermi–Dirac statistic (fermions).

For several years, the Pauli principle represented an important integration of the Bohr–Sommerfeld theory, although without a plausible explanation of its presence. In his papers, Pauli in fact never explained the theoretical reasons for the existence of a fourth quantum number. Only in 1945 when he received the Nobel Prize for physics did Pauli supply in his Stockholm speech a full explanation of the principle in terms of quantum mechanics and not of the old quantum theory. In quantum mechanics, for an atom with two electrons at the a and b levels, the correct wavefunction in which the two electrons are indistinguishable and the function is antisymmetric with respect to the exchange of the two electrons has the form

$$\psi = \psi_1(\mathrm{a})\psi_2(\mathrm{b}) - \psi_1(\mathrm{b})\psi_2(\mathrm{a})$$

and this function vanishes if the two electrons are at the same level, $\mathrm{a} = \mathrm{b}$.

In 1926, the Swedish physicists George Eugene Uhlenbeck (1900–1988) and Samuel Abraham Goudsmit (1902–1978), working at Leyden in Holland under the supervision of Ehrenfest, read the just published Pauli's paper where he mentioned a fourth quantum degree of freedom. Goudsmit was an experimentalist who knew well the anomalous Zeeman effect, whereas Uhlenbeck was a theoretician who had worked in Italy and met Enrico Fermi. It was actually Uhlenbeck who, once he understood that Pauli was looking for a fourth quantum number, realized that this meant the occurrence of another degree of freedom for the electron and that the only possible additional degree of freedom was a spinning motion around its own axis, an idea that Konig had already suggested a year before. The two friends published the spin theory right away (Uhlenbeck and Goudsmit 1925) in papers in which the electron was assimilated to a small sphere of negative electricity rotating around the nucleus and spinning like a small whip top. Being an electric charge in rotation in an orbit, it had to be associated with an intrinsic magnetic moment. The two Dutchmen then applied to the rotation of the electron the condition that the spin angular momentum could only have the value (½)h/2π and that the magnetic moment could be oriented in a magnetic field in only two ways, parallel or antiparallel to the direction of the field (Uhlenbeck et al. 1926). Application of the Pauli exclusion principle then decrees that if two electrons have the same values of the quantum numbers n, ℓ and m must have opposite spins (antiparallels), one with value +1/2 and the other with value $-1/2$. The fourth quantum number therefore became the spin quantum number s that could have only two values, +1/2 and −1/2. The spin theory was later formalized by Pauli in 1927. The introduction of the spin quantum number s for the electron turned out to be of extreme importance for the successive development of quantum chemistry.

At this point, the atomic structure was more or less understood, at least in outline. It was still obscure, however, why the mass of the nucleus did not correspond to the atomic number and that for the same atomic number different isotopes could exist. In 1921, Rutherford had already postulated the existence of a neutral particle of mass equal to that of the proton. The problem was definitively solved in 1932 with the discovery of the neutron by James Chadwick.

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