Chapter 1

The Rise of Atomic Theory

Contents

Our present understanding of the chemistry and physics of matter rests firmly on the idea of atomism and the theories of quantum mechanics and statistical mechanics. The idea of atomism is very old and has assumed different forms throughout the centuries. The theory of statistical mechanics was founded in the nineteenth century. Quantum mechanics is, however, a product of the twentieth century. It was born in the year 1900 and emerged as a result of the efforts spent by chemists and physicists throughout the previous century to make atoms real. The first chapter describes these efforts and the way they connect to our modern view of matter.

1.1 Early Atomic Theories

The idea of atomism, which states that matter is composed of ultimate and indivisible particles (atoms) that move with respect to each other in empty space, can be traced back to the Greek philosopher Leukippos and his pupil Demokritos, in the fifth century B.C. The idea met considerable resistance from the Platonists and the Aristotelians who dominated the philosophical scene for many centuries. Still, it was accepted and further developed by Epicurus (about 300 B.C.), and it was highly praised by the Roman poet Lucretius (about 65 B.C.) in the didactic poem *De rerum natura.* This extensive work is an important source to the understanding of the atomic theories of the classical antiquity.

It is likely that the antique idea of atomism has been familiar to most educated men since the days of Leukippos and Demokritos. The idea was, however, purely philosophical. It was a stimulation to the intellect, but lacked any documented connection with the real world outside the minds of the philosophers. Hence its impact remained very small.

It doesn't seem that the atomic idea played any noticeable role in the Middle Ages, but it was revived during the scientific revolution of the sixteenth and seventeenth centuries, in particular by René Descartes and Pierre Gassendi in France, and by Robert Boyle and Isaac Newton in England. A detailed and interesting contribution was made by the influential Croatian Jesuit scholar Ruder Bošković in his *Philosophiae naturalis theoria* published in 1758.[1] What Bošković tried in his treatise was, *inter alia*, to create a general theory of matter based on the idea of atoms and Newton's concept of force. Unlike the Greeks he assumed the atoms to be point-like, and he also assumed that Newton's law of attraction became a law of repulsion at small distances. This implies that two atoms are pulled toward each other by an attractive force until the distance between them reaches the point where the force starts to become repulsive. At this distance we must have stability of matter because the force is now neither attractive nor repulsive. Bošković even assumed that the force might change sign more than once as the distance between atoms varied, and in this way he

[1] Until 1757 the Roman Catholic Church did not allow the publication of books that supported views implying the motion of the Earth. Between 1616 and 1757, such books were entered in the Index of Forbidden Books (*Index Librorum Prohibitorum*).

could account for the existence of more than one stable form of the same kind of matter in a qualitative way. Thus, the theory proposed by Bošković had some intuitively appealing features, but it was still a purely speculative theory and a theory devoted to generalities. Like its predecessors, it was of little help in the solution of specific problems.

1.2 The Chemical Atom

The first practical atomic theory was put forward by the English chemist and physicist John Dalton during the years 1803 to 1808. The background for this theory was the *law of conservation of mass* and the *law of constant proportions*. The first of these laws had been formulated by the French chemist Antoine Laurent Lavoisier in 1785. It was based on the exact process of weighing and states that there is no measurable change in mass during a chemical reaction. The second law was enunciated by the French chemist Joseph Louis Proust in 1799. It states that different samples of a substance contain its elements in the same proportions.

An element had been defined by Lavoisier as being a substance that cannot be decomposed (by chemical means), and he had given a list of 33 substances that he considered to be elements (among them light and caloric, or heat). Dalton's hypothesis was then that all elements consist of atoms, and that all atoms of the same element have the same weight, but the weights of atoms of different elements are different. Dalton also formulated the *law of simple multiple proportions*. This law states that when two elements combine to form more than one chemical compound, the weights of one element that combine with the same weight of the other are in the ratio of small integers. The meaning that Dalton gave to this law was that a chemical compound consists of units of a characteristic number of atoms.

The radically new in Dalton's atomic theory, as compared to earlier atomic theories, was its quantitative element. It was based on the process of weighing. This made it a practical theory that could grow and expand over the years to come.

The first addition to the theory was proposed in 1811 by the Italian physicist Amadeo Avogadro, and independently in 1814 by the French physicist André Marie Ampère. It is known as *Avogadro's hypothesis*. It gives independent existence to the smallest units of a compound by referring to them as molecules and states that any two gases, taken under the same conditions of temperature and pressure, contain in the same volume the same number of molecules. The hypothesis was, however, relatively unnoticed for many years. Its implication for the determination of a rational table of atomic weights was in fact not fully appreciated until 1858, when the Italian chemist Stanislao Cannizzaro published his *Sketch of a Course of Chemical Philosophy*, and it was only after then that the concept of free molecules gained its immense importance.

But in the meantime, a large number of new elements were discovered, and the atomic theory was enriched with the concept of valency, by the contributions of many chemists. The elements were grouped according to their valencies and general properties, and this allowed the Russian chemist Dmitri Ivanovich Mendeleev to construct his *periodic table of the elements*, in 1869.

Next, the chemical formulae were extended into space. The molecules became three-dimensional. It was in 1874 that the Dutch chemist Jacobus Henricus van't Hoff and the French chemist Joseph Achille le Bel independently documented that the valencies of the carbon atom are directed toward the corners of a tetrahedron of which the carbon atom itself occupies the center.

With the three-dimensional structure of molecules understood, the valence concept became too narrow to account for the binding capacity of all atoms, especially transition metal atoms. It was accordingly supplemented with the concept of coordination number, by the German chemist Alfred Werner, in 1893. This was the last major addition to Dalton's atomic theory in the nineteenth century. The theory of *the chemical atom* had now reached a high level of development and had shown its ability to rationalize a huge amount of chemical data.

But how big were atoms and molecules, and how should they be visualized?

1.3 The Kinetic Molecule

The first serious estimate of the size of atoms and molecules was made by the Austrian physicist Joseph Loschmidt in 1865. It was based on the results of a new science, the *kinetic theory of gases*, which had been initiated by the physicists Rudolf Clausius in Germany and James Clerk Maxwell in England.

Together with the English physicist William Thomson (Lord Kelvin), Rudolf Clausius was the founder of thermodynamics as an exact phenomenological science of energetics. He was the first to formulate the second law of thermodynamics, and the father of the concept of entropy. But he also wanted to understand the mechanical (microscopic) basis of the thermodynamic laws, and he realized that this basis must be statistical.

Thus, the kinetic theory of gases is a statistical theory which deals with the average behavior of an immense number of particles. It operates with concepts like mean free path and collision time, and it allows the derivation of theoretical expressions for coefficients of diffusion, coefficients of thermal conductivity, coefficients of viscosity, etc. Maxwell had shown that the mean free path of a gas could be calculated from measured values of the coefficient of viscosity, and Loschmidt was now able to derive a simple expression for the diameter, s, of a molecule, viz.

$$s = 8\varepsilon l, \tag{1.1}$$

in which l = mean free path, and ε is a *condensation coefficient*, expressing the ratio of the actual volume of condensed gas molecules to the volume they take up in the gas phase. Using the values $l = 1.40 \times 10^{-7}\,\mathrm{m}$ and $\varepsilon = 0.000866$, he obtained $s = 10^{-9}\,\mathrm{m} = 1\,\mathrm{nm}$ as his estimate for the diameter of a molecule of air. This result compares reasonably well with the currently accepted value of about 0.3 nm for the diameter of O_2 and N_2 molecules.

The mean free path is the average distance which a molecule traverses between two collisions, so by combining l with s it is possible to derive the number of atoms or molecules in the volume of $1\,\mathrm{cm}^3$ at standard conditions. This number is referred to as *Loschmidt's constant.* Equivalently, one may calculate the number of atoms or molecules in a molar mass. This number is *Avogadro's constant*, whose value is[2]

$$N_A = 6.02214 \times 10^{23}\,\mathrm{mole}^{-1}. \tag{1.2}$$

The estimate one obtains from Loschmidt's data is $0.4 \times 10^{23}\,\mathrm{mole}^{-1}$.

The kinetic molecule of the nineteenth century was essentially the kind of entity we have just implied, i. e., an impenetrable, perhaps spherical particle without internal structure which moves according to the laws of Newtonian mechanics and undergoes collisions with other particles. This was a simple picture, and it did not distinguish between atoms and molecules, but in the hands of some of the great scientists of the time it was a very fruitful one. The foremost of these scientists was the Austrian physicist Ludwig Boltzmann.

Boltzmann studied the mechanics of collisions between the particles of a gas in great detail, and as a result he succeeded in constructing a statistical function that he could identify with the entropy of the gas. Entropy, he stated, is a measure of the disorder of a physical system, and he showed (1877) that

[2] An abbreviated list of the values of the fundamental constants of physics and chemistry is given in the back of this book.

if the physical system is left to itself its statistical entropy will always either increase in time or remain constant, rather than decrease. Thus, he had given the second law of thermodynamics an intuitively clear formulation.

Boltzmann's definition of entropy is contained in the equation

$$S = k \ln W \tag{1.3}$$

where S is the entropy and W the so-called thermodynamic probability, i. e., the number of microstates which are compatible with the same macroscopic properties. k is *Boltzmann's constant*, with the value

$$k = 1.38065 \times 10^{-23}\,\mathrm{J\,K^{-1}}. \tag{1.4}$$

Actually, Boltzmann never specified the constant k, nor did his analysis allow him to, for his counting of microstates was necessarily relative rather than absolute. It was the German physicist Max Planck who first wrote Eq. (1.3) in this explicit form and obtained the numerical value of k, in his important work on the black-body radiation that we shall discuss in the next chapter.

Eq. (1.3) is not only a central equation in the kinetic theory of gases. It is also a fundamental equation in the broader theory of *statistical mechanics* which deals with a general macroscopic system. The remarkable development of this science during the second half of the nineteenth century was also to a large extent due to Boltzmann. The other great contributor was the American physicist Josiah Willard Gibbs.

Boltzmann arrived at his definition of entropy and his interpretation of the second law of thermodynamics through his studies of the kinetic theory of gases, and it was the simplistic assumption of kinetic molecules without internal structure that allowed him to carry his analysis so far. This did not imply, however, that molecules were actually believed to be devoid of internal structure. Rather, motion of a particle was imagined to mean motion of its center of mass.

Both Maxwell and Boltzmann, as well as several others, considered a molecule to be a rotating and vibrating cluster of atoms, and they tried to estimate the heat capacity of molecules from this picture, by using the general relations of statistical mechanics. For a diatomic molecule, for instance, this resulted in the value $C_V = 3.5\,R$ for the molar heat capacity of a gas at constant volume, where R is the general gas constant, with the value

$$R = 8.31447\,\mathrm{J\,K^{-1}mole^{-1}} = kN_A. \tag{1.5}$$

The value $3.5\,R$ is made up of separate contributions from the various *degrees of freedom*. There are three degrees of freedom which correspond to the motion of the center of mass along the three coordinate axes, and each of these contribute $0.5\,RT$ to the molar internal energy at absolute temperature T, according to the kinetic theory of gases, and hence $0.5\,R$ to C_V. In addition, there are two rotational degrees of freedom according to the two angles that describe the direction of the internuclear axis in space, and by a general assumption about equipartition of energy each of these also contribute $0.5\,R$ to C_V. Finally, there is one vibrational degree of freedom corresponding to the variation of the internuclear distance. By the equipartition theorem this gives a contribution of $1.0\,R$ because kinetic and potential energy contribute separately to C_V. Adding up the various contributions, we arrive at the value $C_V = 3.5\,R$. This value for C_V is, however, only observed at very high temperatures (several thousand degrees), whereas at normal temperatures the molar heat capacity of diatomic gases is only about $2.5\,R$.

The failure of statistical mechanics to describe the temperature dependence of C_V was, of course, a serious shortcoming. It remained a riddle until the advent of quantum mechanics.

1.4 The Spectroscopic Atom

The nineteenth-century attempts to determine the heat capacity of molecular gases from first principles were, as we have seen, only modestly successful. The situation was, however, even worse when it came to the understanding of the optical spectra of atoms and molecules.

Optical spectroscopy became a well-developed subject during the nineteenth century. It was realized early that elements liberated from a chemical compound in a flame or an electric arc would emit light at discrete and characteristic wavelengths, and in 1859 the German chemist Robert Wilhelm Bunsen and his colleague, the physicist Gustav Robert Kirchhoff founded the method of spectral analysis based on this fact. The presence of many elements could now be verified by their line spectra. The elements rubidium, cesium, indium, and thallium were, in fact, discovered spectroscopically, and helium was detected by observation of the sun (1868) long before it was found on the earth (1895).

The line spectrum of an element has in general a very complex structure, but with marked constellations of lines. The simplest line spectrum is that of atomic hydrogen. It consists of three lines in the visible part of the spectrum, a red line called H_α, a blue-green line called H_β , and a violet line called H_γ. On the photographic plate it is found that the spectrum continues in the ultraviolet region with a large number of close-lying lines which form a *spectral series* that converges to a limiting wavelength of 364.6 nm. It was of course a challenge to try to represent the series by some simple arithmetic law, and in 1885 the Swiss school teacher Johann Jacob Balmer succeeded in showing that the following formula would reproduce the series,

$$\lambda = 364.6 \frac{m^2}{m^2 - 2^2} \, \mathrm{nm}, \tag{1.6}$$

where λ is the wavelength and m is an integer parameter that runs from 3 to ∞. The visible lines are reproduced by putting m equal to 3, 4, and 5. If, instead of λ, we introduce the *wavenumber*, $\tilde{\nu} = 1/\lambda$, the formula becomes

$$\tilde{\nu} = R_H \left(\frac{1}{2^2} - \frac{1}{m^2} \right) \tag{1.7}$$

where R_H is the so-called *Rydberg constant*, with the numerical value

$$R_H = 1.097 \times 10^7 \, \mathrm{m}^{-1}. \tag{1.8}$$

The constant is named after the Swedish physicist Johannes Robert Rydberg who generalized Eq. (1.7) to other series and other simple atoms. For the hydrogen atom, the set of all spectral series may be represented by the general formula

$$\tilde{\nu} = R_H \left(\frac{1}{n^2} - \frac{1}{m^2} \right). \tag{1.9}$$

For $n = 2$ we get the above *Balmer series*. $n = 1$ gives the *Lyman series* with wavelengths in the ultraviolet part of the spectrum, $n = 3$ gives the *Paschen series* with wavelengths in the infrared region, etc.

Light is electromagnetic radiation, and this was fully understood by the end of the nineteenth century. Maxwell had succeeded in combining all theoretical knowledge about electric and magnetic phenomena into a set of four differential equations (1873). The equations are expressed in terms of electric charges, electric currents, and electric and magnetic fields, and they allow the calculation of the fields once the charges and the currents are specified. The equations show, in particular, that an accelerated charge, for instance an oscillating charge, will generate electromagnetic waves that spread in space with the speed of light. Such waves were first produced and studied by the German physicist Heinrich Rudolf Hertz in 1886.

It was accordingly natural to assume that the emission of light from agitated atoms and molecules was caused by oscillations of electric charge. It was well known from electrochemistry that electric charge was intimately connected with the forces of chemical combination, and chemical affinity had often been ascribed to the attraction between opposite charges. This led, in turn, to the suggestion that both positive and negative electric charge existed in discrete units. But nothing definite was known about the way electric charge operated in the atomic and molecular world, and it was consequently completely impossible to calculate the nature of the light that an atom or a molecule might emit.

It was obvious, however, that the atomic emission of light must reflect some internal structure of the atom, and speculative suggestions as to what this structure might possibly be were certainly made, also prior to the appearance of Maxwell's equations, and independent of the assumption of charges. Thus proposed William Thomson, in 1867, that atoms should be thought of as being vortex rings in the omnipresent ether. The motion and mutual interactions of such vortices, he contended, could account for the kinetic behavior of atoms. They could be linked together to form molecules, and their fundamental vibrations could supposedly account for the spectral lines of an atomic gas.

The vortex atom was an intelligent construction, and it was highly regarded by several scientists. But it had to be abandoned as a working model, because it was unable to give a quantitative description of the real world after all. No other model could do better either.

1.5 Antiatomism

As we have discussed it in the previous sections, chemistry, experimental spectroscopy, and statistical mechanics were highly developed sciences at the end of the last century. But nobody had been able to unite the various aspects of atomic behavior met in these sciences into a single and coherent picture of the atom. As a result, there were several scientists who did not believe in the physical reality of atoms and molecules, and some of them were very influential indeed, like the German chemists Hermann Kolbe and Friedrich Wilhelm Ostwald, and the Austrian physicist Ernst Mach.

The criticism by these scientists was both deep and varied. The cardinal point was their objection to the metaphysical aspect of atomic theories. These theories, they said, work with forces whose existence we cannot prove between atoms that we cannot observe. So it is better to consider atoms and molecules as purely formal, albeit useful entities and concentrate on what we can in fact measure, and on the pure energetics of processes.

The strong opposition of the antiatomists led to many fierce debates and much bitterness. And their attitude survived long into the twentieth century, but quite unwarranted, for soon new experimental results provided unambiguous proofs of the reality of atoms.

1.6 The Discovery of the Electron. The Planetary Atom

The experimental study of the interaction of an electric current with chemical substances in a melt or a solution played a considerable role for the development of chemistry and chemical ideas during the nineteenth century. The process of decomposing a chemical compound by an electric current is known as *electrolysis*, and the first quantitative laws concerning this process were formulated in 1834 by the English scientist Michael Faraday who also introduced the notion of ions for the carriers of the current. The laws state that the amount of matter decomposed by an electric current is proportional to the amount of electricity which passes, and that the weights of different substances produced by the same quantity of electricity are proportional to the equivalent weights of the substances. (The equivalent weights of different substances are defined in chemistry as the weights than can combine with each other or a same third substance, to saturate a single unit of valence.)

It is, of course, tempting to speculate from Faraday's laws, that if chemical compunds are composed of atoms, then electricity too, positive as well as negative, is divided into discrete units which attach themselves to the atoms and thus behave like atoms of electricity. This possibility was suggested by the English scientist George Johnstone Stoney in 1874 and, with great strength, by the German scientist Hermann von Helmholtz in 1881. The postulated unit of electricity was given the name *electron* by Stoney in 1891. By hypothesis, an ion will either accept or deliver an integer number of elementary electric units at an electrode during electrolysis. Hence, we may refer to N_A electrons as one mole of electrons and conclude, from the quantitative measurements by Faraday and other scientists, that the electric charge of one mole of electrons is 96485 C. This gives us *Faraday's constant*,

$$F = 96485\,\mathrm{C\,mole^{-1}}. \tag{1.10}$$

We also conclude, that if the charge of the electron is denoted by e and the mass of a hydrogen atom by M, then e/M is approximately equal to F (since the atomic weight of hydrogen is almost exactly equal to 1).

Toward the end of the century, several studies were performed on electrical discharges in gases and on the conductivity of gases subjected to radiation. The experiments were carried out in glass tubes fitted with electrodes and at different gas pressure. It was then found that when a tube was evacuated, rays were observed to cross the tube from a negative electrode (the cathode) to the positive electrode (the anode). These rays were given the name cathode rays. There was much discussion as to the nature of the rays, but in 1897 the physicists Emil Wiechert in Germany and Joseph John Thomson in England demonstrated that they were in fact negatively charged particles. By a very careful study, which involved deflections of the rays by both electric and magnetic fields, J. J. Thomson succeeded in determining the ratio of the electric charge (e) to mass (m) for cathode rays, showing that e/m was at least 1000 times as great as the value for hydrogen mentioned above. Later, the value was corrected to become almost twice as large.

This experiment is considered to mark the discovery of the electron.

The study of cathode rays only allowed the determination of the e/m ratio and not the values of e and m separately. Approximate values for e and m were estimated, but exact values were not determined until 1909. In that year the American physicist Robert Andrews Millikan succeeded in determining the value of e to within 1%, by measuring the velocity in an electric field, of falling oil drops charged with electrons that had been produced by irradiating the air with a beam of X-rays. With the value of e thus determined, the value of m could of course be found from the e/m ratio.[3]

X-rays had been discovered already in 1895, by the German physicist Wilhelm Konrad Röntgen, and the next year the French physicist Henri Becquerel had discovered the phenomenon of radioactivity. During the following years it was found that radioactivity involved no less than three distinct types of radiation. They were called α (alpha) radiation, β (beta) radiation, and γ (gamma) radiation respectively. It was also found that beta rays consist of electrons, wheras gamma rays and X-rays are electromagnetic waves like visible light, but with much shorter wavelengths. Alpha rays were shown, by the British physicist Ernest Rutherford, to be the dipositive ions of helium atoms, moving at high speed. He showed this, partly by measuring the deflection of the rays in electric and magnetic fields, partly by shooting the rays through a thin metal foil into a chamber and demonstrating the presence of helium in the chamber.

[3]Millikan's determination of the electronic charge became also the first truly direct determination of Avogadro's constant, by comparison of e with the known charge of the Faraday.

Much work was done on the scattering of the newly discovered rays by matter. J. J. Thomson derived a formula which showed that the scattering of X-rays should be proportional to the number of electrons in the target, and this led to the experimental finding that the number of electrons in an atom equals its atomic number, Z. Studies of radioactive decay, by Rutherford and others, pointed in the same direction. But if an atom contains Z electrons each of charge $-e$, then by charge neutrality it must also contain a positive charge Ze. And because the mass of Z electrons is only a tiny part of the atomic mass, the positive charge and the majority of the atom's mass must belong together. But how is this positive charge and remaining mass distributed within the atom?

J. J. Thomson, who incidentally had been working on Kelvin's theory of vortex atoms several years earlier, made the simplest possible assumption. He suggested that the mass and the positive charge was uniformly distributed within a sphere with an approximate radius of 10^{-10} m, a value supported by the kinetic theory of gases and other evidence. The electrons were then supposed to form an electrostatically stable constellation inside the sphere. This model of the atom is referred to as Thomson's model, and thus its name also does justice to Kelvin who earlier had presented some ideas of a similar type.

Thomson's atomic model was of course unable to account for the large number of spectral lines and laws like those hidden in Balmer's and Rydberg's formulae. It was again a new model based on speculation and incomplete knowledge.

The final step toward a correct picture of the atom was taken by Rutherford in 1911. It was based on experimental results on the scattering of alpha rays, obtained in 1909 by his collaborators Hans Geiger and Ernest Marsden. Geiger and Marsden had allowed a beam of alpha particles to pass through a thin gold foil and observed that most of the particles showed very slight deviations from a straight path. However, a small fraction of the particles showed deflections through very large angles. Rutherford went carefully through the dynamics of possible collision processes and showed that such large deflections could come only from a collision of a heavy particle with another particle of comparable mass, and at such a small distance that the electric force of interaction was extremely great.

On the basis of his analysis, Rutherford introduced his model of the *planetary atom*, or *solar atom*, according to which the positive charge and the majority of the atomic mass is concentrated in a tiny *nucleus* at the center of the atom. The electrons, on the other hand, are distributed throughout a sphere of atomic dimensions.

Rutherford's analysis marked the end of a long search for an objective model of the atom, a search in which both chemists and physicists had taken part, and a search during which several false models had emerged and led the way for some time. The new atom became the principle of unification for chemistry and physics, but so far only its constitution was known. To understand its internal dynamics it became necessary to enter a whole new world, the world of quantum mechanics, in which the classical laws of motion lose their validity. Thus, the end of a long development also became the beginning of a new epoch for science.

It is this epoch that the present exposition is about. But before we enter the discussion of quantum mechanics, let us update the description and give a brief sketch of our present picture of the constitution of atoms and molecules and their interactions.

1.7 The Constituents of Atoms and Molecules. The Modern View

The constituents of atoms and molecules are electrons and atomic nuclei. The present section specifies the basic physical parameters of these particles.

Modern physics considers the electron to be a *true* elementary particle, i. e., it is believed that the electron cannot be divided into smaller constituents. Its mass is

$$m_e = 9.10938 \times 10^{-31}\,\mathrm{kg}. \tag{1.11}$$

The electron is a carrier of the negative elementary electric charge $-e$, where

$$e = 1.60218 \times 10^{-19}\,\mathrm{C}. \tag{1.12}$$

As to the spatial extension of the electron, its radius is known to be less than 10^{-18} m. There is in fact nothing in our present knowledge that conflicts the assumption that the electron is contracted into a point.

However, it is incorrect to consider the electron to be merely a charged mass point. The contraction into a point is such that it produces an anisotropy which, in a certain sense, allows us to talk about the orientation of an electron. This orientation is defined by the so-called *spin* of the electron and the magnetic dipole accompanying this spin. The spin, which we shall consider in much more detail later, is the intrinsic angular momentum of the electron. It has the magnitude $\hbar/2$ where

$$\hbar = h/2\pi \tag{1.13}$$

and h is *Planck's constant* (the quantum of action), with the numerical value

$$h = 6.62607 \times 10^{-34}\,\mathrm{J\,s}. \tag{1.14}$$

The introduction of this natural constant will be the first thing to be discussed in the following chapter.

The magnetic dipole accompanying the spin has a magnetic moment whose magnitude is almost exactly given by

$$\mu_B = e\hbar/2m_e = 9.27401 \times 10^{-24}\,\mathrm{J\,T^{-1}}. \tag{1.15}$$

This quantity is called the *Bohr magneton.*

Unlike the electron, atomic nuclei are composite particles, the constituents being protons and neutrons. The masses of the proton and the neutron are

$$m_p = 1.67262 \times 10^{-27}\,\mathrm{kg} = 1836.15\,m_e \tag{1.16}$$

and

$$m_n = 1.67493 \times 10^{-27}\,\mathrm{kg} = 1838.67\,m_e, \tag{1.17}$$

respectively. The proton carries the positive electric charge e, whereas the charge of the neutron is zero. Protons and neutrons are collectively referred to as nucleons. The number of nucleons in a nucleus consisting of Z protons and N neutrons is therefore

$$A = Z + N. \tag{1.18}$$

A is called the mass number and Z the atomic number.

Protons and neutrons are each composed of three so-called quarks and are not point-like. They both have a radius of approximately $10^{-15}\,\mathrm{m}$. The volume of a nucleus increases essentially linearly with its mass number A, and in accordance with this it is found that the approximate radius of a nucleus may be represented by the formula

$$R = 1.1 \times 10^{-15} A^{1/3}\,\mathrm{m}. \tag{1.19}$$

The nuclear surface is, however, often deformed from the spherical shape and, in addition, it should be considered as diffuse rather than sharp.

Just like the electron, a nucleon has a spin and a magnetic dipole associated with it. The spin is the same as for the electron, but the magnetic moment is three orders of magnitude smaller than that of the electron. It is expressed in terms of the so-called *nuclear magneton*

$$\mu_N = e\hbar/2m_p = 5.05078 \times 10^{-27}\,\mathrm{J\,T^{-1}}. \tag{1.20}$$

Both the spin and the magnetic dipole are vector quantities, and when the nucleus is formed, these quantities add like vectors. This implies that the resulting spin and magnetic dipole of the nucleus may be zero or only a few times larger than the spin and magnetic dipole of a free nucleon.

Electric charge is, however, a scalar quantity, and the total electric charge of a nucleus with atomic number Z is consequently Ze. Such a nucleus may bind Z electrons to form a neutral atom.

The radius of a neutral atom is of the order of 10^{-10} m. This is five orders of magnitude larger than the radius of the nucleus. In discussing the properties of the electronic cloud, it is accordingly an extremely good first approximation to consider the nucleus as point-like.

An atom, X, with only $Z - n$ electrons is referred to as the positive ion X^{n+}, and an atom, X, with $Z + n$ electrons is referred to as the negative ion X^{n-}. For a positive ion, n may take any value between 1 and Z. On the other hand, no free negative ion is known for which n is larger than one.

An atomic nucleus consists of *nucleons in interaction*. The nuclear forces that govern this interaction will not be discussed in the present text. Such a discussion belongs in the realm of nuclear physics. Hence, we shall always express nuclear properties in terms of parameters like charge, magnetic moment, and electric moments describing the shape of nuclei.

As a result of this simplification, we may now treat an atom or a molecule as a *collection of nuclei and electrons in interaction*. The forces responsible for this interaction are the electromagnetic forces between the particles.

In spite of the complexity of the problem, we shall see that quantum mechanics allows us to obtain a clear and exact description of atoms and molecules in their various internal states, on the basis of the above picture of nucleons and electrons in interaction. This description moves naturally from the smaller systems toward the larger ones. Thus, we obtain the so-called shell structure of atoms, and the picture of molecules as assemblies of atoms. But we also learn that shells in atoms, and atoms in molecules, are soft concepts that must be used with care.

1.8 External Interactions. Photons

Experimentally, one studies the structure and properties of atoms and molecules by letting them interact with each other in a vessel or a beam, and letting them interact with external media. An external medium may, for instance, be a static electric or magnetic field, or it may be a beam of free particles like electrons and neutrons. But the most widely applied external medium is electromagnetic radiation.

Electromagnetic radiation is, for instance, produced in light bulbs, electric arcs, lasers, X-ray generators, and synchrotrons. As we shall discuss it in the following chapter, it consists of *photons* of distinct energy.

Like the electron, the photon is a true elementary particle. It has a spin of magnitude $\hbar$, but its mass is zero and it has no intrinsic magnetic moment. It may have any energy, but it always moves with the speed of light which, in vacuum, is defined as

$$c = 299\,792\,458\,\mathrm{m\,s^{-1}}. \tag{1.21}$$

A photon of energy ε carries a linear momentum whose direction is the direction of propagation, and whose magnitude is

$$p = \varepsilon / c. \tag{1.22}$$

When a photon interacts with an atom or molecule, there may be three different outcomes. Thus, the photon may leave the region of interaction with its energy unchanged, but with a different direction of its momentum. Such a process is called elastic scattering. Or the energy, and hence also the magnitude of the photon's momentum, may be changed. This is the process of inelastic scattering. Finally, the photon may be destroyed as a result of the interaction. Its energy and momentum are absorbed by the atom or molecule affected. We call this an absorption process.

The reverse of the process of absorption is the process of emission, during which an atom or a molecule emits a photon and loses corresponding quanta of energy and momentum.

Although electromagnetic rays are composed of photons, and although interaction processes are elementary events that only involve one or a few photons at a time, it is usually possible to represent a ray composed of many photons by an electromagnetic wave. This is certainly the case for all situations studied in the nineteenth century. All such situations are, as we know, governed by Maxwell's equations which predict electromagnetic radiation to be true wave motion. For a ray consisting of photons with energy ε, the frequency ν that characterizes the wave is given by the relation

$$\varepsilon = h\nu. \tag{1.23}$$

The corresponding wavelength is related to the frequency through the general equation

$$\nu\lambda = c \tag{1.24}$$

which simply states that an electromagnetic wave propagates with the speed of light.

Eqs. (1.23) and (1.24) allow us to write Eq. (1.22) as

$$p = h/\lambda. \tag{1.25}$$

The remarkable *dualism* between particle properties (ε and p) and wave properties (ν and λ), expressed by Eqs.(1.23) and (1.25), is a genuine and general feature of quantum mechanics. It also plays a most fundamental role in the description of electrons and nucleons and will be properly discussed in the following chapters.

The elastic scattering of photons is observed as Rayleigh scattering and Thomson scattering, the inelastic scattering as Compton scattering and Raman scattering. The measurements of photon absorption and photon emission are called absorption and emission spectroscopy, respectively. Depending on the energy of the photons, and the nature of the atomic or molecular changes brought about through the interaction with the photons, different experimental techniques are used, and thus many different branches of spectroscopy have developed. This has, in turn, led to a natural division of the so-called *electromagnetic spectrum* into subregions.

The *spectrum* of a physical quantity is the set of values that the quantity may take. This set may be discrete or continuous, or it may have both a discrete and a continuous part. The energy of a photon may take any value between zero and infinity (in arbitrary units). The energy spectrum is accordingly continuous. It is this energy spectrum that is called the electromagnetic spectrum. It may, of course, equally well be characterized by the possible values of ν, or the possible values of λ, for the associated wave, and this is common practice. The range of values is again from zero to infinity, and so is the range for the so-called wavenumber

$$\tilde{\nu} = 1/\lambda = \varepsilon/hc \tag{1.26}$$

Table 1.1: The Electromagnetic Spectrum

λ	Spectral region
$< 10\,\text{pm}$	γ-ray
$10\,\text{pm} - 10\,\text{nm}$	X-ray
$10 - 180\,\text{nm}$	Vacuum ultraviolet
$180 - 400\,\text{nm}$	Quartz ultraviolet
$400 - 760\,\text{nm}$	Visible region
$760 - 1000\,\text{nm}$	Photographic infrared
$1 - 5\,\mu\text{m}$	Near infrared
$5 - 40\,\mu\text{m}$	Medium infrared
$40 - 400\,\mu\text{m}$	Far infrared
$> 400\,\mu\text{m}$	Micro- and radiowaves

which we already introduced in Section 1.4. It is a frequently used quantity in spectroscopy.

A coarse division of the electromagnetic spectrum into subregions is shown in Table 1.1. Each subregion may, of course, be further divided. The visible region may, for instance, be divided into subregions according to the various colors.

We shall now return to our historical approach and discuss how the study of electromagnetic radiation in equilibrium with matter led to quantum mechanics, and hence to the discovery of the photon and the dynamics that governs the behavior of the particles in the atomic and molecular world.

Supplementary Reading

The bibliography, entries [1], [2] and [3].

Problems

1.1. From your favorite physics textbook, repeat the classical description of the harmonic oscillator, i. e., a particle with mass m and position coordinate x, bound to the origin ($x = 0$) by the elastic force $F = -kx$. Set up Newton's second law and determine x as a function of time. Express the frequency of oscillation in terms of k and m.

1.2. In the atomic model suggested by J. J. Thomson (page 12), the hydrogen atom is imagined to consist of a positive charge e, uniformly distributed inside a sphere with radius R, and an electron with the negative charge $-e$, originally placed at the center of the sphere, O.

a. Write down the expression for the force acting on the electron if it is pulled out to a distance $r < R$ from O. (According to the laws of electrostatics, one may calculate this force by assuming that the positive charge inside the sphere of radius r is concentrated at O, while the positive charge outside this sphere is neglected.)

b. Show that the force just calculated is a harmonic force (Problem 1), and write down the expression for the frequency of the oscillations that the electron may execute under the influence of this force.

c. Assume that $R = 0.53 \times 10^{-10}$ m, corresponding to the radius of the first Bohr orbit defined in the following chapter. Determine the numerical value of the frequency of oscillation under this assumption. Calculate also the corresponding wavenumber $\tilde{\nu}$ and relate it to the Rydberg constant defined by Eq. (1.8).

The Thomson model has a quantum-mechanical parallel in the so-called *jellium model* which is sometimes used as a first description of large systems, for instance a crystal or a cluster of atoms. The sum of nuclear charges is uniformly distributed over the region of the crystal or the cluster. The motion of the electrons is then modelled by solving the Schrödinger equation with the electrostatic potential arising from the positive "jellium".