# 2

# On the Constitution of Atoms and Molecules

Atomic theory experienced a dramatic shift with the publication in the summer of 1913 of Niels Bohr's model of the atom. Although in some respects with roots in the Thomson tradition and 'based on the methods of mid-Victorian Cambridge physics',[1] it also marked a break with this tradition. The model initiated an entirely new and immensely fruitful development in the study of atomic, subatomic, and molecular phenomena. First of all, it made crucial use of the quantum theory of Planck and Einstein, making it clear that an understanding of atomic structure had to build on principles of a non-classical nature. How these principles related to the existing quantum theory remained unclear, but with his treatise of 1913 Bohr made a most important contribution to the process that eventually led to quantum mechanics.

Bohr's atomic theory is often conceived in a rather narrow way, essentially referring to his model of hydrogenic atoms governed by the quantum postulates of stationary states and the mechanism for emission and absorption of light by transitions from one quantum state to another. This is the historical legacy of the theory, which proved to be viable and of central importance in the construction of our current picture of the atom built on quantum mechanics. A century later, Bohr's visualizable planetary atom is still a favoured model, which for pedagogical reasons appears in physics and chemistry textbooks at high school level. However, it is important to recall that Bohr's three papers, comprising a total of 71 pages in *Philosophical Magazine*, carried the common title 'On the Constitution of Atoms and Molecules', thus indicating that the work was meant to be more than just a new physical theory of the structure of the hydrogen atom. Molecules—and thereby chemistry—were an important part of Bohr's very ambitious theory of matter, which also included aspects of radioactivity, X-rays, optics, magnetism, and more. The sequence of papers covered a broad spectrum of subjects, and only some of them successfully as seen from a later perspective.

In this chapter we shall follow the scientific path of the young Danish physicist, from his early studies at the University of Copenhagen to the publication of his so-called trilogy. Bohr did not originally have an interest in atomic structure, a subject that was foreign to him until he became a research assistant under Rutherford in the early spring

of 1912. On the other hand, his research into the electron theory of metals made him well prepared to look at atoms through different eyes to his contemporaries. Rutherford's role in the creative phase of Bohr's theory is well documented and was of the utmost importance to the ambitious Dane, who in the summer of 1912 had ready a framework for his new conception of atomic structure: what is known as the Manchester memorandum. However, it took the best part of a year before he was able to hand Rutherford the complete manuscripts of his three papers. What these papers were about will be explained in the four last sections of this chapter, which direct particular attention to those aspects that related to spectroscopy and atomic chemistry.

## 2.1 THE TRAINING OF A YOUNG PHYSICIST

Niels Henrik David Bohr was born in Copenhagen in 1885.[2] His mother, Ellen Adler, belonged to a wealthy and influential Jewish banking family, while his father, Christian Bohr, was a promising physiologist who had done postdoctoral studies in Leipzig under the anti-vitalistic German physiologist Karl Ludwig. On the basis of his innovative studies on the physiology of respiration, in 1890 he was appointed professor at Copenhagen University. Internationally recognized for his work on the exchange of oxygen and carbon dioxide between living organisms and the environment, Christian Bohr was twice nominated for the Nobel Prize in physiology or medicine. However, in neither of the cases did he receive the prestigious prize. Young Niels Bohr was raised in an intellectually stimulating environment, which not only included his father and his circle of friends from the university and the Royal Danish Academy of Sciences and Letters, but also his younger brother Harald, with whom he had and continued to have a very close relationship. While Niels pursued a career in physics, the equally bright Harald chose pure mathematics as his calling and soon became an internationally known mathematician with strong connections to David Hilbert and his famous school of mathematics in Göttingen.

In 1903 Niels Bohr enrolled at Copenhagen University to study physics as his major subject and mathematics, astronomy, and chemistry as his minor subjects. At that time Denmark could boast only a single university professor in physics. Christian Christiansen, a colleague and friend of Christian Bohr, enjoyed an international reputation both as a textbook writer and researcher. His *Elemente der Theoretischen Physik*, which appeared in 1894, was a translation of a Danish original from 1887–1889, which marked the beginning of theoretical physics in Danish science. Written in the tradition of Kirchhoff and Helmholtz, the book was remarkable for its inclusion of the most recent international research. It appeared in a revised edition as late as 1921, although by that time it was outdated.[3] As a textbook for Danish students Christiansen wrote *Lærebog i Fysik* (*Textbook in Physics*), the third edition of which formed the basis of the course he taught young Bohr and the few other physics students in Copenhagen. His most

significant contribution to physics was an experimental investigation of anomalous dispersion, a subject that came to play an important role in the electron theories of the late 1890s and later also in the new quantum theory. Another of his important experimental studies, dating from 1884, resulted in the insight that cavities with small holes provide a method to produce nearly blackbody-distributed radiation. Christiansen published these works in internationally recognized journals, such as the *Annalen der Physik und Chemie*, for which reason they attracted the attention of leading physicists including Helmholtz and Boltzmann.

Niels Bohr's view of physics was to some extent influenced by his teacher Christiansen, for whom he had great respect. As to his more general outlook and interests, he received inspiration from other sources as well. Together with his brother Harald, from whom he was inseparable, he was for several years active in a discussion group called 'Ekliptika', a circle of twelve young Copenhagen students founded in 1905. The group met regularly to read and debate a wide range of issues, many of them of a general philosophical nature. The organizer of the Ekliptika group was Edgar Rubin, who was later to become a professor of psychology. Several of the members of Ekliptika, including Niels Bohr, were influenced by the philosophy professor Harald Høffding, who at the time had won international recognition and was Denmark's best-known philosopher. Much of what Bohr knew of philosophy came to him from Høddfing, with whom he was also acquainted through his father. A great deal has been written about the controversial Bohr–Høffding relationship, especially in connection with the later complementarity principle and sometimes also the correspondence principle. The only relevance to the present context, limited as it is to early atomic theory, is the suggestion that Bohr's idea of acausal and discontinuous quantum jumps was somehow indebted to the thoughts of the famous Danish nineteenth-century existentialist philosopher Søren Kierkegaard. The influence, if there was one, was supposed to have been mediated through Høffding.[4] Suffice to say that this is a speculative hypothesis that lacks documentation as well as, in my view, plausibility. Whatever the influence of Høffding (and Kierkegaard, or other philosophers) on Bohr's later thinking, there is no reason to believe that his atomic theory of 1913 was even remotely inspired by what he happened to know of philosophy prior to that year.

While still a student in Copenhagen, Bohr published his first scientific paper, which was based on a prize problem on methods of determining the surface tension of liquids that the Danish Academy of Sciences had proposed. In early 1907 Bohr won the Academy's gold medal for his predominantly experimental research, and the following year he prepared a more elaborate version of his work for publication. His prize essay resulted in two papers, both published in the *Philosophical Transactions* of the Royal Society.[5] The first and longer of them, which appeared in early 1909, was mainly experimental, while another paper of 1910 was purely theoretical. Both of these early papers involved a heavy dose of mathematical analysis. The same year that Bohr's first paper appeared in print he completed his master's degree, which included the writing of

a paper on a problem set by the professor, Christiansen. The problem that Christiansen chose for his student dealt with the application of electron theory to explain the physical properties of metals. With a satisfactory essay and equally satisfactory oral examinations, Bohr earned his master's degree at the end of 1909. By that time he had become seriously interested in the electron theory of metals, as shown by a letter to his brother in the spring of that year: 'At the moment I am wildly enthusiastic about Lorentz's (Leiden) electron theory'.[6] This was a subject he wanted to examine in depth in a forthcoming doctoral dissertation, which at the time was the necessary entrance ticket for admission to the academic world.

The electron theory of metallic conduction was established on a new basis with an ambitious theory proposed by the Leipzig physicist Paul Drude in 1900.[7] Drude assumed the existence of electric carriers of both charges in metals, some of them free and others bound; he pictured the first as constituting a kind of gas, which could be analyzed by applying the kinetic theory of gases developed by Maxwell and Boltzmann. In this way he was able to derive a theoretical expression for the Wiedemann–Franz law established on an empirical basis in 1853. According to this law the ratio of the heat conductivity $K$ and the electrical conductivity $\sigma$ was the same for all metals at the same temperature, that is, $K/\sigma \cong$ const. In 1872 the Danish physicist Ludvig Lorenz generalized the law to $K/\sigma \cong \text{const} \times T$, where $T$ is the absolute temperature. Drude found theoretically the expression

$$\frac{K}{\sigma} = \frac{4}{3}\left(\frac{3R}{2e}\right)^2 T,$$

where $R$ denotes the gas constant and $e$ the elementary charge. He thus derived from theory the Wiedemann–Franz–Lorenz law and explained the empirical constant appearing in it.

While Drude assumed 'electrons' of both charges, within the next five years Hendrik Antoon Lorentz developed a more sophisticated theory on the assumption that the negative electrons were the only carriers of electric conduction. He further assumed that the positive particles (ions) remained fixed in the metal and that ion–electron collisions could be treated as collisions between elastic hard spheres. Although Lorentz's theory was mathematically attractive and more complete than Drude's, its empirical success was limited. For example, Lorentz derived the Wiedemann–Franz–Lorenz law, but unfortunately with a numerical factor (8/9 rather than 4/3) that made the agreement with measurements less precise. There were other empirical and conceptual problems with Lorentz's theory, such as there were with the alternative theories proposed by J. J. Thomson, William Sutherland, James Jeans, Richard Gans, and others. One of the most serious problems was its inability to account for the specific heats and their variation with temperature, a phenomenon which had been explained by Einstein in 1906 in terms of quantized thermal vibrations of the atoms. In Einstein's theory the electrons did not contribute to the specific heat.

Another of the problems related to the new and poorly understood quantum theory, which at the time essentially meant Planck's radiation law for heat radiation. Planck's experimentally confirmed law ought to be derivable from electron theory, or at least be compatible with it, but apparently it was not. To make things worse, in a lecture of 1908 Lorentz proved rigorously that existing electron theory must lead to the classical Rayleigh–Jeans law, which reproduces the observed blackbody spectrum only for long wavelengths.[8] By 1910 the electron theory of metals was a focal point for theoretical physicists—promising and at the same time intriguingly problematic. Bohr's choice of topic for his dissertation was just right.

On 13 May 1911 Bohr successfully defended his doctoral thesis, a thorough and densely written work that impressed his opponents and Denmark's small physics community. In accordance with the university statutes it was written in Danish and for this reason it was not well known, or known at all, by physicists outside Scandinavia. (Only in 1921 did it become possible to write dissertations in German, French, or English, and even then only by permission.) It had deserved better, for at the time it was the most complete and critical analysis of the electron theory of metals in the physics literature.

What makes Bohr's dissertation of more than passing interest is its comprehensiveness, its sharp critical perspective, and his acute awareness that important parts of classical physics were irreparably in trouble. It is also worth pointing out that it was a highly mathematical work and thus contradicts, like other of his early publications, the claim that Bohr was a poor mathematician.[9] Moreover, the dissertation is of interest because it provides information about what Bohr knew at the time and how he assessed contemporary physicists and problems in physics. For example, he was familiar with Thomson's *Corpuscular Theory of Matter* and thus also with the Thomson atomic model, although at the time there is no indication that he showed interest in the internal constitution of atoms. Thomson's book included two substantial chapters on the theory of metallic conduction, followed by a chapter on 'the arrangement of corpuscles in the atom' in which Thomson gave a thorough if largely qualitative account of his atomic theory. One can assume that Bohr read the former chapters with greater interest than the latter. Another physicist to whom Bohr referred in his dissertation was Einstein, whose papers of 1909 and 1910 signified that 'it seems impossible to explain the law of heat radiation if one insists upon the fundamental assumptions underlying the electromagnetic theory'. Bohr continued:

> This is presumably due to the circumstance that the electromagnetic theory is not in accordance with the real conditions and can only give correct results when applied to a large number of electrons (as are present in ordinary bodies) or to determine the average motion of a single electron over comparatively long intervals of time (such as in the calculation of the motion of cathode rays) but cannot be used to examine the motion of a single electron within short intervals of time.[10]

The problem with the electromagnetic theory was that it did not apply to the interaction between electrons or interactions between electrons and the radiation field. On the other hand, Bohr never doubted that the theory was valid for the radiation field itself.

The aim of Bohr's thesis was, as he said, 'to carry out the calculations for the various phenomena that are explained by the presence of free electrons in metals in as great generality as possible, while retaining the fundamental points of view underlying the theory of Lorentz'. While he admitted Lorentz's theory to be 'mathematically very perfect', he also noted that 'the physical assumptions on which it is based can hardly be expected to be valid, even approximately, for actual metals'.[11] His extension of the existing theory consisted in part in assuming that the force between ions and electrons varied with the distance according to $r^{-n}$, where $n$ is arbitrary. With this generalization he was able to improve on some of Lorentz's results. More importantly, he realized that several phenomena were outside the reach of the electron theory, irrespective of its degree of sophistication and level of generality. There was something seriously wrong—something fundamental. In the introduction he wrote that there were

> . . . many properties of bodies impossible to explain if one assumes that the forces which act within the individual molecules . . . are of such a kind [mechanical]. Apart from several generally known examples of this, for instance calculations of the heat capacity of bodies and of the law of heat radiation for short wavelengths, in what follows we shall encounter another example of it, namely in our discussion of the magnetic properties of bodies.[12]

Bohr discussed at length the problems of magnetism, namely that neither free nor bound electrons contributed to the magnetic properties of matter, at least not to diamagnetism. This he considered a crucial failure, and he returned to it in the very last sentence of the thesis: 'It does not seem possible, at the present stage of development of the electron theory, to explain the magnetic properties of bodies from this theory'.[13] Bohr realized that the classical laws of physics were inadequate when applied to rapidly moving electrons, but he did not yet relate the difficulties to the structure of atoms, a topic he does not seem to have been interested in at the time.

Bohr had effectively discovered that according to classical statistical mechanics the net magnetization of a collection of electrons in equilibrium will vanish. It follows that classical physics cannot account for magnetism, whatever its form. The importance of this insight was not noticed at the time, although to Bohr it indicated that magnetism was a quantum phenomenon. Only in 1921 did the Dutch physicist Hendrika J. van Leeuwen independently rediscover what in modern physics literature is referred to as the Bohr–van Leeuwen theorem.[14]

For Bohr, now a doctor of philosophy ('dr. phil.'), it was natural to continue his studies into the electron theory abroad, and his chosen destination was Cambridge, where Thomson resided. Although critical of Thomson's electron theory of metallic conduction, he had the greatest admiration for the famous English physicist who, so he said in his dissertation, 'has contributed so much to the *experimental* foundation of electron theory'.[15] Financed by a stipend from the Carlsberg Foundation, in September

1911 Bohr arrived in Cambridge, eager to work with Thomson and secure his career in theoretical physics.

## 2.2 FROM CAMBRIDGE TO MANCHESTER

Bohr's stay in Cambridge did not live up to his high expectations. In an interview shortly before his death in 1962, he recalled the period as 'absolutely useless'.[16] This must be considered an exaggeration, but on the other hand there is no doubt that after a month or two his initial enthusiasm had evaporated and been replaced by a growing disappointment. J. J. Thomson, his hero, showed little interest in the ideas of the young and awkward Dane. Thomson's primary research field was no longer the electron theory of metals but exciting experiments with positive rays, which were of an entirely different nature and far from Bohr's interests. The busy director of the Cavendish Laboratory did not particularly welcome the fact that his new research student criticized his work on conduction in metals. In a long and informative letter of 1 December 1911 to Carl Wilhelm Oseen, a young Swedish physics professor with whom Bohr had close relations, Bohr pointed out a serious error in Thomson's theory: 'I mentioned it to Thomson three weeks ago. He said he would think about it, but I have not heard from him since'.[17] The Bohr brothers had first met Oseen in the summer of 1911 at a congress of Scandinavian mathematicians in Copenhagen. The Swedish physicist, who had read Niels Bohr's dissertation with interest (as a Swede he had no difficulties with the Danish language), was among the first to recognize the genius of his colleague in Copenhagen.

Nor was Thomson seriously interested in the complex arguments of Bohr's dissertation: 'Thomson has so little time; I gave him the [translation of the] dissertation when I came, but he hasn't read it yet. I have only talked with him a few moments about certain points, and I don't yet know whether he will agree with me or not'.[18] The fruitless and time-consuming efforts to get the dissertation published in English was a constant source of worry for him, both in Cambridge and during his subsequent stay in Manchester. He attempted to get it published first by the Royal Society and then by the Cambridge Philosophical Society, but none of these plans worked out.[19] In spite of his lack of fruitful interaction with Thomson, he continued to value him. Thus after having visited Rutherford he wrote in a letter to his fiancée, Margrethe Nørlund, that Rutherford was not quite of the same caliber as the Cavendish physicist: 'J. J. Thomson is a tremendously great man, and I have learnt such an enormous amount from his lectures; I like him so much . . . '[20]

Although Bohr's stay in Cambridge was far from what he had looked forward to, it was not quite as 'absolutely useless' as he recalled late in life. For one thing, he attended lectures by Thomson, Larmor, and Jeans, although at the time he did not speak with either Larmor or Jeans. More importantly, he established contacts with several

physicists of the younger generation who shared some of his own research interests. One of them was Australian-born William Lawrence Bragg, who was Bohr's junior by five years and in 1915 would become the youngest Nobel laureate ever. At the time a student in Cambridge, Bragg followed some of the same courses as Bohr, including Jeans' course on statistical mechanics and radiation theory. He happened to meet Bohr after one of Jeans' lectures, a meeting he reported to his father, William Henry Bragg: 'I got an awful lot from a Dane who had seen me asking Jeans questions, and after the lecture came up to me and talked over the whole thing. He was awfully sound on it, and most interesting, his name was Böhr, or something that sounds like it'.[21] In later recollections Bragg wrote: 'J. J. Thomson gave us stimulating fireworks. I also got very excited over some lectures of Jeans, because they opened up a new world of statistical mechanics. After them a strange young man used to draw me aside and explain at enormous length just where Jeans was wrong. This was Bohr!'[22]

During his stay in Cambridge Bohr also met with Nicholson and the Birmingham physicist Samuel McLaren, both of whom had recently published papers on the electron theory of metals. Whereas Bohr praised the methods used by McLaren as 'extremely interesting', he bluntly dismissed Nicholson's paper as 'perfectly crazy'. About his conversation with Nicholson, he wrote to Oseen: 'He was extremely kind, but with him I shall hardly be able to agree about very much'.[23] At that time Nicholson had just published his atomic theory, but apparently the subject did not enter their conversation. Bohr only became aware of Nicholson's planetary theory of atoms about a year later, as we shall see in Section 2.3.

Bohr's letter to Oseen ended with a remark of considerable interest. 'At the moment I am very enthusiastic about the quantum theory (I mean its experimental aspects)', he wrote; 'but I am not yet sure if this is not because of lack of knowledge; the same I can say, but only to a still higher degree, about my relation to the magneton theory'. The 'magneton' Bohr referred to was a unit magnetic moment $M_0$ that the French physicist Pierre Weiss, director of the physics laboratory at the Zurich Polytechnic, had recently introduced as a way to explain his measurements of the magnetic properties of various salts.[24] Weiss's hypothesis of the magneton as a physical reality, and not merely a number, aroused immediate interest. It was discussed during the Solvay congress from 30 October to 3 November 1911, where Paul Langevin, interpreting it in terms of revolving electrons and linking it to Planck's constant, derived an expression of $M_0$ in rough agreement with Weiss's experimental data. The Weiss–Langevin magneton was the quantity

$$M_0 = \frac{e}{12mc}\frac{h}{2\pi}.$$

Bohr, who was aware of the Solvay discussions, may have been thinking along similar lines.[25] For an orbiting electron the magnetic moment is given by $M = (e/2mc)L$, where $L$ is the angular momentum and $e$ the charge of the electron. Bohr hinted at a connection between the magneton and the quantum of action, possibly by applying

Planck's relation to the kinetic energy $E_k$ of the orbiting electron; that is, $E_k = h\nu$. Now the kinetic energy and angular momentum of a circulating electron are related as $E_k = \pi\nu L$, where $\nu$ is the orbital frequency. It then follows that the magneton is

$$M_0 = \frac{e}{2mc}L = \frac{e}{mc}\frac{h}{2\pi},$$

or twelve times the Weiss–Langevin magneton. Bohr may have seen the discreteness of $M$ and $L$ as a possible solution to the dilemma of the existing electron theory of metals, namely its inability to account for magnetism. What is presently known as the Bohr magneton, a quantity first defined by 20-year-old Wolfgang Pauli in 1920, is one half of the magneton considered by Bohr in 1912.[26]

In March 1912 Bohr terminated his stay in Cambridge and moved to Manchester to do research under Rutherford, whom he had first seen at a dinner in the Cavendish Laboratory in October 1911. The following month, while spending a weekend in Manchester with the physiologist James Lorrain Smith, a friend of Bohr's father, he got a chance to meet Rutherford personally.[27] On this occasion the two physicists talked about the recent Solvay conference, but not about Rutherford's nuclear atom. The transfer to Manchester was not motivated by a desire to work on atomic structure, radioactivity, or any of the other topics that Rutherford and his group cultivated so successfully. In the spring of 1912 the main focus of Bohr's mind was still on the electron theory of metals, not on the structure of the nuclear atom. On the other hand, in Manchester he also worked experimentally on radioactivity, a subject he soon came to see as closely related to the structure of the atom. In this line of work he received much help and inspiration from George von Hevesy, a Hungarian physical chemist who worked in Rutherford's group and with whom Bohr established a lifelong friendship.

'I remember, as if it were yesterday', Bohr said in his Faraday Lecture of 1930, 'the enthusiasm with which the new prospects for the whole of physical and chemical science, opened by the discovery of the atomic nucleus, were discussed in the spring of 1912 among the pupils of Rutherford'.[28] More clearly than other scientists at the time, Bohr realized that while radioactive disintegration was rooted in the nucleus, the ordinary physical and chemical properties of matter had to be explained by the surrounding system of electrons. The general view in Manchester was that beta particles had their origin in the extra-nuclear cluster of electrons,[29] but this was not a view shared by Bohr. He believed that they came from the nucleus, as he argued in public in his trilogy of 1913 (see Section 2.7). Moreover, he came to the conclusion that while in alpha decay a radioactive element descends in the periodic system by two units, in beta decay it raises by one unit (in terms of the atomic number, $\Delta Z = -2$ and $\Delta Z = 1$). At about the same time similar ideas were suggested by Soddy, Fajans, and a few other scientists, but without associating them with Rutherford's nuclear model as Bohr did.

On the other hand, Hevesy, who in the autumn of 1912 investigated the chemical properties of elements involved in radioactive transformations, was acquainted with and sympathetic to the ideas of Rutherford and Bohr. He was consequently inclined to interpret his results in accordance with these ideas. In January 1913 he wrote to Bohr regarding a new paper he had written on the valencies of radioactive elements: '*Where* do these [alpha and beta] particles come from, was the question you were so much occupied with .... My results seem to support the view that they stem from the interior of the atoms'.[30] He further commented in a somewhat surprising way on Bohr's new version of the hydrogen atom. Hevesy could understand how an atom with many electrons arranged in rings could be in an equilibrium state, but 'How can a positive atomic nucleus and *one* rotating electron be in equilibrium? I cannot imagine at all what would prevent the electron from falling into the centre of the atom?' In his letter of reply Bohr expressed his agreement with Hevesy's suggestion that radioactivity was purely a nuclear phenomenon:

> The beautiful results were exactly what I had expected according to the point of view I hold on the constitution of the atoms... By the phenomena of radioactivity we observe an explosion of the nuclei ... the chemical and physical properties of the new elements formed will only depend of the charge of the new nuclei; which latter again will depend on the charge of the rays expelled. The latter relation is just the one you have found in your experiments; and your results were therefore what I had expected and hoped.[31]

In a letter to Fajans from the spring of 1913, Rutherford informed him about the ongoing work of the Danish physicist: 'Bohr of Copenhagen has been working at the general theory of atoms built on my model and appears to have made definite progress.... He is a very capable fellow, and there will soon appear a very interesting paper by him in the Phil. Mag'.[32] In fact, it was only after having studied Bohr's very interesting paper that Fajans became convinced of the truth of the nuclear atom. In a letter to Rutherford of 13 December 1913 he said: 'I have followed Bohr's papers with extraordinary interest, and now I no longer doubt the complete correctness of your atomic theory. The reservations I expressed in my last letter have been entirely removed by Bohr's work'.[33]

It is difficult to know precisely what Bohr's thoughts were on these matters since he only published them over a year later, when he included them in the second part of his great trilogy. Concerning the relationship between radioactivity and the periodic system, Hevesy said in a letter of October 1913: 'Though [Alexander] Russell was already interested in the problem and I started the valency experiments when Bohr came to Manchester, no doubt he encouraged us both very much and if we trace the origin of the above ideas to their origin, we will find them in Bohr's mind, as pointed out to me by himself in his usual modest way'.[34] In fact, Bohr wanted to publish his innovative ideas in 1912, but was dissuaded by Rutherford who 'warned with characteristic caution against overstressing the bearing of the atomic model and extrapolating from comparatively meagre experimental data'.[35]

What really changed Bohr's mind in the direction of atomic structure was not so much radioactivity as it was absorption theory. The change was to a large extent caused by a paper on the absorption of alpha particles written by Charles Galton Darwin, a 25-year-old theorist working with Rutherford (and a grandson of *the* Charles Darwin, of evolution fame). The aim of Darwin's paper was to examine theoretically the energy loss of alpha particles as they were absorbed in or scattered on thin metal foils and air. Naturally for a Manchester physicist (but not for other physicists) he adopted Rutherford's nuclear model, which 'supposes the atom to consist of a cluster of electrons held by an unknown field of forces round a central charge'.[36] As to the cluster of electrons he made parallel calculations assuming that they were either distributed homogeneously in a spherical atomic volume or over the surface of the sphere. Darwin's analysis rested on a couple of further assumptions, in particular that the atomic electrons could to a good approximation be considered to be free. Contrary to scattering, which was thought to be due to the nucleus, the free electrons were chiefly responsible for the absorption.

The result of Darwin's analysis was a formula for the loss of energy that included two atomic parameters: the atomic radius and the number of electrons outside the nucleus. Comparing the formula with experimental data he obtained a rough agreement, but not one that was quantitatively convincing. For example, he found atomic radii that decreased with atomic weight and differed substantially from the commonly accepted values derived from the kinetic theory of gases. Assuming the hydrogen atom to contain only one electron, his formula resulted in an atomic radius of about $5 \times 10^{-8}$ cm, an order of magnitude too large.

In a letter to Harald of 12 June Bohr reported that Darwin's theory was 'very unsatisfactory in the basic conception', although not in its reliance on the nuclear atom to which he referred for the first time: 'In the last few years he [Rutherford] has worked out a theory of atomic structure which seems to have a much more solid basis than anything that we had formerly'.[37] Only a week later, in another letter to his brother, Bohr explained that he was now working on atomic structure and what he had found so far was 'perhaps a little bit of reality'.[38] Sensing that his ideas were important and that other physicists might be on the same track, he was 'eager to finish it in a hurry'. However, his critical improvement of Darwin's absorption theory proved more difficult than expected and only reached completion after he had left Manchester and returned to Copenhagen. The paper, communicated to *Philosophical Magazine* by Rutherford, was dated August 1912 but it took until January 1913 before it appeared in print.

Bohr objected to Darwin's theory that the loss of velocity of an alpha particle would depend on the motion of the electrons during the collision and, for this reason, the electrons could not be considered as free. Instead he treated the electrons as bound to the nucleus by an elastic force, hence oscillating with characteristic frequencies. As he saw it, it should be possible to get 'information about the internal structure of atoms' from the experimentally determined velocity loss of alpha particles, namely information in the form of frequencies. Importantly, he related the frequency of the oscillators to Planck's quantum hypothesis:

> According to Planck's theory of radiation we further have that the smallest quantity of energy which can be radiated out from an atomic vibrator is equal to $v \cdot k$, where $v$ is the number of vibrations per second and $k = 6.55 \cdot 10^{-27}$. This quantity must be expected to be equal to, or at least of the same order of magnitude as, the kinetic energy of an electron just sufficient to excite the radiation.[39]

The quantity $k$ is obviously Planck's constant, which was usually denoted $h$. From an empirical point of view Bohr's theory was an improvement over Darwin's, although its agreement with experiments was far from perfect. Relying on data for dispersion and refraction in gases obtained by Clive and Maude Cuthbertson at University College, London, he concluded 'with great certainty' that a hydrogen atom contained only one electron and helium two electrons. This he interpreted as support of Rutherford's nuclear atom:

> The value $r = 2$ for the number of electrons in a helium atom, indicated by experiments on dispersion and on absorption of $\alpha$-rays, is what we, adopting Rutherford's theory of atoms, necessarily must conclude from the behaviour of $\alpha$-rays, according to which helium atoms formed from $\alpha$-particles will contain 2 electrons outside the central nucleus.[40]

Bohr was aware that this number of electrons in helium did not agree with the value inferred from Drude's dispersion theory of 1904, from which he calculated $r = 2.3$. However, as he wrote in a letter to Clive Cuthbertson: 'As to the question of the interpre[ta]tion of the result according to Drude's theory, I am of the opinion . . . that the number of electrons per atom calculated from the theory need not to be whole numbers, as the theory in question uses assumptions as to the motions of the electrons which hardly are fulfilled in the actual atoms'.[41] By that time Bohr had reached the conclusion that atomic electrons did not perform mechanical oscillations, as assumed in Drude's theory, but that dispersion was a quantum phenomenon to be explained in terms of transitions between stationary energy states.

Apart from hydrogen and helium, for the lighter atoms Bohr obtained reasonably good values for the number of electrons, such as 14 for aluminium and 18 for molecular oxygen, to be compared with $A/2 = 13.5$ and $A = 16$. For the heavier elements the agreement was less satisfactory: tin = 38, gold = 61, and lead = 65, as compared to $A/2 = 59.3$, 98.5, and 103.5, respectively.

## 2.3 THE MANCHESTER MEMORANDUM

In late June and early July 1912, shortly before returning to Copenhagen, Bohr prepared a draft document in which he summarized in a rather sketchy fashion his most recent ideas about atomic structure. He may have sent it to Rutherford on 6 July, for a short letter of that date says that 'I send the remarks concerning the structure and stability of molecules for which you kindly asked'.[42] The handwritten notes, consisting of six sheets of paper and often referred to as the Manchester memorandum, were evidently written

in haste. They carried the title 'On the Constitution of Atoms and Molecules', the very same title that he chose for the trilogy of articles that appeared in *Philosophical Magazine* a year later.[43] In this important document the structure and stability of atomic systems were indeed the key issues.

Bohr started by briefly outlining Rutherford's atomic model, or rather his own version of it—a positive nucleus surrounded by one or more rings of electrons. (Rutherford had not suggested a ring model.) He then noticed that in such an atom mechanical stability requires the electrons to be rotating around the nucleus. 'By an analysis analogous to the one used by Sir J. J. Thomson', he said, 'it can very simply be shown that a ring [such] as the one in question possesses no stability in the ordinary mechanical sense . . . and the question of stability may [must] therefore be treated from a quite different point of view'.[44] It should be emphasized that the 'question of stability' dealt with by Bohr in the memorandum was restricted to mechanical stability. He did not mention the radiation instability caused by the accelerating electrons, although he was undoubtedly aware of it. Radiative instability would soon become an important issue, but by the summer of 1912 this was not yet the case (Figure 2.1).

Not only did Bohr find that the Rutherford ring atom was mechanically unstable, he also noticed that it had no characteristic radius to define the size of the atom. 'There is nothing to determine a quantity of dimension, a "length" ', and nothing 'to allow from mechanical considerations to discriminate between the different radii and times of vibration [rotation].' Considering a ring determined only by the charge of the nucleus and the number of electrons, he wrote that it 'can rotate with an infinitely great number of different times of rotation, according to the assumed different radius of the ring; and there seems to be nothing . . . to allow from mechanical considerations to discriminate between the different radii and times of vibration'. This was an important point, for all experience indicates that the size of real atoms does not vary arbitrarily, and nor does the frequency of the radiation they emit. Without providing calculations, Bohr discussed how many electrons a single ring could contain before its became unstable. It is 'immediately seen', he said, that the number is seven, for this is the largest number for which the total energy of an electron (the sum of the kinetic energy and the potential energy) remains negative and thus allows it to be in a bound state with the nucleus.

> This, together with the fact that inner rings of electrons in Prof. Rutherford's atom-model will have only very little influence (and always to the worse) on the stability of outer rings seems to be a very strong indication of a possible explanation of the periodic law of the chemical properties of the elements (the chemical properties are assumed to depend on the stability of the outermost ring, the 'valence electrons') by help of the atom-model in question.

That is, Bohr argued that because the addition of electrons within a ring would reduce its stability, the building up of the electron system would at some stages occur with the formation of a new external ring. This idea connected the outermost electrons with the valence of the elements in an attractive way, in contrast to the case in Thomson's

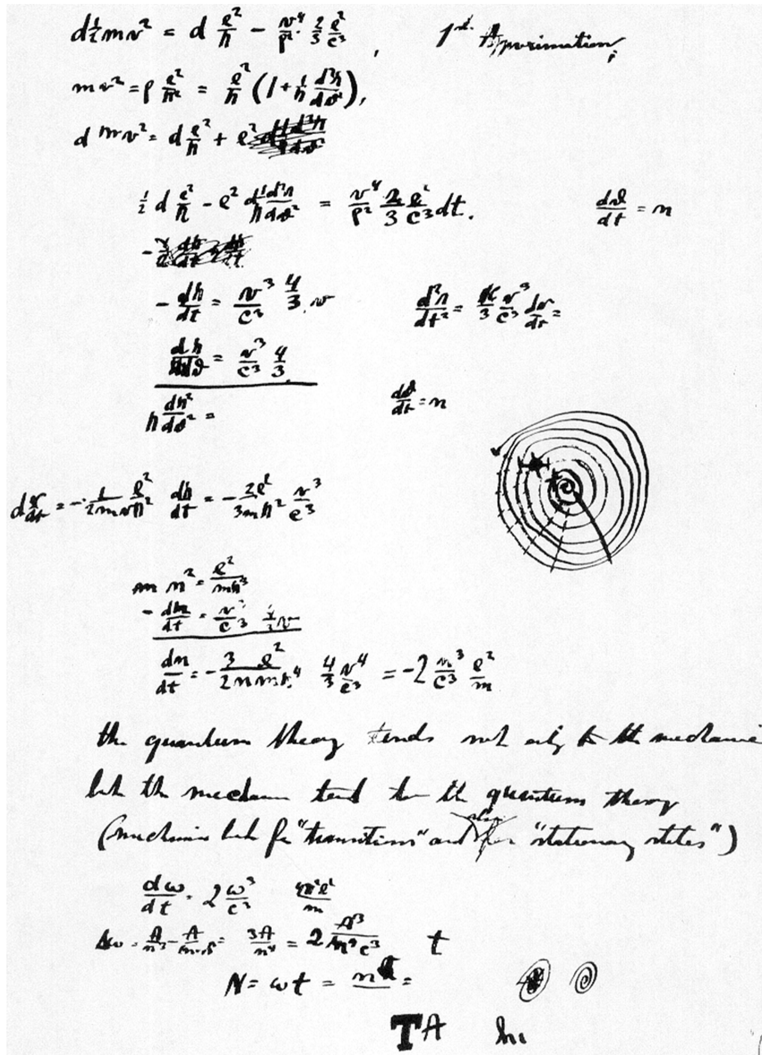

**Fig. 2.1.** Bohr's draft calculations from 1913 of the radiation emitted by a rotating electron, causing it to spiral towards the nucleus. The sentence reads: 'The quantum theory tends not only to the mechanics but the mechanics tend to the quantum theory (mechanics both for "transitions" and for "stationary states")'.

model of the atom. Recall that in the Thomson atom valency and other chemical properties were assumed to depend on the number of electrons in the internal rings. Bohr realized the advantage of his scheme over that of Thomson, as he explained in a footnote: 'The difference in this respect between the atom-model considered and J. J. Thomson's atom-model is very striking, and seems to make it impossible to give a satisfactory explanation of the periodic law from the last mentioned atom-model'.

With regard to the problem of fixing a definite size of the atom, Bohr felt it necessary to introduce a new hypothesis:

> This hypothesis is: that there, for any stable ring (any ring occurring in the natural atoms), will be a definite ratio between the kinetic energy of any electron in the ring and the time [frequency] of rotation. This hypothesis, for which there will be given no attempt of a mechanical foundation (as it seems hopeless), is chosen as the only one which seems to offer a possibility of an explanation of the whole group of experimental results which gather about and seem to confirm conceptions of the mechanism of the radiation as the ones proposed by Planck and Einstein.

In agreement with what he had already stated in his dissertation of 1911, he added that classical mechanics was known to fail in the domain of atoms: 'It seems to be rigorously proved that the mechanics is not able to explain the experimental facts in problems dealing with single atoms'. Bohr explained his special hypothesis in connection with his discussion of the hydrogen molecule, stating it in the Planck-like form

$$E = K\nu,$$

where $E$ denotes the kinetic energy of an electron moving in a ring with radius $r$, given by $E = \frac{1}{2}mv^2 = \frac{1}{2}m(2\pi\nu r)^2$. $K$ is a new constant and $\nu$ denotes the electron's frequency of revolution. Bohr's relation $E = K\nu$ is of course very similar to Planck's formula, but nowhere in the memorandum did Bohr indicate the value of $K$; nor is there any reason to suspect that he knew it, except that he assumed $K \approx h$. However, it is quite likely that he adopted the relationship $K \cong 0.6h$ and that he based it on empirical data.[45] Only in his paper of 1913 did he provide theoretical arguments that $K = \frac{1}{2}h$.

For a ring in a state of equilibrium the centrifugal and attractive forces must be the same, meaning that

$$m(2\pi\nu)^2 r = X\frac{e^2}{r^2},$$

where $X = 1$ if there is only a single electron and $X > 1$ for more electrons. For example, Bohr calculated $X = 1.75$ for the helium atom and $X = 1.049$ for the hydrogen molecule. The equation does not determine the radius or the frequency, but only the product $r^3\nu^2$ of the two quantities. Introducing the $E = K\nu$ hypothesis yields expressions for $r$ and $\nu$ that depend only on the constant $K$, the computable factor $X$, and the atomic constants $m$ and $e$. It also leads to an expression for the work required to remove an electron from the ring, namely

$$W = X^2 \frac{me^4\pi^2}{2K^2}.$$

Bohr did not write down this expression, but he stated that for one mole of matter 'the energy of a system containing a ring of $n$ electrons acted on by a central force $e^2/r^2X$ is

equal to $-nX^2A$, where $A$ is approximately equal to $1.3 \times 10^{-11}$ erg and $NA = 1.9 \times 10^5$ cal'. The quantity $N$ denotes Avogadro's number, close to $6 \times 10^{23}$, and 1 erg = $10^{-7}$ J = $0.24 \times 10^{-7}$ cal. The formula enabled him to calculate the heat released when two moles of hydrogen atoms combine into one mole of diatomic molecules according to $H + H \rightarrow H_2$. The value he obtained, $3.8 \times 10^4$ cal, was of the right order of magnitude. Using the same kind of reasoning, he calculated that the corresponding process for helium, $He + He \rightarrow He_2$, would be endothermic by about $3 \times 10^5$ cal, implying that diatomic helium molecules cannot exist in nature. This agreed with experimental knowledge, as no such molecules had ever been detected. Bohr further proposed electronic structures—'figurations' as he called them—for the molecules $O_2$ and $O_3$, and also for the compounds $H_2O$, $CH_4$, and $C_2H_2$, but in these cases only in qualitative versions (see also Sections 2.4 and 2.6).

The stability and heat of formation of simple compounds such as $H_2$ constituted one class of phenomena that Bohr thought provided support for his ideas of atomic structure. Ever careful to connect his theoretical ideas with experimental data he cited three other relevant relations:

1. the periodic variation of the atomic volume, meaning the ratio between atomic weight and density, that the German chemist Lothar Meyer had first demonstrated in 1870—this variation could be qualitatively understood on the basis of Bohr's assumption that external electron rings were successively added to the atom as it grew heavier;
2. 'Whiddington's law', due to the Cambridge physicist Richard Whiddington, according to which the minimum velocity of electrons capable of exciting characteristic X-rays was proportional to the element's atomic weight;
3. 'Bragg's law', named after W. Henry Bragg, that the stopping power of metal foils for alpha rays was approximately proportional to the square root of the atomic weight.

Bohr did not account for these laws in the memorandum, but he would return to them in his published paper of the following year. Parts II and III of his trilogy were to a large extent elaborations of issues dealt with in the 1912 memorandum to Rutherford.

In general the Manchester memorandum was full of ideas, which were, however, sketches and proposals rather than explicitly worked out. The only exception was the case of the hydrogen molecule, which at the time could not be compared with experiments on the heat of formation. The main message of the memorandum was that the stability of the atom required the introduction of quantum considerations, as preliminarily given by the $E = K\nu$ hypothesis.

Soon after having returned to Copenhagen Bohr became the teaching assistant to Martin Knudsen, the new professor of physics who had been appointed after Christiansen's retirement. Knudsen was internationally known for his experimental investigations of gases at very low pressure and one of the chosen few who had been invited to the 1911 Solvay meeting where the quantum theory had been the main issue. However,

he had no interest in the new quantum theory or, for that matter, in other areas of theoretical physics that occupied the mind of Bohr, some fourteen years younger.[46] Busy with his duties as lecturer and teaching assistant, Bohr had little time to develop the ideas that had germinated during his fruitful stay in Manchester. In a letter to Rutherford of 4 November 1912 he expressed the hope of finishing his 'paper on the atoms' in a few weeks, but this turned out to be much too optimistic. Among the reasons for the delay were not only his teaching obligations, but also that he kept changing the plan and content of his paper as he came across new experiments and theories of relevance to it.

One of the problems concerned the number of electrons in the simplest atoms and their relation to dispersion data, about which he wrote to Rutherford on 6 July 1912: 'I saw some difficulties in the explanation of the experimental results concerning the dispersion, which I had not seen before'.[47] The difficulties were not easily solved, and Bohr returned to them four months later:

> I have made some progres[s] with regard to the question of the dispersion. The number of electrons in a Hydrogen- and a Helium-atom calculated from the dispersion seems thus to work out nearer to respectively 1 and 2, if the forces acting on the electrons are assumed to vary inversely as the square of the distance, than if they, as in Drude's theory, are assumed to be of the elastic type. I have however just in this calculation met with some serious trouble arising from the instability of the system in question which has not allowed the execution of the calculation in the extension desirable.[48]

Bohr found that the use of a Coulomb force instead of an elastic force was insufficient to give the right number of electrons in both hydrogen and helium, and it took him some time to obtain a reasonably satisfactory solution. 'My suggestion is now', he reported to Rutherford in a letter of June 1913, 'that the frequency of vibration perpendicular to the plane of the ring (which frequency according to the theory can be calculated on the ordinary mechanics) in a hydrogen-molecule is of the same order of magnitude as the frequencies in the plane of the ring, but in a helium-atom much greater and therefore of no sensible influence on the dispersion'.[49]

Importantly, at the end of 1912 Bohr became aware of Nicholson's atomic theory, realizing its disturbing similarity to his own view of the constitution of the atom. At first he thought that the two theories could not both be right, presumably because the radii and frequencies deduced by Nicholson were so very different from those he found on his own model. However, he soon reached a different conclusion. As he wrote in a Christmas postcard to his brother Harald, Nicholson's theory was not incompatible with his own but rather stood in a complementary relationship to it. 'For, the latter's [Bohr's] calculations should be valid for the final or classical state of the atoms, while Nicholson seems to be concerned with the atoms while they radiate, i.e., while the electrons are about to lose their energy, before they have occupied their final positions.'[50] This is also what he said in a letter to Rutherford about a month later, where he pointed out the similarities and dissimilarities between the two conceptions of the nuclear atom:

> In his calculations, Nicholson deals, as I, with systems of the same constitution as your atom-model; and in determining the dimensions and the energy of the systems he, as I, seeks a basis in the relation between the energy and the frequency suggested by Planck's theory of radiation. The state of the systems considered in my calculations are however—between states in conformity with the relation in question—characterized as the one in which the systems possess the smallest possible amount of energy, i.e. the one by the formation of which the greatest possible amount of energy is radiated away. It seems therefore to me to be a reasonable hypothesis, to assume that the state of the systems considered in my calculations is to be identified with that of the atoms in their permanent (natural) state . . . According to the hypothesis in question the states of the systems considered by Nicholson are, contrary, of a less stable character; they are states passed during the formation of the atoms, and are states in which the energy corresponding to the lines in the spectrum characteristic for the element in question is radiated out.[51]

Bohr emphasized the difference between Nicholson's theory, which was essentially concerned with the spectra and formation of atoms, and his own theory dealing with the permanent state of atoms: 'I do not at all deal with the question of calculation of the frequencies corresponding to the lines in the visible spectrum'. Considering the nature and content of Bohr's theory as it appeared in print half a year later, this is a most remarkable statement. But notice that Bohr does not speak of spectral lines in general, only of those in the visible part of the spectrum.[52]

Only in mid-February 1913 did Bohr realize that his ideas of atomic constitution could be fruitfully extended to a theory of light emission. A letter to Hevesy dated 7 February reveals no sign of change but merely summarizes Bohr's ideas as stated in the Manchester memorandum. Although in this letter Bohr relates the energy of the radiation emitted during the binding of an electron and 'the frequency of rotation of the electron considered in its final orbit' in the form $E = h\nu$, this does not amount to a quantum theory of light emission. For Bohr adds that the constant in front of the frequency 'is not exactly equal to Planck's constant, but differ[s] from it by a numerical factor'.[53] Thus in the early days of February 1913 Bohr's picture of the radiation mechanism was still essentially classical and in line with the commonly accepted view. This view was that the spectral lines are produced by electrons vibrating or rotating with the same frequencies that appear in the spectrum. The mechanical frequencies of atomic oscillators—at the time generally taken to be electrons—correspond to the optical frequencies. Bohr's view was also fairly orthodox in another respect, since he thought that atoms must be ionized or dissociated before they would emit radiation.

'As soon as I saw Balmer's formula, the whole thing was immediately clear to me'.[54] This was what Bohr told Léon Rosenfeld, his later assistant and close collaborator, and what he said at several other occasions. The spectral laws of Balmer and Rydberg were well known and frequently discussed during the first decade of the century. They not only appeared in scientific papers but also in textbooks, one of

them being the textbook by Christiansen that Bohr used while a student (Figure 2.2).[55] Here the formula of the Swiss schoolteacher Johann J. Balmer, dating from 1884, was stated in the standard form

$$\lambda = A \frac{n^2}{n^2 - 4},$$

with $A = 3647$ Å and $n = 3, 4, \ldots$ It is therefore remarkable that Bohr insisted that he did not know about the formula before he was made aware of it by his colleague Hans Marius Hansen in February 1913. In an interview shortly before his death, he recalled:

> I didn't know anything about the spectral formulae. Then I looked it up . . . I discovered it, you see. Other people knew about it, but I discovered it for myself. And I found then that there was this very simple thing about the hydrogen spectrum. I was just reading the book of Stark, and at that moment I felt now we will just see how the spectrum comes.[56]

Bohr might not have 'known' Balmer's formula in the sense that he took notice of it as relevant for his own work, but it is most unlikely that he was literally unaware of it. Although he had undoubtedly seen the formula, he might have forgotten about it. At any rate, as far as we can tell it was during a conversation with Hansen that he realized its significance. According to one of the versions of Balmer's formula, the frequencies of the visible lines in the hydrogen spectrum can be written as

$$\nu = cR\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \; n = 3, 4, \ldots$$

where $R$ is the empirical Rydberg's constant. Around 1910 it was known that Balmer's formula could be extended to other series in the hydrogen spectrum, and some spectroscopists followed the Swiss physicist Walther Ritz in suspecting a generalized formula of the form $\nu = cR(1/m^2 - 1/n^2)$, $n > m$.[57] Balmer's formula was an eye-opener to Bohr, who immediately realized that it could be interpreted as the difference between two energy terms. Not only did Balmer's formula indicate as much in the case of hydrogen, but Rydberg had also shown that the frequencies of various spectral series could be expressed as the difference between two spectral terms, namely in the form

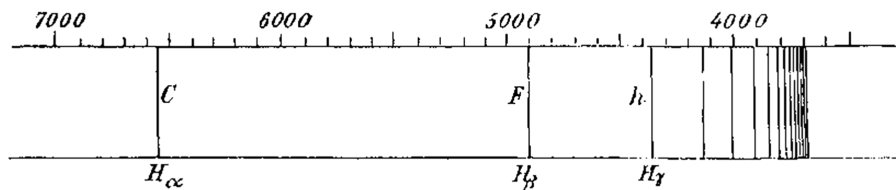


**Fig. 2.2.** The Balmer spectrum as reproduced in the 1910 edition of C. Christiansen's textbook in physics, which Bohr had studied. The same illustration was used in Kramers and Holst 1923, p. 58. *Source*: Christiansen 1910, p. 354.

$$\nu = \frac{cR}{(1+p_1)^2} - \frac{cR}{(m+p_2)^2},$$

where $m = 2, 3, 4, \ldots$ and $p_1$ and $p_2$ are constants that characterize the series and the element in question. Formulae of this kind were discussed in Stark's *Atomdynamik*, where Bohr may have met them. We do not know precisely how he reasoned,[58] but as early as 6 March he sent a letter to Rutherford that included a revised first part of his paper. In contrast to the earlier drafts and letters, the new version was 'mainly dealing with the problem of emission of line spectra', as he informed Rutherford. Bohr continued:

> I have tried to show that it from such a point of view seems possible to give a simple interpretation of the law of the spectrum of hydrogen, and that the calculation affords a close quantitative agreement with experiments. (I have given reasons which show, that if the foundation of the theory is sound, we may assume that
>
> $$\frac{2\pi^2 me^4}{h^3} = 3.290 \times 10^{15}$$
>
> Putting your value $e = 4.65 \times 10^{-10}$, I get $h = 6.26 \times 10^{-27}$. Putting Millikan's value $e = 4.87 \times 10^{-10}$, I get $h = 6.76 \times 10^{-27}$. Unfortunately, however, Planck's constant is hardly known with any great accuracy.) The second chapter deals with the atoms, the third with molecules, and the last chapters with magnetism and some general considerations. I hope you will find that I have taken a reasonable point of view as to the delicate question of the simultaneous use of the old mechanics and of the new assumptions introduced by Planck's theory of radiation.[59]

With the new insight into the origin of line spectra, Bohr's theory differed even more markedly from Nicholson's than earlier. However, he suggested that perhaps the celestial spectra investigated by Nicholson were not the result of true emission of light but rather due to scattering of radiation. In that case, 'Nicholson's theory would fit exceedingly well in with the considerations of my paper', he reported to Rutherford.[60] The final version of the paper, only completed after Bohr had gone to Manchester to discuss it with Rutherford, was submitted to *Philosophical Magazine* on 5 April. This was the first part of the sequel of three papers that is collectively known as Bohr's trilogy.

## 2.4 QUANTUM JUMPS

Bohr's trilogy did not start with the two later postulates that were to become so famous, which he only introduced after he had offered the first of his derivations of the energy of an atomic state.[61] Instead he prefaced the first of the papers by

emphasizing that all his considerations rested on Rutherford's nuclear atom, according to which 'the atoms consist of a positively charged nucleus surrounded by a system of electrons kept together by attractive forces from the nucleus'. As mentioned above, this view of the atom was at the time only accepted by a minority of physicists outside Manchester. In contrast to the Thomson atom, the electrons in Rutherford's atom were not in mechanically stable states. This problem Bohr associated with another one, namely that whereas Thomson's model included a natural length as given by the radius of the positive sphere, Rutherford's did not, because it is not possible to determine an atomic length solely by the charges and masses of electrons and nuclei.[62] As Bohr saw it, this necessitated the introduction of 'a quantity foreign to the classical electrodynamics, i.e. Planck's constant, or as it often is called the elementary quantum of action'. He reasoned that, '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'.[63]

To establish the mechanism of how an electron became bound to a nucleus, Bohr considered the simplest atom of the Rutherford type, an electron (charge $-e$) revolving with orbital frequency $\omega$ around a nucleus of charge $E$ in a stationary orbit with a major axis of $2a$. Assuming that the electron, in spite of its accelerated motion, radiated no energy, he found from classical mechanics the frequency and major axis as given by the total energy $W$ of the atom; that is, the energy necessary to remove the electron to a distance infinitely far from the nucleus. The expressions

$$\omega = \frac{\sqrt{2}}{\pi} \frac{W^{3/2}}{eE\sqrt{m}} \quad \text{and} \quad 2a = \frac{eE}{W} \tag{1}$$

show that all possible values for $\omega$ and $a$ can be obtained by varying $W$. However, the distinct spectral lines indicate that $a$ and $\omega$ assume definite values, implying that the energy of atoms must be restricted to definite values as well. Bohr next noted that according to Maxwellian electrodynamics the electron will radiate energy in agreement with Larmor's formula, with the result that $W$ increases and $a$ diminishes until the electron coalesces with the nucleus. The energy dissipated in this way, he noticed, 'will be enormously great compared with that radiated out by ordinary molecular processes'.[64] This was a problem that had played no role in either the Manchester memorandum or other of his earlier sketches, but now it became of pivotal significance.

As a remedy against the potential disaster of atomic radiative instability he appealed to Planck's quantum hypothesis in the version Planck had developed during the years 1911–1912, a version known as Planck's 'second theory'. Assuming—but not justifying—that during the binding of an electron a monochromatic radiation of frequency $\nu = \omega/2$ is emitted ($\omega$ is the orbital frequency in 'the final orbit'), he reasoned that 'the amount of energy emitted by the process considered is equal to $\tau h\nu$, where $h$ is Planck's constant

and $\tau$ an entire number' (p. 5). This he formulated as an energy quantization for stationary orbits,

$$W = \tau h \frac{\omega}{2} \tag{2}$$

From equation (1) he then obtained the values of $W$, $\omega$, and $a$ in terms of atomic constants:

$$W = \frac{2\pi^2 me^2 E^2}{\tau^2 h^2}, \qquad \omega = \frac{4\pi^2 me^2 E^2}{\tau^3 h^3}, \qquad a = \frac{\tau^2 h^2}{4\pi^2 meE} \tag{3}$$

That is, according to Bohr even the simplest atom should be capable of existing in an infinite number of distinct states, characterized by varying sizes and amounts of energy (Figure 2.3). Atoms existing in states given by high quantum numbers (values of $\tau$) might even be fairly large, say with radii about 0.01 mm. This was a picture of the atom quite different from what physicists had been used to. The large hydrogen atoms described by Bohr's formula were later called 'Rydberg atoms'. Isolated Rydberg atoms were first observed in 1965, when scientists at the National Radio Astronomy Observatory in the USA detected radiation from hydrogen atoms in interstellar space undergoing transitions between levels near $\tau = 100$.

We are, Bohr said, 'led to assume that these configurations will correspond to states of the system in which there is no radiation of energy; states which consequently will be stationary as long as the system is not disturbed from outside'. In the case of the ground

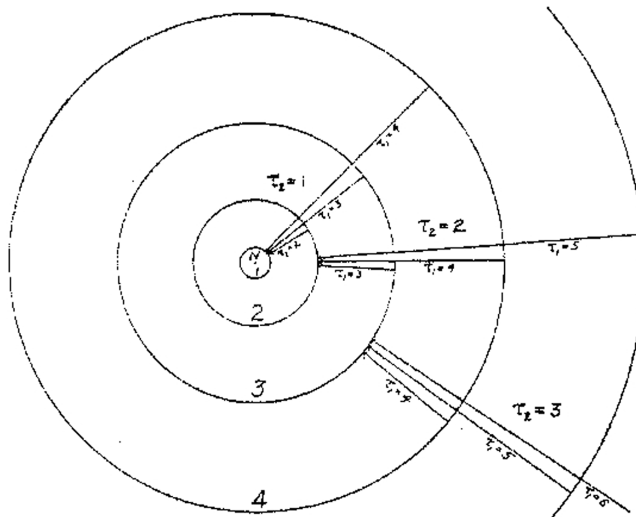


**Fig. 2.3.** Bohr's atomic model of hydrogen, possibly the first picture of its kind, as depicted in a paper of early 1915.

*Source*: Harkins and Wilson 1915, p. 1406.

state $\tau = 1$ he found the numerical values $a = 0.55 \times 10^{-8}$ cm, $\omega = 6.2 \times 10^{15}$ s$^{-1}$, and $W = 13$ eV. The values of $a$ and $\omega$ were of the same order of magnitude as the linear dimension of atoms and the optical frequencies, respectively. More interestingly, $W$ corresponded to the ionization energy of hydrogen, a quantity which at the time was only roughly known from experiments. As Bohr pointed out in the second part of the trilogy, Thomson had recently measured $W \cong 11$ eV in experiments with positive rays, a value that a few years later turned out to be inferior to the one predicted by Bohr's atomic theory.[65]

Before proceeding to the hydrogen spectrum Bohr dealt at some length with Nicholson's atomic theory, which he praised for its precise predictions of the spectral lines supposed to originate in the hypothetical nebular and coronal elements. However, he also raised serious objections against the theory, in particular that it rested on the classical assumption that the radiated frequency was the same as a mechanical frequency in the atomic system:

> As a relation from Planck's theory is used, we might expect that the radiation is sent out in quanta; but systems like those considered, in which the frequency is a function of the energy, cannot emit a finite amount of a homogeneous [monochromatic] radiation; for, as soon as the emission of radiation is started, the energy and also the frequency of the system is altered.[66]

Later in the paper Bohr, adopting a reconciliatory strategy, suggested that the difficulties of Nicholson's theory 'may be only formal'. Much as he had done in his earlier letters to Rutherford, he now proposed that the spectra studied by Nicholson were not due to emission but to scattering of radiation. In that case, 'we immediately understand the entirely different form for the laws connecting the lines discussed by Nicholson and those connecting the ordinary line-spectra considered in this paper'.[67]

In Bohr's original interpretation of equation (2) it meant that the atom emitted $\tau$ quanta of the same frequency $h\omega/2$, which would, however, imply a monochromatic radiation in contradiction of experience. Having critically examined Nicholson's theory he now realized that the radiation process must yield a *single* quantum corresponding to the reinterpretation

$$W = \tau\left(h\frac{\omega}{2}\right) = h\left(\tau\frac{\omega}{2}\right).$$

Thus, during the binding of a free electron to orbit number $\tau$ only one energy quantum of frequency $\tau\omega/2$ is emitted. Bohr now formulated what he called the two 'principal assumptions' upon which his own theory rested, namely:

1. that the dynamical equilibrium of the systems in the stationary states can be discussed by help of the ordinary mechanics, while the passing of the systems between different stationary states cannot be treated on that basis;

2. that the latter process is followed by the emission of a *homogeneous* radiation, for which the relation between the frequency and the amount of energy emitted is the one given by Planck's theory.[68]

As to the second assumption or postulate, Bohr remarked that it is 'in obvious contrast to the ordinary ideas of electrodynamics, but appears to be necessary to account for experimental facts'. The derivation of Balmer's formula was now an easy matter, as he just had to write down the energy difference between two stationary states and equal it to a quantum of energy,

$$W(\tau_2) - W(\tau_1) = h\nu. \tag{4}$$

For the hydrogen atom, where $E = e$, the result is

$$\nu = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2}\right). \tag{5}$$

Two consequences followed immediately. Not only does the formula reproduce the ordinary Balmer series for $\tau_2 = 2$ and $\tau_1 = 3, 4, \ldots$ and the Paschen series in the ultraviolet for $\tau_2 = 3$ and $\tau_1 = 4, 5, \ldots$, it also predicts new series in the extreme ultraviolet ($\tau_2 = 1$) and infrared ($\tau_2 > 3$) regions 'which are not observed, but the existence of which may be expected'. In addition, what had hitherto been an empirical quantity, the Rydberg constant, was now derived theoretically as $cR = 2\pi^2 me^4/h^3 = 3.290 \times 10^{15}\ \mathrm{s}^{-1}$, the same value Bohr had reported to Rutherford in his letter of 6 March. The numerical value of Rydberg's constant was $R = 109\,740\ \mathrm{cm}^{-1}$, in excellent agreement with the measured value $R = 109\,675\ \mathrm{cm}^{-1}$. (The two numbers are identical to the accuracy within which the constants $m$, $e$, and $h$ were known at the time.) As we shall see, many physicists were impressed by Bohr's derivation of Rydberg's constant, which according to Bertrand Russell 'was perhaps the most sensational evidence in favour of Bohr's theory when it was first published'.[69]

Bohr also came up with a clever explanation of why only 12 of the Balmer lines had been found in experiments with vacuum tubes, while astronomers had observed as many as 33 lines. The proposed explanation, based on the increased size of the atoms when in highly excited states, as given by equation (3), led him to conclude that spectral lines arising from hydrogen atoms in high quantum states required a large space of very small density. In the rarefied atmosphere of the stars there must exist hydrogen monster-atoms about thousand times as large as those of Earth ($2a = 1.3 \times 10^{-5}$ cm, corresponding to $\tau = 33$), a result of the large volume and low density. He therefore predicted that the large number of Balmer lines found in the emission spectra of celestial objects would never be observed in the laboratory, although it might be possible to detect the absorption lines.

Realizing that the relation $W = \frac{1}{2}\tau h\omega$ was conspicuously ad hoc, Bohr suggested a different and, he thought, more satisfactory way to derive it. This derivation was the first germ of what would later become the correspondence principle. Instead of equation (2) he assumed the more general relation

$$W = f(\tau)h\omega$$

and argued that, to agree with the form of the Balmer expression, the function $f(\tau)$ had to be proportional to the integer $\tau$; that is $f(\tau) = b\tau$. He then considered a transition from the state $\tau = N$ to the state $\tau = N - 1$. The frequency of the radiation emitted becomes

$$\nu = \frac{\pi^2 me^2 E^2}{2b^2h^3}\frac{2N-1}{N^2(N-1)^2},$$

while the frequency of revolution of the electron in the stationary state $\tau = N$ is

$$\omega_N = \frac{\pi^2 me^2 E^2}{2b^3h^3N^3},$$

and similarly for $\tau = N - 1$. The ratio between the mechanical frequencies of the two states is given by

$$\frac{\omega_N}{\omega_{N-1}} = \frac{(N-1)^3}{N^3},$$

which tends towards unity when $N >> 1$. 'If $N$ is great the ratio between the frequency before and after the emission will be very near equal to 1; and according to the ordinary electrodynamics we should therefore expect that the ratio between the frequency of radiation and the frequency of revolution also is very nearly equal to 1' (p. 13). This gives the result that $b = \frac{1}{2}$, justifying the factor of $\frac{1}{2}$ introduced in the original derivation. For a passage from $\tau = N$ to $\tau = N - n$, where $n$ is small compared to $N$, the result is $\nu = n\omega$. Foreshadowing the correspondence principle, he commented (p. 14):

> The possibility of an emission of a radiation of such a frequency may also be interpreted from analogy with the ordinary electrodynamics, as an electron rotating round a nucleus in an elliptical orbit will emit a radiation which according to Fourier's theorem can be resolved into homogeneous components, the frequencies of which are $n\omega$, if $\omega$ is the frequency of revolution of the electron.

The new interpretation of $W = \tau h\omega/2$ was 'not that the different stationary states correspond to an emission of different numbers of energy-quanta, but that the frequency of the energy emitted during the passing of the system from a state in which no energy is yet radiated out to one of the different stationary states, is equal to different multiples of $\omega/2$, where $\omega$ is the frequency of revolution of the electron in the state

considered'. The earlier interpretation was now dismissed as only preliminary (which makes one wonder why he included it in the first place).

Bohr justified his result in yet another way, namely by quantizing the angular momentum $L$ of the revolving electron. As mentioned in Section 1.4, Nicholson had previously restricted changes in the angular momentum to units of $h/2\pi$. Moreover, in a paper dealing with the quantum theory of diatomic gases that was published shortly before Bohr's, Paul Ehrenfest in Leiden had independently assumed the angular momentum of a rotating molecule to be quantized according to

$$\tfrac{1}{2}J(2\pi\omega)^2 = \tau\frac{h\omega}{2},$$

where $J$ denotes the moment of inertia. However, he did not formulate the quantization as a general principle.[70] Noting that 'there obviously can be no question of a mechanical foundation of the calculations given in this paper', Bohr nonetheless interpreted his calculations 'by help of symbols taken from the ordinary mechanics'. For the case of an electron moving in a circular orbit he found

$$L = ma^2(2\pi\omega) = \tau\frac{h}{2\pi} \tag{6}$$

In Bohr's words: 'The angular momentum of the electron round the nucleus in a stationary state of the system is equal to an entire multiple of a universal value, independent of the charge on the nucleus'. Since $\pi L = W/\omega$ for a circular orbit, the quantization of $L$ is equivalent to the result of equation (2). While the quantization of the angular momentum played only a secondary role in the first part of the trilogy, in the second part it had become the 'main hypothesis' of the theory.[71]

In a section on absorption of radiation Bohr argued that his theory was able to account not only for the emission of light but also for absorption phenomena. These he regarded as the reverse of emission; that is, he attributed them to a transition from a lower-energy state to a higher one, whether bound or free. His general hypothesis was that 'a system of electrons will absorb a radiation of a frequency different from the frequency of vibration of the electrons calculated in the ordinary way'. Considering an electron in a stationary state to receive an energy quantum $h\nu$—as 'in experiments on ionization by ultra-violet light and by Röntgen rays'—he argued that in these cases it would enter an unbound state. If $W$ denotes the negative of the binding energy, the ejected electron will acquire a kinetic energy $E_{\text{kin}} = h\nu - W$, which is just Einstein's formula of 1905 for the photoelectric effect. Bohr further argued that experiments made by the American physicist Robert Williams Wood at Johns Hopkins University on absorption of light by sodium vapour could be qualitatively explained along similar lines. According to Bohr, Wood's results could be interpreted as a transition of the valence electron in the sodium atom from a bound to a free state.[72]

In the later literature Bohr's famous frequency relation $W_1 - W_2 = h\nu$ was sometimes seen as the reverse of Einstein's hypothesis of energy generation by absorption of light, and for this reason was referred to as the 'Einstein–Bohr condition'. For example, Sommerfeld called Bohr's condition 'a counterpart to Einstein's photoelectric equation'.[73] However, although there is an obvious formal similarity between the two equations, from a conceptual and historical perspective they are quite different. For one thing, Einstein's $h\nu$ was a light quantum, a parcel of energy, whereas Bohr's was the energy of a monochromatic electromagnetic wave. Moreover, Einstein's light quantum hypothesis was independent of any atomic model, while Bohr's frequency condition was an integral part of his theory of atomic structure, dependent as it was on the notion of stationary states.

While Bohr's theory of the hydrogen atom agreed impressively with spectroscopic measurements, the agreement did not amount to a confirmation of his prediction of the many discrete energy levels in the atom. In 1913 the experimental data necessary for a direct confirmation did not exist, but they were obtained in later experiments measuring the resonance potentials required to raise the electron from the ground state to higher states. Table 2.1 shows data from experiments on the radiation from atomic hydrogen made in 1923 by P. S. Olmstead and Karl T. Compton at Princeton University. As the two American physicists pointed out, 'the agreement with . . . the Bohr theory is exact'.[74] By that time this was a conclusion that surprised no one.

The hydrogen atom and other one-electron atomic systems constituted the core of Bohr's theory as he presented it in the first part of his trilogy. However, he also discussed systems in which more electrons were arranged in a ring, as he did in greater detail in the second part.[75] This he did by following the stability calculations of Thomson and Nicholson, but with the important difference that he did not base his

**Table 2.1** Comparison of energy levels (in eV) in atomic hydrogen between measured values and values predicted by Bohr's theory. The last row corresponds to ionization.

| Quantum transitions | Observed voltage | Calculated voltage |
|---|---|---|
| 1–2 | 10.15 | 10.154 |
| 1–3 | 12.05 | 12.034 |
| 1–4 | 12.70 | 12.692 |
| 1–5 | 13.00 | 12.997 |
| 1–6 | 13.17 | 13.162 |
| 1–7 | 13.27 | 13.262 |
| .... | .... | ... |
| 1-∞ | 13.54 | 13.539 |

*Source*: Olmstead and Compton 1923.

conclusions solely on mechanical considerations. His hypothesis was that 'the stability of a ring of electrons rotating round a nucleus is secured through the above condition of the universal constancy of the angular momentum, together with the further condition that the configuration of the particles is the one by the formation of which the greatest amount of energy is emitted' (p. 23). In a brief section on the spectra of elements with several electrons he pointed out that his theory provided an immediate explanation of the so-called combination principle formulated in 1908 by Ritz.[76] According to the Swiss physicist, the wave numbers (or frequencies) of the spectral lines of an element can in all cases be written as the difference between two spectral terms, each of which depends on an integer. Let $n_1$ and $n_2$ be two integers, and $F_r$ and $F_s$ two functions of these numbers. Then:

$$\frac{1}{\lambda} = \frac{\nu}{c} = F_r(n_1) - F_s(n_2).$$

By focusing attention not on the spectral lines, but on the terms, Ritz's combination principle greatly helped spectroscopists in organizing the spectra, but until Bohr's theory it remained phenomenological, without a basis in physical theory.

In the second part of the trilogy Bohr offered a more elaborate analysis of the distribution of electrons in coplanar rings round a nucleus. In the case of a single ring his calculations showed that the number of electrons increased only slowly with the nuclear charge. A ring of $n$ electrons 'cannot rotate in a single ring round a nucleus of charge $ne$ unless $n < 8$', he concluded, just as he had done in the Manchester memorandum a year earlier. To accommodate eight electrons in the same ring a nuclear charge of $Z \geq 10$ was required, implying a positive ion instead of a neutral atom. Bohr furthermore considered the tendency of separate rings of electrons to coalesce into a single ring. He argued that such coalescence will only occur when the rings contain the same number of electrons, and 'accordingly the numbers of electrons on inner rings will only be 2, 4, 8, . . . .'.[77] As we shall see in Section 2.6, these and similar results provided the seeds for a possible explanation of the periodic system on the basis of Bohr's new theory.

Bohr was not very happy about either of the derivations of the Balmer formula given in the trilogy as outlined above. In a lecture before the Danish Physical Society on 20 December 1913 he reconsidered his model of the hydrogen atom and its connection to Planck's quantum theory.[78] By that time he thought it was misleading to base the atomic model on Planck's second theory and preferred to use only the two postulates. As he pointed out, while in Planck's theory the frequency of an oscillator was independent of the amount of energy contained in the system of oscillators, in his own theory the frequency of revolution depended on the energy according to the Keplerian relationship $\omega^2 \sim W^3$. Moreover, while Planck assumed that an oscillator could emit several quanta of the same frequency at once, in Bohr's theory only a single quantum of energy was emitted during a transition.

While in the first part of the trilogy Bohr had emphasized that 'The foundation of the hypothesis [quantization of angular momentum] has been sought entirely in its relation with Planck's theory of radiation' (p. 25), he now endeavoured to loosen this relation. Although he kept to the concept of energy quanta as given by $E = h\nu$, he wanted to do without the Planckian notion of atomic oscillators. Already in the conclusion of the third part of the trilogy he had expressed his misgivings about 'The assumption of such vibrators . . . [which] involves the assumption of quasi-electric forces and is inconsistent with Rutherford's theory, according to which all the forces between the particles of an atomic system vary inversely as the square of the distance apart'.[79]

'We can not expect', he said in Copenhagen, 'that all cases of disagreement between the theoretical conceptions hitherto employed and experiment will be removed by the use of Planck's assumption regarding the quantum of the energy momentarily present in an oscillating system'.[80] As far as Planck's theory was concerned it only appeared indirectly in the fundamental assumption of quantum jumps, which can be written

$$\nu = \frac{1}{h}(W_1 - W_2). \tag{7}$$

Bohr further stressed that there were no observational reasons to keep to Planck's picture of oscillating charges. He appealed to empiricism: 'We stand here almost entirely on virgin ground, and upon introducing new assumptions we need only to take care not to get into contradiction with experiment'. What does 'direct observation' tell us about the mechanism causing the blackbody spectrum so precisely expressed by Planck's formula? According to Bohr, nothing:

> No one has ever seen a Planck's resonator, nor indeed even measured its frequency of oscillation; we can observe only the period of oscillation of the radiation which is emitted. It is therefore very convenient that it is possible to show that to obtain the laws of temperature radiation it is not necessary to make any assumptions about the systems which emit the radiation except that the amount of energy emitted each time shall be equal to $h\nu$, where $h$ is Planck's constant and $\nu$ is the frequency of the radiation.[81]

In his lecture of December 1913 Bohr did not attempt to derive Balmer's formula, but only the coefficient appearing in it; that is, the Rydberg constant. This he did by comparing equation (7) with Balmer's formula, which suggests $W = Rhc/n^2$ for the $n$th stationary state. Adopting a correspondence approach similar to the one used in the trilogy, he expressed the frequency of the radiation arising from a transition from state $(n + 1)$ to state $n$ as

$$\nu = Rc\left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right).$$

For large values of $n$ this gives approximately $\nu = 2Rc/n^3$. According to the correspondence view this radiation frequency is equal to the frequency of revolution. Inserting $W = Rhc/n^2$ in equation (1) then gives

$$\omega^2 = \frac{2R^3h^3c^3}{\pi^2 e^4 mn^6} = \frac{4R^2c^2}{n^6}.$$

From this expression it follows that $R = 2\pi^2 me^4/h^3c$, the same expression that he had found in the trilogy.

Bohr's new atomic theory was a somewhat strange mixture of classical and quantum ideas based on two postulates that were only justified by the empirically successful use he made of them. Bohr himself, much aware of the arbitrary and unsatisfactory features of the theory, emphasized its 'preliminary and hypothetical character'.[82] In his Copenhagen address he was even more direct: 'The fact that the deficiencies of the atomic model we are considering stand out so plainly is . . . perhaps no serious drawback; even though the defects of other atomic models are much better concealed they must nevertheless be present and will be just as serious'. Bohr furthermore admitted that what he was proposing was not really an explanation, in the causal sense of the term, of how light is emitted from atoms. 'I am by no means trying to give what might ordinarily be described as an explanation', he said; 'nothing has been said here about how and why the radiation is emitted'.[83] This was a point to which he would return at later occasions. Thus, in 1922 he emphasized that his atomic theory 'does not attempt an "explanation" in the usual sense of this word, but only the establishment of a connexion between facts which in the present state of science are unexplained'.[84]

In Chapter 3 we shall see that many of Bohr's contemporaries found the theory to be puzzling for this reason; but we shall also see that they were nonetheless impressed by its explanatory and predictive power over a broad domain and in spectroscopy in particular.

## 2.5 SPECTROSCOPIC PUZZLES

According to Robert Millikan, the eminent American experimentalist and a Nobel laureate of 1923 for his measurements of the photoelectric effect and the electron's charge, the period 1912–1914 was 'comparable in importance with the period of the laws of Galilean–Newtonian mechanics some three centuries earlier'. Looking back on the development to which he had himself contributed so importantly, Millikan highlighted Bohr's theory as a major reason for the revolutionary change in the period: 'For the immense field of spectroscopy was essentially an unexplored dark continent prior to the advent of Bohr's theory. Bohr's equation has been the gateway through which hundreds of explorers have since passed into that continent until it has now become amazingly well mapped'.[85]

Indeed, Bohr's atomic theory scored its first and most spectacular successes in the area of optical spectroscopy, more precisely with respect to the spectra of hydrogen and other one-electron atomic systems. As mentioned above, in the trilogy he had predicted—or, as he phrased it, 'expected'—the existence of hydrogen lines arising from electron transitions to the states $\tau = 1$ and $\tau > 3$. In the early 1920s physicists at the Johns Hopkins University detected lines in the infrared region that agreed precisely with Bohr's predictions: In 1922 Frederick Brackett found the first two lines belonging to $\tau = 4$, and also three new members of the Paschen series. Two years later August Pfund found a single line representing the $\tau = 5$ series.[86] While these discoveries were unsurprising—given that Bohr's theory was solidly established at the time—the discovery of the ultraviolet series belonged to a different category.

In 1914 the experienced spectroscopist Theodore Lyman at the Jefferson Laboratory of Harvard University reported the observation of two new hydrogen lines in the ultraviolet region, but without mentioning Bohr or his theory.[87] Indeed, he may well have been unaware of the theory. Even after Bohr had become aware of the lines and referred to 'the series in the ultra-violet recently discovered by Lyman' as further confirmation of his theory,[88] Lyman refrained from considering the theoretical relevance of his discovery. While he did not refer to atomic theory in 1914, in papers of 1915 and 1916 he briefly mentioned that the spectra of hydrogen and helium 'have recently come into prominence through the theoretical researches of Bohr, Nicholson, and others'.[89] In his paper in the *Astrophysical Journal* he called the relations between the spectra of the two elements 'a fascinating subject for speculation' and said: 'In connection with Bohr's speculations it is important to observe that $\lambda$ 1217, which forms the first member of the Ritz [Lyman] series, occupies exactly the same position when obtained from helium as when it is produced in hydrogen'.[90] In none of his papers did he credit Bohr's formula and he ignored his atomic theory. The American spectroscopist obviously preferred to deal with experimental facts rather than 'speculations'.

In a paper of 1896, also in the *Astrophysical Journal*, the American astronomer Edward Pickering at the Harvard College Observatory reported spectral lines (including $\lambda = 5411$, 4541, and 4200) from the star $\xi$ Puppis. These followed a Balmer-like expression. He and Rydberg consequently attributed them to a new hydrogen series.[91] (Initially he thought that the lines might be due to a new element.) The series discovered by Pickering converged to the same limit as the Balmer series, which was one reason why Rydberg identified it as the diffuse series of hydrogen, supplementing the sharp Balmer series. What was generally thought to be new hydrogen lines were studied in the laboratory by Alfred Fowler, an astrophysicist at the Imperial College, London, and a former assistant of Norman Lockyer. In 1912 he succeeded in reproducing the line $\lambda = 4686$ Å in a discharge tube with a mixture of hydrogen and helium.[92] This line also appeared prominently in $\xi$ Puppis and in the spectra from many nebulae.

Although Fowler was unable to find the 4686 line and other of Pickering's lines in tubes filled with hydrogen only, he persuaded himself (and others) that the new series

was indeed due to hydrogen and not to helium. It seemed natural to assume that the 4686 line was the first of the lines in hydrogen's principal series. The wavelengths of the Pickering–Fowler series extended the Balmer–Ritz formula in the sense that they followed an expression of the form

$$\frac{1}{\lambda} = R\left(\frac{1}{(n_2/2)^2} - \frac{1}{(n_1/2)^2}\right). \tag{8}$$

For example, the 4686 line corresponded to $n_1 = 4$ and $n_2 = 3$. Obviously, this was an expression for the hydrogen spectrum that flatly disagreed with Bohr's interpretation, where the denominators necessarily have to be integers. Half-integral quantum numbers would eventually turn up in quantum theory, and then cause problems of their own, but within the context of Bohr's early one-quantum atomic model they were strictly inadmissible.

As early as 6 March 1913, in his letter to Rutherford, Bohr argued that the lines found by Fowler were really due to helium and that the presence of hydrogen was only of indirect significance. 'Dr Bjerrum suggested to me that if my point of view was right the lines might also appear in a tube filled with a mixture of helium and chlorine (oxygen, or other electronegative substances); indeed it was suggested, that the lines might be still stronger in this case'.[93] Since the laboratories in Copenhagen were not equipped for doing such an experiment, Bohr asked Rutherford if it could possibly be performed in Manchester. Two weeks later Rutherford responded:

> Your ideas as to the mode of origin of spectrum and hydrogen are very ingenious and seem to work out well; but the mixture of Planck's idea with the old mechanics make [sic] it very difficult to form a physical idea of what is the basis of it. There appears to me one grave difficulty in your hypothesis, which I have no doubt you fully realise, namely, how does an electron decide what frequency it is going to vibrate at when it passes from one stationary state to the other? It seems to me that you would have to assume that the electron knows beforehand where it is going to stop. . . . I was much interested in your speculations in regard to Fowler's spectrum. I mentioned the matter to Evans here, who told me that he was much interested in it, and I think it quite possible that he may try some experiments on the matter when he comes back next term.[94]

In the first part of the trilogy Bohr explained that 'we can account naturally for these [Pickering–Fowler] lines if we ascribe them to helium' (p. 10). He simply took $E = 2e$ in equation (3) and could then rewrite the expression (8) as

$$\frac{1}{\lambda} = 4R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \quad \text{with} \quad R = \frac{2\pi^2 me^4}{h^3 c}.$$

In this way Bohr accommodated the new spectral series, interpreting it as due to the formation of $He^+$ ions. He further suggested reasons why the spectrum was not observed in ordinary helium tubes. Bohr did not simply ascribe the new lines to

quantum transitions in the $He^+$ ions. In accordance with ideas common at the time he thought that the atoms first had to lose both of their electrons; the lines would then be emitted as an electron was captured to form $He^+$ in one or other stationary state.

In agreement with what Rutherford had told Bohr in his letter of 20 March, the question of the origin of the 4686 line was investigated by his assistant Evan Jenkin Evans, who succeeded in detecting the line in helium discharge tubes with no trace of hydrogen. 'For some time I have been investigating the origin of the 4686 line', Evans said in a preliminary report, stating that 'the experiments already carried out support Bohr's theory'.[95] Unconvinced that Bohr had really explained the 4686 line and other lines in the supposed hydrogen series, in the autumn of 1913 Fowler pointed out that the theoretical values, although very close to those observed, did not quite agree with them. Bohr's response to the challenge from London was to modify his analysis by taking into account the finite mass of the nucleus, which he did by replacing *m* with the reduced mass as given by

$$\mu = \frac{mM}{m+M} = \frac{m}{1+m/M},$$

where *M* is the mass of the nucleus. In this way the Rydberg constant will depend slightly on the mass of the element and, as Bohr showed, the discrepancies disappear.[96] The ratio of the Rydberg constants for a very heavy one-electron atom and the hydrogen atom becomes

$$\frac{R_\infty}{R_H} = 1 + \frac{m}{M_H}.$$

Fowler now conceded that Bohr's atomic theory gave a correct explanation. As he wrote to Bohr, 'Your letter published in last week's "Nature" struck me as a valuable addition to your Phil. Mag. paper of July'.[97] Although this was not the last word in the case of Fowler's lines, the dispute did much to promote Bohr's theory and make it known among British physicists at an early date. It took a little longer in Germany, but there, too, the resolution of the 4686 puzzle came to be seen as convincing evidence for Bohr's theory. 'Only now do I see that Bohr's theory is exactly right', Friedrich Paschen wrote to Sommerfeld. 'There is no doubt that Bohr's final formula is as accurate as the measurements can be made'.[98] Using a special kind of helium tube, Paschen succeeded in photographing the ionised helium components and showed that they agreed perfectly with the ones calculated on Bohr's theory (Table 2.2).

In his letter to *Nature* in which he introduced the reduced mass correction, Bohr pointed out that 'according to the theory helium must be expected to emit a series of lines closely, but not exactly, coinciding with the lines of the ordinary hydrogen spectrum'. The lines would correspond to transitions from $n_1 = 6, 8, 10, \ldots$ to $n_2 = 4$. Experiments

**Table 2.2** Bohr's helium lines. The second column gives the wavelengths of the Pickering series as calculated by Bohr, and the third column the experimental values published by Paschen in 1916. The fourth column contains stellar lines found by Harry Plaskett in 1921. The table is adapted from Plaskett 1922.

| Balmer hydrogen lines | Helium lines, Bohr theory | Helium lines, laboratory | Helium lines, stars |
|---|---|---|---|
| 6562.79 | 6560.15 | 6560.13 | 6560.04 |
| | 5411.53 | 5411.55 | 5411.62 |
| 4861.33 | 4859.35 | 4859.34 | 4859.09 |
| | 4541.62 | 4541.61 | 4541.67 |
| 4340.47 | 4338.70 | 4338.70 | 4338.79 |
| | 4199.86 | 4199.86 | 4200.06 |
| 4101.74 | 4100.00 | 4100.05 | 4100.26 |

with pure helium conducted by Evans in late 1914 confirmed the series predicted by Bohr, which was one more spectroscopic triumph for the new atomic theory.[99]

While Fowler fully recognized Bohr's explanation of the 4686 line as due to 'proto-helium', he remained ambiguous with respect to the theory on which the explanation was based. As he wrote to Bohr:

> Evans's detection of the components near the Balmer lines seems to me to complete the evidence for the helium origin of the 4686 and Pickering lines. But, as I said in the Bakerian lecture (p 258), the assignment of the lines to proto-helium is 'independent of Bohr's theory'. . . . Your theory has the great merit of accounting for the lines in positions slightly different from those calculated by Rydberg, and of predicting Evans's lines. But perhaps we may find that some other theory will do the same thing. Meanwhile I am a warm supporter of your theory.[100]

Fowler's recognition that the 4684 line was indeed due to ionized helium, as predicted by Bohr, did not quite close the case. In some quarters doubts remained as to whether this was the true explanation. In a paper from March 1915 Thomas Ralph Merton, a spectroscopist at Imperial College, London, observed that Bohr's theory 'has given rise to a considerable amount of theoretical discussion'.[101] Spectroscopic experiments based on a new interference method suggested to him that the evidence provided by Evans was inconclusive and that the mass of the atom from which the 4686 line originated was much smaller than that of the helium atom. He found that it was only about one-tenth of the mass of a hydrogen atom and thus 'due to systems of subatomic mass'. What these unlikely systems might be, Merton wisely refrained from saying. Nor did he spell out the theoretical significance of his conclusion, although it obviously contradicted Bohr's explanation as well as other parts of established atomic physics.

Just as Bohr had reinterpreted the Pickering–Fowler lines in agreement with his theory, so he did with another series of spectral lines that Nicholson in early 1913 had

suggested belonged to the hydrogen spectrum and had interpreted according to his own atomic theory.[102] The British astrophysicist had found that the frequencies of some hitherto unidentified lines in the spectra of a class of stars known as Wolf–Rayet stars could be expressed in a manner similar to the Balmer and Pickering–Fowler lines, namely as

$$\nu = Rc\left(\frac{1}{4} - \frac{1}{\left(n \pm \frac{1}{3}\right)^2}\right)$$

However, as Bohr saw it, the lines were more likely to be due to the doubly charged lithium ion $Li^{2+}$, just as the Pickering–Fowler lines were due to the $He^+$ ion. He simply rewrote Nicholson's expression as

$$\nu = Rc\left(\frac{1}{(n_2/3)^2} - \frac{1}{(n_1/3)^2}\right) = 9Rc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

where the factor 9 comes from the square of the charge of the lithium nucleus ($E = 3e$). Nicholson did not accept Bohr's reinterpretation, based as it was on a model of the lithium atom with two electrons in the inner ring and one electron in the outer ring. According to Nicholson, this model was dynamically impossible (see further discussion in Section 3.6). The cases of $He^+$ and $Li^{2+}$ were different in the sense that whereas Bohr's prediction of the $He^+$ lines was confirmed experimentally, this was not the case with his reinterpretation of Nicholson's lines. There were no experimental data on the doubly charged lithium ion.

Bohr was well aware that if the atomic electrons revolved with velocities comparable to the velocity of light it might be necessary to replace the constant mass $m$ with the varying relativistic mass $m(v)$ as given by Einstein's formula

$$m(v) = \frac{m}{\sqrt{1 - v^2/c^2}}$$

However, in the trilogy he saw no reason to introduce the small relativistic modification.[103] He only this this in a letter to Fowler of 15 April 1914 in which he reported the more general but still approximate formula for the spectral lines emitted by an electron bound to a nucleus of mass $M$ and charge $Ne$.[104] The modified formula he offered was this:

$$\nu = \frac{2\pi^2 Mme^4N^2}{(M+m)h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\left\{1 + \frac{\pi^2e^4N^2}{h^2c^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\right\}$$

Although the relativistic effect was very small ($\pi^2e^4/h^2c^2 \cong 1.3\times\ 10^{-5}$) it was not negligible, and it became important in connection with precision experiments made by William Edward Curtis, an astrophysicist and student of Fowler. According to Curtis's measurements of the Balmer spectrum the wavelengths of the lines deviated slightly

from those predicted by the Balmer–Bohr formula.[105] Bohr hoped to explain the deviations by means of his relativistic modification, but had to admit that it only accounted for about one third of the deviations observed by Curtis. 'Might not the disagreement as to $H_\alpha$ in some way be connected with the doubling of the line?' he asked Fowler.[106] We shall consider the connection between Bohr's theory and the fine structure of the hydrogen spectrum in Section 4.4.

## 2.6 BOHR'S ATOMIC CHEMISTRY

Considerations and results of a chemical nature occupied an important place in Bohr's trilogy, which was after all a treatise on the constitution of atoms *and molecules*.[107] Whereas he dealt with the atomic structure of the chemical elements in Part I, in Part III he focused on the structure of simple molecules. The chemical aspects were in Bohr's mind from the very beginning of his project, undoubtedly in part inspired by his contact with Hevesy. As mentioned in Section 2.3, molecules figured prominently in the Manchester memorandum. In his letter to Hevesy of 7 February 1913, shortly before he became aware of the Balmer spectrum, Bohr said that he could 'explain not only the order of magnitude of the dimensions of the atoms, but also the way in which the atom-volumes vary with the valency of the element considered (i.e. with the number of electrons in the outermost ring)'. He continued:

> Besides a very suggestive indication of an understanding of the periodic system of the elements, the considerations in question leads [sic] to a theory of chemical-combinations, a theory which permits to follow the process of combining of atoms in detail, and applied on the most simple systems immediately gives the result, that 2 Hydrogen-atoms will combine into a molecule, while 2 Helium-atoms wont [sic]. . . . [B]y simple application of considerations as the above indicated, [I] have hope to obtain a knowledge of the structure of the systems of electrons surrounding the nuclei in atoms and molecules, and thereby hope of a detailed understanding of what we may call the 'chemical and physical' properties of matter.[108]

In dealing with atoms containing more than one electron Bohr realized that their constitution could not be fully determined by the conditions he had used in the case of hydrogen, that is, mechanical stability and the constancy of the angular momentum of the electrons. He therefore adopted an alternative approach, which can be reconstructed as consisting of four elements: (i) involved calculations of mechanical stability; (ii) applications of chemical knowledge, such as valency, reactivity, and ionization potentials; (iii) considerations related to spectroscopy; and (iv) simplicity assumptions, including that the electron rings are situated in the same plane through the nucleus even in the case of many electrons. In Bohr's words: 'On the general view of formation of atoms, however, and by making use of the knowledge of the properties of the

corresponding elements, it will be attempted . . . to obtain indications of what configurations of the electrons may be expected to occur in atoms'.[109] There is little doubt that empirical knowledge of a chemical and physical nature played a greater role than calculations based on mechanical and quantum-theoretical principles.

The lightest atoms with atomic number between 2 and 4 were treated separately by Bohr and in general accordance with his treatment of the hydrogen atom. In the case of neutral helium he argued that stability required the two electrons to move in the same orbit, a configuration he referred to as 2(2) and for which he found the radius and binding energy to be $a = 0.571\ a_0$ and $W = 6.13\ W_0$ ($a_0$ and $W_0$ are the values for the hydrogen atom; $W_0 \cong -13$ eV). Since $W$ for the configuration 2(3) turned out to be smaller than for 2(2), he concluded that a negative helium ion could not exist. For the energy of the helium ion $He^+$ he obtained $W = 4\ W_0$, meaning that both electrons were bound to the nucleus more firmly than in the case of hydrogen. The ionization energy for helium amounts to $(6.13 - 4)W_0 = 2.13\ W_0$ or about 27 eV, which Bohr noticed was of the same order of magnitude found experimentally by James Franck and Gustav Hertz in Berlin, namely 20.5 eV.[110] He also claimed to find support for his model in measurements of the ultraviolet absorption frequency in helium, where the Cuthbertsons had found a value of $5.9 \times 10\ s^{-1}$. Bohr's calculations based on the energy difference between He and $He^+$ in their ground states resulted in a frequency parallel to the orbital plane of $6.6 \times 10\ s^{-1}$, and from ordinary mechanics he obtained for the perpendicular frequency $20.3 \times 10\ s^{-1}$. He concluded that the frequency of dispersion 'may be regarded as corresponding to vibrations in the plane of the ring', whereas the perpendicular vibrations had only a negligible influence on dispersion.[111]

Bohr's calculations of helium and other atoms and molecules more complicated than hydrogen were crude and rested on an arbitrary mixture of quantum and classical considerations. In 1913 they did not result in convincing agreement with experiments. Later and much more sophisticated calculations did not materially improve the agreement. As we shall see, the normal helium atom never succumbed to Bohr's theory. His treatment of the lithium atom is another case that may be used to exemplify his eclectic and somewhat opportunistic approach. In this case he calculated the total binding energy for two configurations, one being a two-ring system and another in which the three electrons moved on the same ring. He obtained the values, in his notation,

$$\mathrm{W}[3(2,1)] = -16.02\,W_0 \quad \text{and} \quad \mathrm{W}[3(3)] = -17.61 W_0.$$

This means that the latter configuration is energetically favoured, but of course it contrasts with the chemical properties of lithium. For the $Li^+$ ion Bohr found $W = -15.13\ W_0$, which implied that it should be easier to ionize helium than lithium vapour! Characteristically, Bohr chose to ignore the result of his mechanical calculations and concluded that the (2,1) configuration was the correct one 'from a consideration of the chemical properties' of the element. His model of beryllium was no better,

for here the theory showed that the configuration with four electrons revolving in a single ring was energetically favoured: he got $W = -37.04\ W_0$ for this configuration, and $W = -33.61\ W_0$ for the 4(2,2) structure.[112]

The same willingness to sacrifice mechanical calculations for chemical considerations appeared in Bohr's assignment of electrons in systems of rings. While he had found that the inner ring, to be mechanically stable, could accommodate no more than seven electrons, in the end he chose the number eight. The reason was obviously the known periodicity of the elements, with the first periods including eight elements. As to the number of electrons in the outer ring he did not even pretend to base it on calculations: 'The number of electrons in this ring is arbitrarily put equal to the normal valency of the corresponding element'.[113] This accounts for the change in the building-up scheme at nitrogen, which he assigned the configuration (4,3) rather than (2,5). He gave no reason for this change except that three outer electrons are necessary to account for nitrogen's tervalency. A similar case can be observed for phosphorus, to which he assigned the configuration (8,4,3) rather than (8,2,5).

Bohr also made no attempt to take into regard the distinction between the so-called principal and secondary valences (or normal valence and contravalence), concepts which the German physical chemist Richard Abegg had introduced in 1904. According to Abegg's 'rule of eight' the sum of the two valences was always equal to eight.[114] For example, chlorine has one negative normal valence (as in HCl) and seven positive contravalences (as in $NaClO_4$); similarly, nitrogen displays valencies from −3 (as in $NH_3$) to +5 (as in $N_2O_5$). Shortly after Bohr's paper had appeared, Hevesy asked him: 'How would you explain the difference between principal and secundary valencies. (Haupt und Nebenvalenzen.) Can the first be connected with the outermost ring, and the second one indirectly though with the other rings?'[115] His question remained unanswered.

For the lighter elements, up to manganese with 25 electrons, Bohr suggested configurations that he thought corresponded to the periodic system (Table 2.3). Although he did not assign electron arrangements to atoms heavier than chromium, based on the periodic system he suggested that 'elements of higher atomic weight [than about 60] contain a recurrent configuration of 18 electrons in the innermost rings'. Moreover, he argued that in some cases, such as the rare earth metals, the building up of electrons took place in an inner rather than the outer ring. In this way it would be possible to account for the striking chemical similarity of this group of elements. Finally he indicated an explanation of the 'observed increase of the electropositive character for an increase of atomic weight of the elements in every single group of the periodic system', say from beryllium to radium (p. 497). According to Bohr, this was a result of the increasingly weaker binding of the outer electrons as the number of rings increased.

The ideas of molecular structure included in the Manchester memorandum, and also in his letter to Hevesy of 7 February 1913, were only published in the third part of the

**Table 2.3** Bohr's 1913c proposal of electron rings in chemical elements. In his table in *Philosophical Magazine* he did not assign chemical symbols to the structures.

| | | | | | |
|---|---|---|---|---|---|
| H | 1 (1) | F | 9 (4, 4, 1) | Cl | 7 (8, 4, 4, 1) |
| He | 2 (2) | Ne | 10 (8, 2) | Ar | 18 (8, 8, 2) |
| Li | 3 (2, 1) | Na | 11 (8, 2, 1) | K | 19 (8, 8, 2, 1) |
| Be | 4 (2, 2) | Mg | 12 (8, 2, 2) | Ca | 20 (8, 8, 2, 2) |
| B | 5 (2, 3) | Al | 13 (8, 2, 3) | Sc | 21 (8, 8, 2, 3) |
| C | 6 (2, 4) | Si | 14 (8, 2, 4) | Ti | 22 (8, 8, 2, 4) |
| N | 7 (4, 3) | P | 15 (8, 4, 3) | V | 23 (8, 8, 4, 3) |
| O | 8 (4, 2, 2) | S | 16 (8, 4, 2, 2) | Cr | 24 (8, 8, 4, 2, 2) |

trilogy. Bohr's general idea was to picture the covalent bond as a ring of two or more revolving electrons common to the two atoms forming a diatomic molecule:

> If we thus consider a neutral system containing two nuclei with great charges, it follows that in a stable configuration the greater part of the electrons must be arranged around each nucleus approximately as if the other nucleus were absent; and that only a few of the outer electrons will be arranged differently rotating in a ring round the line connecting the nuclei. The latter ring, which keeps the system together, represents the chemical 'bond'.[116]

For the simple symmetrical case of two nuclei of equal charges $Ne$ and a ring of $n$ electrons between them, he stated the equilibrium condition as

$$b = a\left[\left(\frac{4n}{N}\right)^{2/3} - 1\right]^{-1/2}, \qquad (9)$$

where $2b$ is the distance between the nuclei and $2a$ the diameter of the ring. For systems containing several rings the effect of the inner rings would have to be taken into account, but Bohr chose to disregard this more general case with the excuse that it 'involves elaborate numerical calculations'.

The only molecule he discussed in detail was hydrogen, supposed to consist of two nuclei (protons) kept together by a ring of two electrons placed diametrically opposite. From equation (9) he got $b = a/\sqrt{3}$ and for the total energy of the molecule he calculated

$$-W = -\frac{e^2}{2a}F$$

with the numerical factor $F = 1.049$ (which he had given already in the Manchester memorandum). To determine the radius $a$, Bohr applied the quantum condition of the constancy of the angular momentum, $mva = h/2\pi$. In this way he arrived at the expression

$$W = \frac{4\pi^2 e^4 m}{h^2} F,$$

which he compared with the corresponding value $W_0$ for the hydrogen atom, as derived in the first part of the trilogy. The result was

$$(W - 2W_0) = 2W_0(F^2 - 1) = 0.20\ W_0.$$

Thus, 'it follows that the two hydrogen atoms combine into a molecule with emission of energy'.[117] With a value of Avogadro's number $N_A = 6.5 \times 10^{23}$ the theoretical result for the formation of one mole of $H_2$ came out as 60 kcal.

The American physical chemist Irving Langmuir, a researcher at the General Electric Research Laboratory and a future chemistry Nobel laureate, had recently made experiments from which he inferred the heat of formation of $H_2$ to be about 130 kcal mole$^{-1}$. Compared with Bohr's theoretical value this was of the right order of magnitude, but the numerical agreement was far from convincing.[118] However, a few months after the appearance of Bohr's paper Langmuir informed him that improved experiments had resulted in a value of 76 kcal mole$^{-1}$. Langmuir praised Bohr's theory of the hydrogen molecule as 'valuable and wonderfully suggestive' and found the disagreement between his new measurements and Bohr's calculations to be not intolerably high. (He did however find it 'very improbable' that the correct value could be as low as 60 kcal mole$^{-1}$.) In a letter to Langmuir Bohr described how the experimental results of 1912 had been 'the cause of much doubt for me as to the correctness of my assumptions on the constitution of the hydrogen molecule'.[119] At the same time he offered a recalculation using better values of the constants of nature. Bohr's revised result was $W = 63$ kcal mole$^{-1}$, only 17% away from the experimental value. Considering the tentative character of Bohr's molecular model this was a promising agreement, but the promise did not hold for long. More elaborate and accurate experiments made Langmuir conclude that 'it now becomes impossible to reconcile our experiments with the value $q = 63\,000$ [cal mole$^{-1}$] calculated according to the method of Bohr'.[120] As the final value for the heat of formation at constant volume he arrived at 84 kcal mole$^{-1}$.

Bohr also dealt with absorption lines in molecular hydrogen, assuming them to have their origin in the vibrations of the electron ring and the system of nuclei. In the first case he found an absorption frequency of $3.7 \times 10^{15}$ s$^{-1}$, which he compared with the value $3.5 \times 10^{15}$ s$^{-1}$ calculated from dispersion experiments made by the Cuthbertson couple.[121] Further considering the molecule ions $H_2^-$ and $H_2^+$, with three and one electrons rotating between the nuclei, respectively, he concluded that while the first one was mechanically stable the latter would be unstable against a displacement of the electron perpendicular to the plane of its orbit. Since the $H_2^+$ ion had been identified in Thomson's experiments with positive rays, this 'may therefore at first sight be considered as a serious difficulty for the present theory' (p. 867). However, Bohr suggested a solution, satisfactory to his own mind, that avoided the problem:

> A possible explanation, however, might be sought in the special conditions under which the systems are observed. We are probably dealing in such a case not with the formation of a stationary system by a regular interaction of systems containing single nuclei . . . but rather with a delay in the breaking up of a configuration brought about by the sudden removal of one of the electrons by impact of a single particle.

In another part of his paper he argued that 'in the breaking up of a hydrogen molecule by slowly increasing the distance apart of the nuclei, we obtain two *neutral* hydrogen atoms and not a positively and a negatively charged one' (p. 870).

In accordance with what he had said in the Manchester memorandum, in the trilogy Bohr argued that a helium molecule ($He_2$) would be unable to exist, and so would a chemical combination of helium and hydrogen. Although the hypothetical HeH molecule, bound together by a ring of three electrons, was energetically allowed, he gave reasons why 'the configuration in question cannot . . . be considered to represent a possible molecule of hydrogen and helium' (p. 867). Although Bohr focused on the simple hydrogen molecule, he saw no reason why it should not be possible to understand, at least in principle, other and more complicated molecules along similar lines of reasoning. Admitting that his conception of the covalent bond was premature and might have to be abandoned, he nonetheless proposed structures for the molecules HCl, $H_2O$, and $CH_4$ (Figure 2.4) For methane his structure was tetrahedral, with the C–H bonds represented by four rings each of which carried two electrons; the remaining two electrons were supposed to circle around the central carbon nucleus in an orbit of small radius. Referring to the possible structure of methane and similar compounds, he confessed that his theory was inadequate: 'The closer discussion of such questions, however, is far out of the range of the present theory' (p. 874).

In spite of its obvious inadequacies, Bohr's atomic chemistry of 1913 marked an important advance in chemical philosophy. It was the first theory of real atoms and

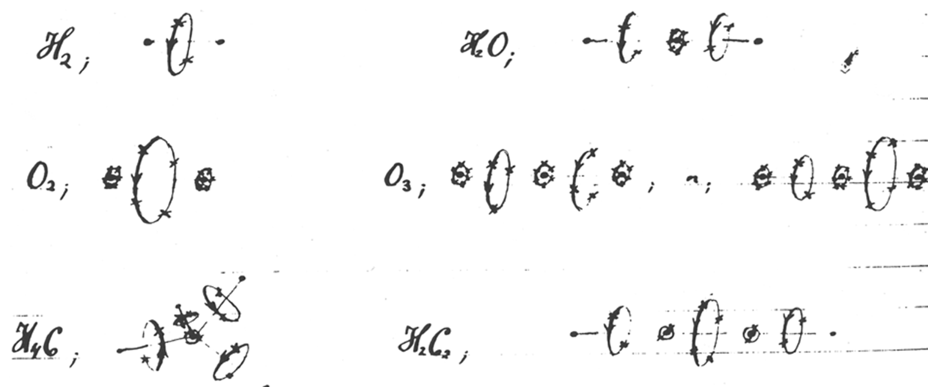


**Fig. 2.4.** Drawings from the Manchester memorandum showing how Bohr conceived the molecular structure of hydrogen, oxygen, ozone, water, methane, and ethyne.
*Source*: Hoyer 1974, p. 160.

molecules that offered an explanation of their structure in terms of configurations of electrons. The dynamical conception of the chemical bond was based on physical calculations which were, however, too complex to be of any use in molecules except the most simple ones. As it soon turned out, the covalent bond did not yield to Bohr's theory, which was, in this respect, a failure.[122] With the exception of a paper of 1919 on the possible existence of triatomic hydrogen (Section 3.2), Bohr did not follow up his ideas of molecular structure. Nor did these ideas catch the attention of contemporary chemists, who generally ignored them. This was not because they were unaware of them, for the three papers of the trilogy were extensively abstracted in the abstract journal of the London Chemical Society.[123] It was rather because they found the theory to be difficult and of little use to chemical problems. Among the very few chemists who responded to Bohr's atomic chemistry was Ernst Buchner at the Chemical Laboratory of the University of Amsterdam, who in 1915 suggested a modification of Bohr's electron configurations of simple molecules.[124] As Buchner pointed out, it was difficult to arrange the electrons in $NH_3$ in accordance with Bohr's principles and, at the same time, represent the radical $NH_4$ (or the corresponding ion $NH_4^+$) in agreement with chemical knowledge.

## 2.7 OTHER ASPECTS OF THE TRILOGY

'On the Constitution of Atoms and Molecules' was a sequel of papers rich in ideas and results. Although the atomic model and its use in explaining simple spectra and the electron configuration of elements had by far the greatest impact, the three papers included other innovative considerations that are worth mentioning.

In the second part of the trilogy Bohr briefly discussed the distinct X-ray lines that Charles Barkla and others had found were characteristic of the elements emitting the X-rays. Bohr suggested that the lines had their origin in a mechanism similar to the one producing the optical lines, only involving electron transitions to the inner rings of the atom. He ascribed the characteristic K-lines, known to have higher frequencies than lines belonging to other series, to electrons settling down in the innermost ring. Disregarding for reasons of simplicity the other atomic electrons, he considered an electron rotating round a nucleus of charge $Ne$. To remove the bound electron by the impact of a cathode-ray electron, the latter particle needs to have a minimum velocity equal to the velocity of the bound electron. According to Bohr's theory, this velocity is given by $2\pi e^2 N/h$. With the generally accepted relation $A = 2N$ between atomic weight and atomic number Bohr obtained

$$v_{\min} = \frac{\pi e^2}{h} A \cong 10^8 \mathrm{cms}^{-1},$$

in full agreement with the experimental result found by Whiddington. Bohr was well aware that his discussion of the atomic origin of the K-rays was only a 'first approximation', as he said to Rutherford. 'I have omitted any attempt to determine the numbers of electrons on the innermost rings, by comparing the characteristic Röntgen-radiation of the different types.'[125] It would soon turn out that Bohr's atom was even more useful in the study of characteristic X-rays than he imagined. But in the summer of 1913 he could not anticipate the results of Moseley's research programme on X-ray spectroscopy.

At the very end of the third part of the trilogy Bohr referred to the relationship between his atomic theory and Weiss's theory of magnetons. This was a subject which interested him greatly and which often turned up in his correspondence. 'I have thought somewhat about magnetism these days', he wrote to Harald in August 1913, 'and I think I have found out a little about it'. However, he decided not to include these thoughts in the paper: 'I had considered including some remarks about it in the proof to Part II; but I give it up after all . . . '.[126] Bohr's ideas about magnetism are known in part from a draft originally intended for Part II in which he considered the magnetic moment arising from an electron moving in a circular orbit. Using the quantum of the angular momentum he calculated the total magnetic moment $\mu$ for a mole of matter containing $N_{\mathrm{A}}$ particles:

$$\mu = N_A M_0 = \frac{N_A eh}{4\pi mc} = 5610.$$

This was almost exactly five times the value of the molar magneton as determined experimentally by Weiss. In his book *The Electron Theory of Matter*, Owen Richardson calculated a value that was six times as large as Weiss's, adding in a footnote: 'I have learned from a conversation (July 1913) with Dr Bohr, who had made similar calculations, that a more exact experimental value of the magneton makes this ratio exactly five'.[127] Bohr thought that the coincidence might be significant: 'This simple relation may be considered as promising for a theory of magnetism based on the assumption used in my former paper; a detailed discussion, however, involves problems of great difficulty as it is necessary to introduce new assumptions about the behaviour of bound electrons in a magnetic field'.[128] He left it at that.

Considering radioactivity to be an integral part of his theory, Bohr included a section on radioactive phenomena in Part II. Most of the section was concerned with beta radiation, which Bohr argued was of nuclear origin. As mentioned in Section 2.2, Bohr had reached this conclusion as early as about June 1912. It was an original view at a time when it was generally assumed by physicists accepting the nuclear model that beta particles came from the rings of electrons surrounding the nucleus. Thus, Rutherford believed that instabilities in the electron system caused by, for example, the emission of alpha particles gave rise to orbital electrons escaping as beta particles. As these free electrons passed the bound electrons in the rings they would lose some of their energy in the form of gamma radiation. He distinguished between 'the instability of the central nucleus and the instability of the

electronic distribution. The former type of instability leads to the expulsion of an $\alpha$-particle, the latter to the appearance of $\beta$ and $\gamma$-rays'.[129] Bohr apparently accepted the gamma ray mechanism, but he stressed that 'On the present theory it seems also necessary that the nucleus is the seat of the expulsion of the high-speed $\beta$-particles'.[130]

For one thing, Bohr argued from the constancy of the angular momentum that when an alpha particle was expelled from the nucleus and traversed the electron system, the result would not disturb the electron rings to such an extent that they became unstable. As he expressed it to Rutherford: 'From the point of view of the theory, the argument of the invariance of the angular momentum of the electron during the expulsion of an $\alpha$ particle seems to me strongly in support of the hypothesis that the $\beta$-rays have their origin in the nucleus'.[131] To this argument he added another one, based on the new notion of isotopy, a word yet to be coined. It was known that some radioactive substances, apparently belonging to the same element, emitted beta rays with different velocities. If the substances were isotopes they would have the very same electron systems and only differ in their atomic weights, meaning their nuclei. The phenomenon 'shows that $\beta$-rays as well as the $\alpha$-rays have their origin in the nucleus' (p. 501).

Bohr's conclusion soon became generally accepted. Rutherford expressed his agreement with his former research student in a letter to *Nature* dated 6 December 1913 in which he said that he had 'thought for some time' that beta rays had the same origin as alpha rays.[132] In his paper introducing isotopes, Soddy arrived at the same conclusion, but without mentioning Bohr. A somewhat similar view was expressed by Marie Curie at the second Solvay conference in 1913, in a discussion about Thomson's new theory of the atom.[133] Curie distinguished between 'essential' and 'peripheral' electrons, with the first residing in the 'nuclear part' of the atom. However, what might look like a reference to Rutherford's nuclear model was really a version of Thomson's. She did not refer to the views of either Rutherford or Bohr.

## Notes for Chapter 2

1. Heilbron 1981, p. 230, according to whom 'Bohr's atomic theory belongs to the program of semiliteral model making initiated by J. J. Thomson and based on the methods of mid-Victorian Cambridge physics'.

2. Major biographies of Niels Bohr include Pais 1991, Moore 1966, and Röseberg 1985. There is also much information of a biographical kind in Rozental 1967 and in the 12 volumes of the *Niels Bohr Collected Works* published between 1972 and 2007.

3. Christiansen and Müller 1921, the content of which did not include either quantum or relativity physics. The book includes a valuable biographical essay by Eilhard Wiedemann on Christiansen's life and career (pp. xi–xxiv).

4. For opposite views on the Bohr–Høffding relationship, that is, whether Høffding significantly influenced Bohr's thinking about quantum physics or not, see Faye 1991 and Favrholdt 1992. The relevant literature can be found in these two works. In agreement with Faye, Wise

1990 argues for a close correlation between Høffding's philosophy and Bohr's ideas of atomic structure, if not necessarily a direct inspiration from the philosopher to the physicist. A stronger (but not more convincing) claim for Høffding's role in forming Bohr's ideas of atomic structure and the correspondence principle has recently been made by Angelino 2010. The suggestion that Kierkegaard's philosophy inspired some of Bohr's ideas appears in Jammer 1966, Holton 1970, and Feuer 1974.

5. The handwritten prize essay and the two papers are reproduced in Rud Nielsen 1972, pp. 21–92.

6. Niels Bohr to Harald Bohr, 26 April 1909, in Rud Nielsen 1972, p. 503.

7. For the history of the electron gas theory of metals, see Kaiser 2001 and the literature cited in this source. See also Hoddeson and Baym 1980.

8. See, for example, Kuhn 1978 and Seth 2004.

9. This claim has been made by Mara Beller, according to whom 'Bohr's mastery of mathematics was very limited' (Beller 1999, p. 259). She further argues that this supposed lack of mathematical skills was partly responsible for his complementarity interpretation of quantum mechanics.

10. Rud Nielsen 1972, p. 378, which contains a full English translation of the dissertation. Bohr first referred to Planck's radiation law and its incompatibility with electron theory in his master thesis of 1909. For an analysis of the dissertation and its role in the formation of Bohr's ideas of atomic structure, see Heilbron and Kuhn 1969. The papers by Einstein that Bohr referred to were on the theory of radiation and light quanta.

11. Rud Nielsen 1972, p. 299.

12. The translation on p. 300 in Rud Nielsen 1972 does not follow the Danish text very well. The quoted translation, which largely agrees with the one in Heilbron and Kuhn 1969, is my own.

13. Rud Nielsen 1972, p. 395.

14. Van Leeuwen 1921, who did not refer to Bohr's earlier work of which she most likely was unaware. The Bohr–van Leeuwen theorem has found use in several branches of modern physics, including plasma physics and electrical engineering.

15. Rud Nielsen 1972, p. 298. Emphasis added.

16. Pais 1991, p. 121.

17. Rud Nielsen 1972, p. 429. See also Niels Bohr to Harald Bohr, 23 October 1911, in Rud Nielsen 1972, pp. 527–32. On Bohr's acquaintance with Oseen, see Rosenfeld and Rüdinger 1967, p. 39. More details on Oseen and his promotion of quantum and relativity physics in Sweden are given in Grandin 1999.

18. Rud Nielsen 1972, p. 427. In the letter to Harald of 23 October: 'In fact, Thomson has so far not been as easy to deal with as I thought the first day. . . . He has not yet had time to read my paper, and I don't know if he will accept my criticism. He has only talked to me about it a few times for a couple of minutes'.

19. As late as 1920 Bohr attempted to get the dissertation published in the United States. For his various unsuccessful efforts, see Rud Nielsen 1972, pp. 103–19.

20. Quoted in Rosenfeld and Rüdinger 1967, p. 45, who provide no date.

21. Undated letter quoted in Caroe 1978, p. 70. W. Henry Bragg was at the time at Leeds University. In 1915 father and son shared the Nobel Prize for their pioneering studies of crystal structures by means of X-rays.

22. W. L. Bragg, Autobiographical Notes, quoted in Jenkin 2008, pp. 319–20. Jeans's lecture course was given in the Lent term 1912.

23. Bohr to Oseen, 1 December 1911, in Rud Nielsen 1972, p. 427.

24. For the history of the magneton, see Hoddeson et al. 1992, pp. 384–94 and Okada 2002. For Weiss's magneton, which turned out to be a mistake, see Quédec 1988.

25. This suggestion is due to Heilbron and Kuhn 1969, where further arguments and sources can be found.

26. See Okada 2002.

27. Wilson 1983, p. 326. Aaserud 2007, p. 108. See also the 1962 interview with Bohr (www.aip.org/history/ohilist/4517_1.html), where Lorrain Smith is transcribed as 'Lawrence Smith'.

28. Bohr 1932, p. 353.

29. In his book on radioactivity completed in the fall of 1912 (preface dated October 1912), Rutherford distinguished between two types of instability, the one rooted in the nucleus (alpha rays) and the other in the outer system of electrons (beta and gamma rays). When an alpha particle is expelled from the nucleus, 'Part of the surplus energy of a ring of electrons is released in the form of a high speed $\beta$ particle and part in the form of $\gamma$ rays'. Rutherford 1913a, p. 622. See further Section 2.7.

30. Hevesy to Bohr, 15 and 29 January 1913, in Hoyer 1981, p. 528. Hevesy 1913.

31. Bohr to Hevesy, 7 February 1913, in Hoyer 1981, p. 530.

32. Rutherford to Fajans, 19 April 1913, as quoted in Peierls 1988, p. 232.

33. Fajans to Rutherford, 13 December 1913, quoted in Jensen 2000, p. 34.

34. Hevesy to Rutherford, 14 October 1913, as reproduced in Eve 1939, p. 225.

35. Bohr 1961, p. 1085. Similarly in the 1962 interview by Kuhn et al. (www.aip.org/history/ohilist/4517_1.html) as quoted in Pais 1991, pp. 126–7.

36. Darwin 1912, p. 901.

37. Rud Nielsen 1972, p. 555. Although this is the first reference to Rutherford's atomic model in Bohr's correspondence, he most likely knew of the model even while at Cambridge.

38. Letter of 19 June 1912, ibid., p. 559.

39. Bohr 1913a, pp. 26–7. The paper is reprinted in Thorsen 1987, pp. 50–71.

40. Bohr 1913a, p. 25. Cuthbertson and Cuthbertson 1910.

41. Bohr to Cuthbertson, 4 April 1913, in Thorsen 1987, p. 666. The letter was a reply to Cuthbertson to Bohr, 23 March 1913.

42. Hoyer 1981, p. 577.

43. The Rutherford memorandum is reproduced in Rosenfeld 1963, pp. xxi–viii and Hoyer 1981, pp. 135–58. Rosenfeld assumes that a page is missing in the extant document preserved at the Niels Bohr Archive. A careful analysis of the memorandum is given in Heilbron and Kuhn 1969, who note some mistakes in Bohr's arguments. Some of my quotations from the memorandum are slightly modified, but only with regard to Bohr's frequent danicisms and spelling mistakes.

44. Hoyer 1981, p. 136. The following quotations are from the same source.

45. For the arguments in support of $K \cong 0.6h$, see Rosenfeld 1963, p. xxxi, and Heilbron and Kuhn 1969, pp. 250–1.

46. Pais 1991, p. 133. Rud Nielsen 1963, p. 22.

47. Bohr to Rutherford, 6 July 1912, in Hoyer 1981, p. 577.

48. Bohr to Rutherford, 4 November 1912, in Hoyer 1981, p. 577.

49. Bohr to Rutherford, 22 June 1913, in Hoyer 1981, p. 587. For Bohr's considerations, see Hoyer 1973, pp. 189–93.

50. Niels Bohr to Harald Bohr, 23 December 1912, in Rud Nielsen 1972, p. 563.

51. Bohr to Rutherford, 31 January 1913, in Hoyer 1981, p. 579.

52. Fujisaki 1982 argues that Bohr was greatly influenced by the theories of Drude and Stark concerning molecular spectra and that he considered the molecular hydrogen spectrum in the ultraviolet and infrared regions months before he turned to the line spectrum of atomic hydrogen. Fujisaki's arguments are circumstantial and have no convincing support in the sources.

53. Bohr to Hevesy, 7 February 1913, in Hoyer 1981, p. 529.

54. Rosenfeld 1963, p. xxxix.

55. Christiansen 1910, where Balmer's formula appears on pp. 353–4. Also the second edition of 1903 included the Balmer formula (p. 456). Incidentally, the fourth edition of the same textbook, from 1915 and revised by Martin Knudsen, mentioned Bohr's new theory in connection with Planck's introduction of the quantum of action: 'This approach has later been used by N. Bohr in a theory which, among other things, provide an explanation of the location of the lines in the Balmer series and other spectral series' (p. 456).

56. Interview of 7 November 1962 by Thomas Kuhn, Léon Rosenfeld, Erik Rüdinger and Aage Petersen (Niels Bohr Library & Archives, American Institute of Physics, www.aip.org/history/ohilist/4517_1.html). It is possible that the book where Bohr looked up Balmer's formula was Stark's *Atomdynamik*, which was in his reference library (Stark 1911). Stark's book introduced the Balmer spectrum and formula on pp. 43–5.

57. This formula was actually inferred by Balmer, but in an unpublished manuscript only. See Banet 1970 for an exposition of Balmer's route to his spectral formulae for hydrogen.

58. A plausible reconstruction of Bohr's analysis in February–March 1913 is offered in Rosenfeld 1963, pp. xl–xli.

59. Bohr to Rutherford, 6 March 1913, in Hoyer 1981, p. 581. I have changed Bohr's spelling of 'vieuw' to 'view'.

60. Bohr to Rutherford, 21 March 1913, in Hoyer 1981, p. 584.

61. There are several analyses of the first part of the trilogy. See in particular Hirosige and Nisio 1964, Jammer 1966, pp. 76–88, Heilbron and Kuhn 1969, pp. 267–83, Hoyer 1974, pp. 131–49, Petruccioli 1993, pp. 50–64, and Arabatzis 2006, pp. 124–44. A concise overview of the trilogy and Bohr's further development of his theory is given in El'yashevich 1986.

62. It was well known at the time that a natural length existed in the form of the radius of the electron, as given by the theory of electromagnetism. However, this length ($e^2/mc^2 \cong 10^{-13}$ cm) involved the speed of light in vacuum.

63. Bohr 1913b, p. 2. Bohr was aware of the discussions at the first Solvay congress, to the published report of which he referred (Langevin and de Broglie 1912). See also Mehra 1975. As mentioned, the problem of the natural length was also included in the earlier Manchester memorandum.

64. Bohr 1913b, p. 4. Bohr calculated the rate of change of radius and frequency of an electron circulating about a nucleus, but did not include the calculations in his published work. See Hoyer 1974, pp. 143–9 and Hoyer 1981, pp. 243–8.

65. Bohr 1913c, p. 488. Thomson 1912, p. 218. In 1914 the German physicist Heinrich Rau, at the University of Würzburg, reported experiments from which he inferred an ionization energy

for hydrogen of about 13 eV (Rau 1914). One year later Bohr narrowed down his theoretical value to 13.6 eV, which remains the accepted value to this day (Bohr 1915a).

66. Bohr 1913b, p. 7. Bohr also referred to Haas's attempt of 1910 'to explain the meaning and the value of Planck's constant on the basis of J. J. Thomson's atom-model'.

67. Bohr 1913b, p. 24. As we shall see in Section 3.6, Bohr's attempt of reconciliation was not accepted by Nicholson, who in 1913–1915 seriously criticized Bohr's theory.

68. Bohr 1913b, p. 7. The two assumptions are generally known as Bohr's postulates, but he did not refer to them as such until several years later (e.g. Bohr 1921a, p. 1).

69. Russell 1927, p. 175.

70. Ehrenfest 1913. While Bohr knew about Nicholson's work, he was not aware of Ehrenfest's in time to include it in his work.

71. Bohr 1913b, p. 15 and Bohr 1913c, p. 477.

72. Bohr 1913b, pp. 16–17. Wood 1911, p. 513.

73. Sommerfeld 1922a, p. 52. In his paper introducing the new quantum mechanics, Heisenberg (1925, p. 879) similarly referred to 'the Einstein–Bohr frequency condition'.

74. Olmstead and Compton 1923.

75. A detailed examination of Bohr's stability calculations is given in Hoyer 1973 and Hoyer 1974, pp. 100–13.

76. Ritz 1908. On Ritz's important works in theoretical spectroscopy, see Carazza and Robotti 2002.

77. Bohr 1913c, p. 482 and p. 495.

78. Bohr's lecture was first published in *Fysisk Tidsskrift* **12** (1914), 97–114. An English translation appeared in Bohr 1922a, pp. 1–19 and is reprinted in Hoyer 1981, pp. 283–301.

79. Bohr 1913d, p. 874. On the relation between Planck's second theory of quanta and Bohr's atomic theory, see Hirosige and Nisio 1964, who argued that Planck's theory was of great importance to Bohr's. On this matter Heilbron and Kuhn (1969, p. 272) disagreed, but Kuhn (1978, note 33 on p. 320) later admitted the importance of Planck's second theory. See also the discussion in Achinstein 1993.

80. Bohr 1922a, p. 10.

81. Ibid., p. 11. Bohr's statement can be seen as an early (if restricted) expression of the observability principle that became important in the final phase of the old quantum theory (Section 8.6).

82. Bohr 1913b, p. 19.

83. Bohr 1922a, p. 10 and pp. 12–13. According to Pais 1991 (p. 148), Bohr's derivation of the Rydberg constant represented 'a triumph over logic'. In his perceptive study of Bohr's theory, Petruccioli calls the theory 'a brilliant demonstration of how all the rules of logic and methodology might be violated in the interests of a cavalier type of theoretical approach' (Petruccioli 1993, p. 63). On the claimed inconsistency of Bohr's atomic theory, see the appendix of the present book.

84. Bohr 1922a, p. v, preface dated May 1922.

85. Millikan 1951, p. 110.

86. Brackett 1922. Pfund 1924. It took until 1953 before the series corresponding to $\tau = 6$ was detected.

87. Lyman 1914.

88. Bohr 1915a, p. 6.

89. Lyman 1915, p. 370 and Lyman 1916, p. 91. The second paper was an extended version of the first. Lyman was guided by a formula of Walther Ritz from 1908, not by Bohr's formula of 1913. For details on the works of Ritz and Lyman, see Konno 2002.

90. Lyman 1916, p. 100.

91. Pickering 1896. For a detailed account of the complex case of the Pickering–Fowler lines, see Robotti 1983. See also Maier 1964, pp. 476–84, and, for a valuable review from a more contemporary perspective, Plaskett 1922.

92. Fowler 1912.

93. Hoyer 1981, p. 582. The chemist Niels Bjerrum, who at the time was a lecturer at the University of Copenhagen and the following year was appointed professor at the Agricultural and Veterinary College, was a personal friend of Bohr. In 1911–1912 he did pioneering work in the new field of chemical physics which included the application of quantum theory to rotating and vibrating molecules (see Section 6.3). Bohr was acquainted with Bjerrum's works and referred to them in the third part of the trilogy, in connection with the hydrogen molecule. On his part, Bjerrum referred to Bohr's atomic theory in a paper of 1914 dealing with the infrared spectra of carbon dioxide and other simple gases. See Bjerrum 1914, p. 749, with English translation in Bjerrum 1949, pp. 41–55.

94. Rutherford to Bohr, 20 March 1913, in Hoyer 1981, p. 583. In Bohr's theory the electron did not 'vibrate', contrary to what Rutherford seems to have thought.

95. Evans 1913, dated 11 August. This may have been the first published reference to Bohr's atomic theory.

96. Fowler 1913. Bohr 1913e. In March 1914 Bohr pointed out that while $R_H = 109\ 675\ cm^{-1}$, the value for the heavier elements would be $R_\infty = 109\ 735\ cm^{-1}$ (Bohr 1914a, p. 512). The philosopher Imre Lakatos (1970, p. 149) referred to Bohr's response as a case of 'monster-adjustment', that is, turning a counterexample into an example.

97. Fowler to Bohr, 27 October 1913, in Hoyer 1981, p. 503. Fowler publicly admitted the agreement in a note accompanying Bohr's paper in *Nature*. In his Bakerian Lecture of 2 April 1914 he used Bohr's expression $R_\infty/R_H = 1 + m/M$ to suggest a proton–electron mass ratio of $M/m = 1836 \pm 12$ (Fowler 1914, p. 258).

98. Paschen to Sommerfeld, 24 February 1915, in Eckert and Märker 2000, p. 500. Paschen 1916.

99. Evans 1915.

100. Fowler to Bohr, 6 March 1915, in Hoyer 1981, p. 509.

101. Merton 1915, p. 383.

102. Nicholson 1913b. Bohr 1913c, p. 490. Ernest Wilson (1916, p. 25) called the new Balmer-like series 'one of the most remarkable and important points of Nicholson's work'.

103. Bohr 1913c, p. 480.

104. Bohr to Fowler, 15 April 1914, in Hoyer 1981, p. 504. Bohr included the formula in a paper of 1915 (Bohr 1915c, p. 334). On Bohr's relativistic calculations, see Hoyer 1974, pp. 241–7, and the sheet reproduced in Hoyer 1981, p. 382. This was the first scientific use of the theory of relativity made by a Danish physicist.

105. Curtis 1914, who referred to Bohr's theory and also to his still unpublished modification of the simple Balmer formula, which he knew from the correspondence between Bohr and Fowler.

106. Bohr to Fowler, 28 April 1914, in Hoyer 1981, p. 506.

107. On these aspects, see Kragh 1977 on which the present section draws. Bohr's atomic chemistry has generally been ignored by historians of chemistry (but see Scerri 2007, pp. 188–97, on Bohr's 1913 version of the periodic system). More will follow in Chapter 6.

108. Bohr to Hevesy, 7 February 1913, in Hoyer 1981, p. 530. Bohr explicitly excluded gravitation and radioactivity from his notion of 'chemical and physical properties of matter'.

109. Bohr 1913c, p. 486.

110. Franck and Hertz 1913.

111. Bohr 1913c, p. 489. For Bohr's use of dispersion data, see Konno 2000.

112. As Langmuir commented: 'Bohr's original theory would thus indicate that lithium and beryllium (and all subsequent elements) should be inert gases having even greater stability than helium' (Langmuir 1921c, p. 341).

113. Bohr 1913c, p. 496.

114. Abegg 1904. Abegg, a professor of physical chemistry at Breslau, was among the first to give an electron treatment of chemical affinity and valence. J. J. Thomson discussed Abegg's rule of eight and its relation to his own atomic theory in *The Corpuscular Theory of Matter* (Thomson 1907, pp. 118–19). He had to admit that his theory was unable to explain the rule. Since Bohr was familiar with Thomson's book he presumably was aware of Abegg's two valences and the relation between them. On Abegg's work and its significance for the early attempts to base the periodic system on arrangements of electrons, see Stranges 1982, pp. 46–8, 80–4.

115. Hevesy to Bohr, 6 August 1913, in Hoyer 1981, p. 532. The spelling is Hevesy's.

116. Bohr 1913d, p. 862.

117. Bohr 1913d, p. 863.

118. Langmuir 1912. Bohr referred to Langmuir's result, which he found difficult to reconcile with his own.

119. Langmuir 1914, p. 188. Langmuir to Bohr, 2 December 1913, and Bohr to Langmuir, 17 December 1913, in Hoyer 1981, pp. 539–40.

120. Langmuir 1915, p. 452.

121. Cuthbertson and Cuthbertson 1910.

122. For more on this failure, see Sections 3.9 and 6.1. Using modern ideas Bohr's theory of molecules can be extended to provide a good picture of the covalent bond and molecular behaviour (Svidzinsky et al. 2005). Interesting as this observation is, from a historical point of view it is of course irrelevant.

123. The first paper was abstracted by J. F. Spencer and the two others by H. M. Dawson (Spencer 1913; Dawson 1913).

124. Buchner 1915, who argued that his revised electron configurations might explain some of the chemical analogies known from inorganic chemistry, such as the analogy between the ammonium ion and the alkali ions. See also Section 6.1. Bohr contemplated a response to Buchner's paper, but his response remained a draft (Archive for History of Quantum Physics, Bohr Scientific Manuscripts).

125. Bohr to Rutherford, 10 June 1913, in Hoyer 1981, p. 586.

126. Niels Bohr to Harald Bohr, 3 August 1913, in Rud Nielsen 1972, p. 565.

127. Richardson 1916 (second edition of Richardson 1914), p. 395.

128. Manuscript on magnetism, reproduced in Hoyer 1982, pp. 254–6.

129. Rutherford 1912, p. 461 and similarly in Rutherford 1913a, p. 622.

130. Bohr 1913c, p. 500.

131. Bohr to Rutherford, 10 June 1913, in Hoyer 1981, p. 586.

132. Rutherford 1913b. However, Rutherford distinguished between primary and secondary beta electrons. He found it 'very likely that a considerable fraction of the $\beta$ rays which are expelled from radioactive substances arise from the external electrons . . . arising from the primary expulsion of a $\beta$ particle from the nucleus'. See also Jensen 2000, pp. 34–7.

133. Soddy 1913. For Curie, see her discussion contribution in Thomson 1921, p. 56.