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NIELS BOHR AROUND 1920

The publishers are grateful to the Bohr family for permission to reproduce this photograph and to Professor L. Rosenfeld for supplying the print.

The Genesis of the Bohr Atom

BY JOHN L. HEILBRON* AND THOMAS S. KUHN**

INTRODUCTION

The following pages offer a reconstruction of a momentous episode in the history of science: Niels Bohr's journey from his doctoral thesis of 1911 to the composition, some two years later, of his famous three-part paper, "On the Constitution of Atoms and Molecules." Parts of this story have been told before, most notably by Léon Rosenfeld, who has published and interpreted the most important of the relevant manuscripts.[1] Informed by its author's long acquaintance with Bohr, Professor Rosenfeld's imaginative and scholarly account will remain an essential source for students of the development of modern physics. Recent writers, however, working principally from published records to which Rosenfeld attached little weight, have suggested the need for significant modifications in his account, particularly in respect to the importance for Bohr of the work of J. W. Nicholson.[2] As a result, though

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[1] L. Rosenfeld, "Introduction" to *On the Constitution of Atoms and Molecules* (Copenhagen, 1963), a reprinting of Bohr's three papers of 1913, hereafter cited as "Rosenfeld." See also L. Rosenfeld and E. Rüdinger, "The Decisive Years, 1911–1918," in S. Rozental, ed., *Niels Bohr: His Life and Work as seen by his Friends and Colleagues* (Amsterdam and New York, 1967), 38–73.

[2] E.g., T. Hirosige and S. Nisio, "Formation of Bohr's Theory of Atomic Constitution," *Jap. Studies Hist. Sci.*, No. 3 (1964), 6–28; J. L. Heilbron, *A History of Atomic Models from the Discovery of the Electron to the Beginnings of Quantum Mechanics*, diss. (University of California, Berkeley, 1964); R. McCormmach, "The Atomic Theory of John William Nicholson," *Arch. Hist. Exact Sci.*, *3* (1966), 160–184. The older literature (e.g., C. E. Behrens, "Atomic Theory from 1904 to 1913," *Am. J. Phys.*, *11* [1943], 60–66, "The Early Development of the Bohr Atom," *ibid.*, 135–147, and "Further Developments of Bohr's Early Atomic Theory," *ibid.*, 272–281; E. T. Whittaker, *A History of the Theories of Aether and Electricity. II. The Modern Theories, 1900–1926* [London, 1953]; and L. S. Polak, "Die Entstehung der Quantentheorie des Atoms (Das Rutherford-Borsche Atommodell)," *Sowjetische Beiträge zur Geschichte der Naturwissenschaft* [Berlin, 1960], 226–242), since its authors were necessarily ignorant of Rosenfeld's account, is not useful for a reconstruction of Bohr's *path*, though it can help to place his work in historical context.

the existing secondary literature is rich in suggestions and documentation concerning particular aspects of Bohr's route to the quantized atom, there exists as yet no treatment of the subject that is at once comprehensive and plausible. Our aim in this paper is to fill that gap, partly by a critical synthesis of suggestions in the existing literature, and partly by an elaboration of some central but previously neglected strands in Bohr's scientific development.

A cursory reading of Bohr's thesis reveals that, when he finished it early in 1911, he was already convinced that some fundamental break with classical physical theory, probably some form of Planck's quantum theory, would be necessary to resolve specific problems in the electron theory of metals. Very likely, as many have noted, that conviction was an essential prelude to Bohr's attempt, begun within a year and a half of his thesis defense, to quantize Rutherford's atom. But, if the prelude prepares the attempt, it explains neither its origin nor its nature. A concern with detailed atom models was not widespread in the years before World War I; Bohr, in any case, does not mention them in his thesis. Nor are they discussed before June 1912 in any of the many extant letters and manuscripts he wrote while a postdoctoral fellow in Cambridge and Manchester. Yet, within six weeks of the earliest surviving sign of his concern with models, Bohr had produced a quantized version of Rutherford's atom and had applied it to several problems. What suddenly turned his attention from electron theory to atom models during June 1912? Why did he then choose to develop the new, little-known Rutherford atom rather than, say, the older, more successful model proposed by J. J. Thomson? Why did he approach the quantization problem in the particular way he did, one which bore impressive fruits at once and which, a year later, began to revolutionize physics?

We are persuaded that the answer to these and to similar questions lies not in the general conviction of the need for quantum theory which Bohr drew from his thesis research, but rather in certain *specific* problems with which he busied himself until almost the end of his year in England. They helped direct his reading and uniquely prepared him to recognize the special potential of the nuclear atom. The first three sections below detail these problems, suggest how they focussed Bohr's attention on the question of atomic structure, and analyze the way they combined with other factors in the formulation of Bohr's first quantized model of the atom. That model is not, however, the one for which Bohr is known: it possessed only a single stationary state and was neither built around nor applied to the problems of atomic spectra. Sections IV and V trace the development of Bohr's radical conception of stationary states, of his concern with spectra, and of his derivations of the Balmer formula together with the first hints of a Correspondence Principle. These are Bohr's most famous contributions, and they are contained entirely in the first part of his famous trilogy, supplemented by a lecture he gave to the Danish Physical Society in December 1913. Less familiar now, but then of equal concern to Bohr, were his speculations about the stable electronic configurations of polyelectronic atoms and molecules which occupy the last two parts of the trilogy. Section VI outlines these speculations and indicates certain difficulties in Bohr's formulation which were soon to challenge those who built upon his principles.

Our reconstruction rests mainly upon the printed record and the Bohr scientific correspondence and manuscripts in the Archive for History of Quantum Physics.[3] In addition, we have been allowed to see portions of the personal papers of the Bohr family. We deeply appreciate the kindness of Professor Aage Bohr, of Mrs. Margrethe Bohr, and of Professors J. Rud Nielsen and Rosenfeld in making this personal correspondence available to us: it has helped us to understand Bohr's transition from cultivator of the electron theory of metals to developer of the nuclear atom. To the Bohr family we are grateful as well for permission to reproduce the many quotations which follow from Bohr's unpublished correspondence and manuscripts. We also wish to thank Paul Forman, Tetu Hirosige, Martin Klein, Russell McCormmach, Malcolm Parkinson and Léon Rosenfeld for their helpful comments on the final draft of our manuscript.

I. STUDIES ON THE ELECTRON THEORY OF METALS: COPENHAGEN, 1911

On 13 May 1911, Niels Bohr successfully defended his doctoral thesis, *Studier over metallernes elektrontheori,* before the philosophical faculty of the University of Copenhagen. The essay had grown out of his master's dissertation, completed in 1909, and so represented the fruit

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[3] For a description, see T. S. Kuhn, J. L. Heilbron, P. Forman, and L. Allen, *Sources for History of Quantum Physics. An Inventory and Report* (Philadelphia, 1967).

of over two years of concentrated effort. It is thorough and erudite; every page displays its author's critical power, his mathematical suppleness, and his firm grasp of physical principles. His "opponents," who, perhaps, were not entirely competent to judge his work, found little to question. The "defense," which might have lasted six hours, was over in a record-making ninety minutes.[4]

The theory Bohr took as his subject traced conductivity and other metallic properties to "free" electrons, i.e., to charged particles unattached to the molecules making up the metals. Though its roots extended deep into the nineteenth century, in the work of Ampère and of Weber, its major development had occurred in the decade following the experimental isolation of the electron. Then it became one of the most exciting, promising, and popular branches of physics. Its power was increased very quickly, for the elaborate techniques of Maxwell and Boltzmann stood ready for application to the electron "gas." In 1905 H. A. Lorentz published the first systematic development of the statistical mechanics of free electrons.[5]

Lorentz' theory rested on two principles: (1) that in the absence of external fields or temperature differences the electron gas and the stationary metal molecules remain in mechanical heat equilibrium, and (2) that, whether subject or not to external forces, the molecules act isotropically on the electrons. These principles in themselves of course did not enable one to calculate; special assumptions about the interactions of the particles were also required. Here Lorentz simplified. He supposed that the electrons bounced elastically off the metal molecules like billiard balls and that the effects of collisions between electrons were negligible, assumptions which, in Bohr's words, could "scarcely hold even approximately in real metals." [6] Lorentz' principles provided the point of departure, and his special assumptions the challenge, of Bohr's thesis. "The goal I have set myself," he wrote, "is to attempt to carry out calculations for the different phenomena which are explained by the presence of free electrons in metals, in the most general manner possible consistent with the principles of Lorentz' theory." [7]

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[4] N. Bohr, *Studier over metallernes elektrontheori* (Copenhagen, 1911); S. Rozental, *Niels Bohr,* 36–37.

[5] H. A. Lorentz, "The Motion of Electrons in Metallic Bodies," *Proc. Amst. Acad., 7:2* (1905), 438–453, 585–593, 684–691.

[6] Bohr, *Studier,* 4. Though we have profited from other translations where they exist, this and all subsequent ones are our own.

[7] *Ibid.*

Now, as Bohr observed, the first of these principles, that of heat equilibrium, implied that the electrons and the molecules interacted according to the usual laws of mechanics, that their motions always satisfied Hamilton's equations. In admitting the principle for *free* electrons, however, he emphasized that it was an assumption of very limited applicability:

> The assumption [of mechanical interaction] is not *a priori* self-evident, for one must assume that there are forces in nature of a kind completely different from the usual mechanical sort; for while on the one hand the kinetic theory of gases has obtained extraordinary results by assuming the forces between individual molecules to be mechanical, there are on the other hand many properties of bodies impossible to explain if one assumes that the forces which act within the individual molecules (which according to the ordinary view consist of systems containing a large number of "bound" electrons) are mechanical also. Several examples of this, for instance calculations of heat capacity and of the radiation law for high frequencies, are well-known; we shall encounter another later, in our discussion of magnetism.[8]

This most interesting passage, which expresses unambiguously its author's conviction of the ultimate incompetence of "the ordinary mechanics" in atomic theory, sets the tone of the thesis. When combined with different special assumptions, Lorentz' principles often gave conflicting results, none of which agreed more than approximately with experiment. By developing the electron theory in the widest generality, Bohr intended to separate the difficulties dependent on each author's special assumptions from those which were fundamental. The former he could diminish or eliminate with other special assumptions. The latter might, though Bohr did not make the hope explicit, furnish the starting point for the necessary revisions of classical mechanics.

The isotropy of molecular action independent of the presence of an external field, Lorentz' second principle, distinguished Bohr's approach from theories like J. J. Thomson's, in which the fields, by acting directly upon bound electrons, disturbed the original spatial symmetry of the molecules.[9] Bohr could have had little confidence in any theory built upon assumptions about the response of bound electrons

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[8] *Ibid.*, 5.

[9] J. J. Thomson, *The Corpuscular Theory of Matter* (London, 1907), 86; cf. W. Sutherland, "The Electric Origin of Rigidity and Consequences," *Phil. Mag.*, *1* (1904), 417–444, esp. 423–435.

to external fields. In the one case in which he did examine such a response, magnetism, he found that ordinary mechanical principles led to absurd results, and he supposed a similar breakdown was responsible for the well-known paradoxes of blackbody radiation. The assumption of isotropy allowed him generally to disregard the conditions within molecules. It also offered a great mathematical convenience, as he could assume, for example, that the molecules acted on the electrons either continuously, with a force inversely proportional to the rth power of the distance, or in separate collisions, as in the elementary kinetic theory of gases. Bohr in fact performed most of his calculations in parallel, first using separate collisions, as had Lorentz, and then the rth power law.

Bohr's most interesting positive results concerned the famous x, the ratio between a metal's thermal and electrical conductivities, and an obscure phenomenon, the transverse temperature difference ΔT accompanying the Hall effect. Lorentz had obtained the wrong sign for ΔT and a number for x about 40 percent less than that observed. Bohr's computations based on the rth power law, however, agreed quite satisfactorily with experiment in *both* these particulars if r were set equal to three. That two such disparate phenomena should thus be brought into harmony with experience and with one another Bohr thought "remarkable."[10] Part of his enthusiasm over this coincidence may have derived, as we shall see, from a model Thomson had proposed just before this time for quite another purpose, a model which likewise required a force varying as the inverse cube.

The problem of heat radiation also claimed Bohr's careful attention. A complete account of the conduction electrons had to include both the electromagnetic waves which, according to Maxwell's electrodynamics, they emit in their violent stops and starts, and also the accelerations they suffer from any radiation to which they are exposed. In a state of steady motion the amount of energy they absorb must equal the amount they radiate, the precise quantities involved depending on the wavelength λ of the radiation and the temperature T of the steady state. Using very simple assumptions about the interactions between free electrons and metal molecules, Lorentz had derived an expression for the ratio of the coefficients of absorption, $\alpha(\lambda, T)$, to those of emission, $\epsilon(\lambda, T)$, valid for long waves.[11] This ratio was of very great

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[10] Bohr, *Studier,* 57–58, 116–117.

[11] H. A. Lorentz, "On the Emission and Absorption by Metals of Rays of Heat of Great Wavelengths," *Proc. Amst. Acad., 5* (1903), 666–685.

interest for, as Kirchhoff had showed, it should be a universal function of λ and T, quite independent of the nature of the emitting and absorbing body. It is in fact very simply related to the energy density of blackbody radiation.

Planck, of course, had felt constrained to introduce the quantum precisely in order to obtain a formula for this energy density good for all values of λ and T. The theoretician of 1911 had thus to adopt one of two conflicting views about heat radiation. If, on the one hand, he believed that a procedure like Planck's was necessary, and that it was wholly irreconcilable with the ordinary principles of electrodynamics, it would follow from the connection between the blackbody spectrum and ϵ/α that no expression for that ratio valid for all λ and T could be deduced from the electron theory of metals. On the other hand, since Lorentz' expression agreed very nicely with experiment for long waves, our theorist might hope that, by postulating an appropriate *mechanical* interaction between electrons and metal molecules, he could extend Lorentz' computations to shorter wavelengths and explain the blackbody spectrum without recourse to Planck's questionable procedure. Thomson and other Cambridge physicists had developed the latter position.[12] Bohr, as we have seen, embraced the former.

He was led to this conviction, which was still a minority view early in 1911, on two grounds.[13] The first, and probably to him the more persuasive, derived from his own lengthy calculations confirming that Lorentz' expression for ϵ/α for long waves also followed from more general principles than those Lorentz had employed. Bohr's familiarity with the computations and his fine feel for valid approximations convinced him that the apparent success of Thomson's program rested on a flawed assumption about the dependence of absorption on frequency. This conclusion he reinforced with an appeal to the law Rayleigh and Jeans had deduced by applying the principle of energy equipartition to the electromagnetic aether conceived as a mechanical system. The Rayleigh-Jeans law, whose consequences Thomson's school, including Jeans himself, had sought to avoid,[14] agreed with Lorentz'

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[12] J. J. Thomson, "On the Electrical Origin of the Radiation from Hot Bodies," *Phil. Mag., 14* (1907), 217–231; "On the Theory of Radiation," *ibid., 20* (1910), 238–247; J. H. Jeans, "The Motion of Electrons in Solids. I," *ibid., 17* (1909), 773–794. Jeans works out examples only for large wavelengths.

[13] Bohr, *Studier,* 77, 103–104.

[14] They argued, for example, that the flow of energy into the higher-frequency vibrations of the field takes so long that heat equilibrium is not established in the experiments on blackbody radiation. Cf. J. H. Jeans, "Temperature-Radiation and the Partition of Energy in Continuous Media," *Phil. Mag., 17* (1909), 229–254.

expression and with experiment for long waves, but failed hopelessly at the other end of the spectrum. Therefore, without applying his generalized Lorentzian procedures to a direct calculation of the *short*-wave limit of ϵ/α, Bohr concluded that all such computations must inevitably fail. In addition, he localized the difficulty: "The cause of failure is very likely this, that the electromagnetic theory does not agree with the real conditions in matter and can only give correct results if it is applied to a large number of electrons (as in ordinary bodies) or to determine the average velocity of a single electron in a comparatively long time (such as in the calculation of the motion of cathode rays), but cannot [as in short-wave radiation], be used to investigate the motion of a single electron in a short time." [15]

Closely linked to this consequence of electrodynamics, which placed the description of the motions of atomic electrons beyond the reach of the ordinary theory, was a more disconcerting failure, whose detection Bohr considered one of the chief results of his thesis. Contemporary theory traced dia- and paramagnetism to the modification of electronic trajectories occasioned by an external field. Bohr found that, if the ordinary mechanics held, neither the free nor the bound electrons contributed at all to the magnetic properties of matter, or at least not to diamagnetism. This question, because it became a *leitmotiv* of Bohr's early post-doctoral work, deserves our close attention.

In 1900 Thomson had suggested that the free electrons might account for diamagnetism, since an external magnetic field would deflect them into circular or helical orbits so oriented as to produce a moment opposed to the sense of the inducing force.[16] But, as Bohr observed, the external field, which does no work, does not alter the distribution of electrons in space or in velocity, and thus cannot create a net moment where none had previously existed. (This argument, which requires some attention to the motions of electrons close to the surface, was apparently advanced simultaneously and independently by Lorentz.[17]) Since the free electrons thus failed to perform magnetically, Bohr turned to the bound, though their consideration lay beyond the

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[15] Bohr, *Studier,* 103.

[16] J. J. Thomson, "Indications relatives à la constitution de la matière fournies par les recherches récentes sur le passage de l'électricité à travers les gaz," *Congrès international de physique. Rapports* (Paris, 1900–01), *3,* 138–151.

[17] According to H. J. van Leeuwen, "Problèmes de la théorie électronique du magnétisme," *Journal de physique et le radium, 2* (1921), 361–377, on 376. See J. H. van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford, 1932), 101–102, for the argument.

professed scope of his thesis. Here the situation was more promising. A theory of the magnetic properties of bound electrons, which Pierre Langevin had proposed in 1905, appeared an adequate explanation of para- and diamagnetism to most physicists of the time.[18]

In Langevin's theory diamagnetism arises from alterations in the velocities of atomic electrons introduced by the external field, while paramagnetism derives from changes in orientation of the electronic orbits. Both effects occur simultaneously. The crux of Langevin's theory is the tacit assumption that, if the orbits are initially so deployed within a given molecule as to yield no average molecular angular momentum and hence no net molecular moment, a field subsequently superposed will not disarrange or reorient the orbits; it will only affect the electrons' velocities, and diamagnetism will result. If, however, the molecule originally possessed a net moment, Langevin supposed that its orientation under the field would obliterate the diamagnetic effect also present, and paramagnetism develop.

We know from Larmor's theorem that the motions of the orbiting molecular electrons under a magnetic field will be precisely the same as their motions in its absence except for a common precession about an axis parallel to it and passing through the molecule's center.[19] The magnitude of the precession is $\omega_L = eH/2mc$, where H, c, e, and m represent, respectively, the magnetic field, the speed of light, and the charge and mass of the electron; the precession is so directed as to increase the velocities of electrons whose magnetic moments oppose, and to decrease the velocities of electrons whose moments parallel the sense of the field. The accelerating force is the electric field necessarily linked with the establishment of a magnetic one; the latter, of course, does no work on an orbiting charged particle. To determine the size of the diamagnetic effect Langevin proceeded roughly as follows. Taking the z axis along H, the z component of the total angular momentum of a molecule is

$$L_z = \Sigma m\rho_i^2\dot{\phi}_i, \tag{1}$$

where ρ and ϕ form with z a cylindrical coordinate system with origin at the molecule's center. By Larmor's theorem, $\dot{\phi}_i = \dot{\phi}_{i0} + \omega_L$ and

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[18] P. Langevin, "Magnétisme et la théorie des électrons," *Ann. de chimie et de physique, 5* (1905), 70–127, esp. 73–97.

[19] The field must be applied adiabatically for this statement to be entirely true. See Van Vleck, *op. cit.* (note 17), 23.

$\rho_i = \rho_{i0}$, where the subscript $_0$ refers to the motion before the application of the field. Averaging equation (1) over time,

$$\bar{L}_z = \Sigma(\overline{m\rho_{i0}{}^2\dot{\phi}_{i0}}) + \Sigma\overline{m\rho_{i0}{}^2\ \omega_L} = \Sigma\overline{m\rho_{i0}{}^2\ \omega_L}, \tag{2}$$

because, by hypothesis, the molecule originally possessed no average angular momentum. Associated with $\bar{L}_z$ is a molecular magnetic moment $\bar{M}_z = -(e/2mc)\bar{L}_z$. Hence the diamagnetic susceptibility, defined as $(N/H)\bar{M}_z$, N being the number of molecules in unit volume, is

$$D \equiv (N/H)\bar{M}_z = -(e^2/4mc^2)N\Sigma\overline{\rho_{i0}{}^2}. \tag{3}$$

Equation (3) agreed approximately with experiment with acceptable values for $\Sigma\overline{\rho_{i0}{}^2}$.

To obtain an expression for the paramagnetic susceptibility P Langevin assumed that all the molecules possessed the same net moment p in the absence of the field H. In the presence of the field each molecule would have a "magnetic energy" $-pH \cos \theta_j$, where θ_j is the angle between **H** and the direction of the moment of the jth molecule.[20] If nothing opposed the orientation of the molecules, they would all line up with **H**, in conflict with experimental results. Langevin, assuming that thermal agitation opposed their alignment, utilized the usual techniques of statistical mechanics to compute an average value for the paramagnetic susceptibility:

$$P = \frac{N\Sigma pH \cos \theta_j \exp\left(\dfrac{pH \cos \theta_j}{kT}\right)}{H\Sigma \exp\left(\dfrac{pH \cos \theta_j}{kT}\right)} \doteq \frac{Np^2}{3kT}. \tag{4}$$

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[20] By "magnetic energy" is meant the increment ΔT in the electron's kinetic energy consequent on application of the field. Let the direction of the electron's original angular momentum **L** make an angle α with **H**; $\Delta T = L\omega_L \cos \alpha = (eH/2mc)L \cos \alpha$, if we ignore a term of the order of H^2. This energy may also be computed using the convenient fiction that a circulating electron produces at great distances a magnetic field equivalent to that of a small magnet placed normal to its orbit, and possessing a moment $\mathbf{M} = -(e/2mc)\mathbf{L}$. Such a magnet would have energy $-\mathbf{H} \cdot \mathbf{M} = +(e/2mc)\mathbf{H} \cdot \mathbf{L} = (eH/2mc)L \cos \alpha = \Delta T$. This second approach is however misleading in that the magnetic field does not exert a torque on the orbit as it would on a magnet. (The accelerating force producing the Larmor precession is the electric field linked to the establishment of the magnetic.) The angle α must be altered by some extraneous influence, say a collision; then, because the magnetic flux through the orbit changes, a transient electric field is set up which alters the electron's kinetic energy by an amount precisely suitable to the new orientation of its orbit. An electron whose **L** originally lies along **H**, and whose **M** therefore directly opposes it, will enjoy the greatest ΔT, or "magnetic energy." But as collisions alter the orbit's orientation, the transient electric fields decelerate the electrons until, when **L** opposes and **M** parallels **H**, it reaches the "stable" position of minimum energy.

(The summations are evaluated as integrals over the solid angle $2\pi \sin \theta \, d\theta$ in the approximation $pH \ll kT$.) Of course the moments p undergo a diamagnetic change also, but in Langevin's theory one ignores the consequent alteration in P. Equation (4) was perhaps the most persuasive feature of Langevin's theory, for it agreed precisely with the temperature dependence of the paramagnetic susceptibility which Pierre Langevin had found in 1895.[21]

Unfortunately Langevin's theory is incompatible with a literal application of the principles of statistical mechanics. Bohr was the first to recognize this incompatibility, at least in respect to diamagnetism. In an extended footnote to his illuminating discussion of the failure of the free electrons to provide a metal with diamagnetic properties, he remarked that the bound electrons are likewise impotent for, if mechanical heat equilibrium is to prevail, the change of velocity introduced during the build-up of the magnetic field must quickly equalize after the field is established. If there is the "least little energy exchange" between the electrons within a molecule then, according to Bohr, Langevin's theory of diamagnetism falls to the ground. Of course, one might appeal to an agency, like the emission of radiation, which could prevent mechanical heat equilibrium from establishing itself among the bound electrons, but even so diamagnetism would remain an enigma: as Bohr observed, Thomson and Gans had on that assumption obtained only a paramagnetic effect.[22] To save Langevin's diamagnetic theory one must suppose (though Bohr does not make this consequence explicit) some non-mechanical freezing of the velocity changes derived from the field, some principle that prevents the equalization demanded by the mechanical theory of heat.

Bohr's compressed discussion of these difficulties is not complete. As noted earlier, one cannot ignore the effects of the established field because the changing magnetic flux through the electronic orbits does do work when the orbits are shifted by collisions. Such shifts, there-

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[21] P. Curie, "Propriétés magnétiques des corps à diverses températures," *Ann. de chem. et de phys.*, *5* (1895), 289–405.

[22] Bohr, *Studier,* 103, 108; J. J. Thomson, "The Magnetic Properties of Corpuscles Describing Circular Orbits," *Phil. Mag.*, *6* (1903), 673–693; R. Gans, "Zur Elektronentheorie des Ferromagnetismus," *Gött. Nachr.* (1910), 197–273, esp. 213–230; cf. *supra,* note 20. (Incidentally Thomson, *op. cit.,* 687–688, concluded that a collection of parallel, *non-interacting* electron rings would produce no diamagnetic effect, an error arising, as Bohr, following Langevin, observed [*Studier,* 108], from neglect of the electric force accompanying the establishment of the magnetic field. Thomson's paper was nevertheless of very great importance for the theories of radiation and atomic structure.)

fore, have diamagnetic as well as paramagnetic consequences, as they change both the magnitude and the orientation of the electronic moments. In fact, these alterations just compensate one another when the angular moments of the electrons are considered statistical quantities. (Bohr may have seen, but did not describe this effect.) It is not legitimate to require, as Langevin had done, that these moments p remain sensibly constant (excepting the "small" diamagnetic effect) during the establishment of the field and the reorientation of orbits. The ordinary statistical mechanics does not restrict the values of the moments; the p under the summation sign in equation (4) should itself be averaged, and when it is D and P exactly cancel.[23]

Though his criticism of Langevin's theory is incomplete and occupies but a small portion of his thesis, Bohr clearly considered his discovery of the impotence of the ordinary mechanics in respect to magnetism one of his most important results. He refers to it in two prominent places: among the theses, or original propositions, at the end of the *Studier,* and in the Introduction, where he juxtaposes it to a recognized enigma, the ultra-violet catastrophe.[24] Indeed, Bohr thought the two difficulties intimately related, apparently because absurd results followed for radiation as well as for magnetism *if one supposed mechanical heat equilibrium to prevail* over the processes producing those phenomena. At the very least the difficulty with magnetism strengthened and confirmed Bohr's conviction that the usual mechanical laws broke down when applied to rapidly moving electrons; and, even more than the radiation problem, it isolated the breakdown in the behavior of electrons bound into atoms. We conjecture that it did much more. It left Bohr with a specific, important, and easily conceived problem, an enigma of his own creation, whose study and eventual solution promised a clue to the fundamental revisions of contemporary theory he thought inevitable. He addressed himself to this great matter from the moment he finished his thesis, if not before.

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[23] This argument is essentially that first given by Miss Leeuwen, *op. cit.* (note 17), 373–375; cf. Van Vleck, *op. cit.* (note 17), 94–100. Miss Leeuwen did not know Bohr's thesis until after she had completed her own, of which the paper cited is an abstract.

[24] *Studier,* 5, 108, 120; cf. *supra,* 215. The magnetic difficulty also figures prominently in a resumé of his results which Bohr read the Cambridge Philosophical Society in November 1911 (*infra,* 228). Towards the end of his life he mentioned it first among examples of the fruits of his thesis and of the "enormous problems" he was then engaged with; Interviews I, 1, 5. (The roman numeral refers to the number, the arabic to the page, of the transcripts of the five interviews with Bohr conducted by the project "Sources for History of Quantum Physics" in the fall of 1962. For details see Kuhn *et al., Sources* [note 3, *supra*].)

Though the spectacular results he obtained two years later came largely from an unexpected quarter and no doubt greatly exceeded his expectations, the problem—or rather *his* problem—of magnetism had then already had an important influence on the direction of his thoughts. It had focussed his attention on the question of bound electrons, which would ultimately become, for him, the problem of atomic structure. And it had led him to consider the nature of the non-mechanical "law" which, perhaps in the form of a restriction like Planck's quantization rule, might fix the motions of the bound electrons in the manner Langevin's theory tacitly made essential to a successful derivation of the Curie law.

II. CONTINUATION OF THE ELECTRON THEORY: CAMBRIDGE AND MANCHESTER, SEPTEMBER 1911–JUNE 1912

Just as, for Bohr, the master's dissertation entailed the doctoral thesis, the latter inexorably led to a year abroad. He had two obvious alternatives: Leiden with Lorentz, or Cambridge with Thomson. He did not hesitate. His father had instilled in him a love for things English, and his wide reading had given him the greatest respect for Thomson, a pioneer of the electron theory of metals and the acknowledged world master in the design of atomic models. Cambridge also boasted Larmor and Jeans, whose work touched Bohr's in many places. "I considered first of all Cambridge as the center of physics," Bohr later said of his decision to study there, "and Thomson as a most wonderful man . . . , a genius who showed the way for everybody."[25]

In September 1911, Bohr reached his Mecca. "I found myself rejoicing this morning," he wrote his fiancée just after his arrival, "when I stood outside a shop and by chance happened to read the address 'Cambridge' over the door."[26] Thomson received him politely, and promised to read his thesis, of which he had brought a rough English translation. The promise completed Bohr's happiness. "I have just talked to J. J. Thomson," he wrote his brother, "and I explained to him as well as I could my views on radiation, magnetism, etc. You should know what it was for me to talk to such a man. He was so very kind to me; we talked about so many things; and I think he thought

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[25] Interviews II, 6.

[26] NB to Margrethe Nørlund, 26 Sept 1911, quoted without date by Rosenfeld and Rüdinger, *op. cit.* (note 1), 39–40. Prof. Rosenfeld has kindly supplied the date.

there was something in what I said. He has promised to read my thesis, and he invited me to have dinner with him next Sunday at Trinity College, when he will talk to me about it. . . . I can't tell you how happy and thankful I am that [the translation of] my dissertation was finished and I could give it to Thomson." [27]

Unfortunately the exchange of views Bohr desired did not take place. Thomson probably never read through his enthusiastic visitor's thesis. In subsequent interviews he occasionally promised to examine a particular question, but only one, heat radiation, gave rise to any discussion.[28] That conversation came to nothing, as we may gather from Bohr's report of it to his brother, written six weeks after his arrival in Cambridge:

> [Thomson] has not yet had time to read my thesis, and I still don't know if he will agree with my criticisms. He has only chatted with me about it a few times for a couple of minutes, and that was on a single point, my criticism of his calculation of the absorption of heat rays. You may remember I remarked that in his calculation of absorption (as opposed to emission) he does not reckon the time taken up in the collisions, and that therefore he gets a value for the ratio of emission to absorption which is the wrong order of magnitude in the case of high frequencies. Thomson said that he could not see that the collision time could have so great an influence on the absorption; I tried to explain, and the following day gave him a very simple example (an example corresponding to his calculation of the emission), which showed it very clearly. Since then I've talked with him for only a moment, and that a week ago. I think he thinks my calculation is correct, but I'm not sure he doesn't believe that one can design a mechanical model to explain the law of heat radiation on the usual electromagnetic principles. . . .[29]

Bohr was never able to effect Thomson's conversion, and thus failed of one of the chief objectives of his Cambridge sojourn.[30]

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[27] NB to Harald Bohr, 29 Sept 1911 (BPC). ("BPC" signifies Bohr's Personal Correspondence, for which see "Introduction," above.)

[28] NB to S. B. McLaren, 17 Dec 1911; to C. W. Oseen, 1 Dec 1911 (BSC). (The notation "BSC" refers to the Bohr Scientific Correspondence in the Archive for History of Quantum Physics, for which see Kuhn *et al., op. cit.* [note 3].)

[29] NB to Harald Bohr, 23 Oct 1911 (BPC).

[30] Jeans also remained beyond Bohr's reach, declining to discuss the thesis before it appeared in English; NB to Harald Bohr, 23 Oct 1911 (BPC). Bohr did receive some welcome confirmation of his views on heat radiation at about this time from S. B. McLaren (*ibid.;* S. B. McLaren, "The Emission and Absorption of Energy by Electrons," *Phil. Mag., 23* [1911], 66–83, and *Scientific Papers,* ed. J. Larmor [Cambridge, 1925], 22–27).

Part of his problem in communicating with Thomson must have come, as Bohr always believed, from his poor command of spoken English; Bohr could state the errors he had discovered but was unable fully to explain his arguments. Doubtlessly Thomson, unprepared for a recent graduate as thorough and erudite as Bohr, failed to recognize that conversation with his unusual student might repay a little linguistic straining. In any event he had ceased active cultivation of the electron theory of metals some time before Bohr's arrival. By 1911 his primary interest was the study of positive rays, a subject on which he set Bohr a little experimental problem that regrettably proved pointless. Thomson surely did not enjoy hearing his ancient errors rehearsed by a tenacious foreigner whose English he could hardly understand.

Even had language and divergent interests not been barriers, one doubts that the intellectual communion Bohr sought could ever have developed. Bohr's lifelong practice was to refine his ideas in lengthy conversations, which often became monologues, with informed individuals. Whether his colloquist was a full collaborator, a sounding board, or an amanuensis, he required some human contact at almost every stage of his work, even in writing. He dictated his papers, at first (as with his thesis) to his mother, then to his wife, and ultimately to a series of secretary-collaborators beginning with H. A. Kramers.[31] Thomson's method could not have been more different. He seldom solicited his students' views on scientific problems, nor did he develop his own through extended conversations with others. Bohr found that Thomson, though friendly and receptive to questions, would invariably "break off in the middle of a sentence, after a moment's conversation, when his thoughts ran on something of interest to himself." [32] Though he closely followed that part of the literature which interested him, Thomson worked very much alone, a method appropriate to the "genius that showed the way for everybody," but one fatal to anyone who lost the way, as Thomson did increasingly after 1910.

The two men also differed profoundly in their approach to physics. Already in his thesis Bohr seems to display the trait which would characterize so much of his later work. Confronting a fundamental difficulty in existing theory, he would group together problems he thought related to it and subject the complex to a slow, careful, and

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[31] Rozental, *Niels Bohr,* 30.

[32] NB to Harald Bohr, 23 Oct 1911 (BPC).

repetitious analysis. He expected thereby to achieve a coherent new position which, expressed in consistent models, would yield results in exact quantitative agreement with experiment. Thomson's interests lay elsewhere and his expectations were more modest. To him models were mere analogies, and fundamental problems of little interest. He did not anticipate or require exact quantitative agreement between experience and calculations based upon models, nor consistency among the different pictures he employed. As Bohr said later, "Things needed not to be very correct [for Thomson], and if it resembled a little, then it was so."[33] If Thomson's imprecise, often conflicting models helped him and suggested further experiments, they fully served their purpose.[34] Their incompatibility did not disconcert him.

The design of atomic models provides a relevant example of Thomson's practice. In 1904 he suggested the familiar model called after him, in which a crowd of electrons, arranged in concentric, coplanar rings, circulated within a neutralizing sphere of positive electricity of constant charge density.[35] This picture, as he often emphasized, was doubly artificial. In real atoms the electrons must be distributed in three dimensions; he restricted them to a plane because the mathematics of a spatial distribution lay beyond his reach. The sphere of constant charge density was likewise a convenient fiction, amenable to calculation because its linear restoring force permitted mechanically stable deployments of the electrons. The artificiality of the picture notwithstanding, Thomson used it first to elucidate qualitatively the periodic table of the elements and the nature of radioactivity and then, in subsequent years, such other phenomena as chemical combination and the scattering of β rays.[36] He used other pictures concurrently. One of these, "the doublet model," which Thomson introduced in 1910 to explain the photo-effect, particularly interested Bohr and may well have influenced his later work.[37] It therefore claims our attention.

The model consisted of an electron describing a circular orbit under the influence of, and coaxial with, an electric dipole of moment

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[33] Interviews II, 6–7.

[34] Cf. Russell McCormmach, "J. J. Thomson and the Structure of Light," *Br. J. Hist. Sci., 3* (1967), 362–387; Lord Rayleigh, *The Life of Sir J. J. Thomson* (Cambridge, 1942), 202.

[35] J. J. Thomson, "On the Structure of the Atom . . . ," *Phil. Mag., 7* (1904), 237–265.

[36] E.g., J. J. Thomson, *Corpuscular Theory of Matter;* "On the Scattering of Rapidly Moving Electrified Particles," *Proc. Camb. Phil. Soc., 15* (1910), 465–471.

[37] J. J. Thomson, "On the Theory of Radiation," *Phil. Mag., 20* (1910), 238–247.

P. Not all such orbits are possible: only if θ, the angle between the axis and the line drawn from the dipole's center to the electron, equals $\tan^{-1}\sqrt{2}$, will the force normal to the orbit's plane vanish. Any right section of a cone of half-angle θ with apex at the dipole's center is thus a possible orbit. The balance of centrifugal and centripetal force in the plane,

$$mv^2/r = 3\,Pe \cdot \sin^4\theta \cdot \cos\theta/r^3, \tag{5}$$

does not further define the path, as it only gives the orbital radius r in terms of the electron's velocity v. All values of kinetic energy $mv^2/2$ and of orbital frequency $\nu = v/2\pi r$ are therefore possible. But by a peculiar property of the dipole's inverse-cube force, the *ratio* $(mv^2/2)/\nu$ is independent of the orbital parameters; in fact, a simple manipulation of equation (5) yields

$$mv^2/2 = (2.76\sqrt{Pem}) \cdot \nu. \tag{6}$$

Now in his calculation of heat radiation—the calculation Bohr found faulty—Thomson traced emission to the interaction of free electrons with doublets in the metal molecules; and, by comparing his results with a well-known characteristic of the radiation, Wien's displacement law, he was able to infer a value for the doublet's moment P. That value made the expression in parentheses in equation (6) $2.1 \cdot 10^{-27}$ erg-sec, smaller than Planck's constant by a factor of three. Thomson thought this agreement extremely suggestive: with the coefficient of ν approximately equal to h, equation (6) gives Einstein's expression for the photo-effect. A photo-electron is released, according to Thomson, when light of frequency ν disrupts an unstable dipole system, sending the circulating electron on its way into the world with something like its orbital kinetic energy. From equation (6) this quantity, $mv^2/2$, is just about $h\nu$!

Bohr was interested in this representation for two reasons. First, it harmonized strikingly with the chief positive result of his thesis, the fact that the ratio of thermal to electric conductivity and the sign of the transverse temperature difference accompanying the Hall effect both agreed with experiment if the force between free electrons and molecules were assumed to vary with the inverse cube of the distance. An electric dipole produces such a force. Bohr did not miss the connection. In his thesis he had explicitly noticed the "remarkable" agreement between the ratio x, the sign of ΔT, and Thomson's dipole.[38] And at Cambridge he continued to call attention to it. Outlining his thesis to the Cambridge Philosophical Society in November 1911, he told his auditors that his result calling for a dipole force "is perhaps of some interest, because Prof. Sir J. J. Thomson has shown that some of the optical phenomena of the metals can be explained by assuming the existence of such electrical doublets." [39]

The incorporation of Planck's constant in the dipole model would also interest Bohr, who had already decided that the quantum was implicated in the behavior of bound electrons. To be sure, Thomson's handling of h scarcely harmonized with the spirit of Bohr's thesis. For Thomson, h was a *derived* quantity, simply related to constants characterizing the electron and to a new basic parameter, the elementary dipole moment P. He, like several of his contemporaries, considered h shorthand for a product of mechanical quantities, and in no wise fundamental.[40] Bohr, on the contrary, very probably already regarded h as an unanalyzable given, and perhaps also suspected that it helped determine atomic structure in a manner he aimed to uncover.[41] If he took equation (6) seriously, he would have to read it not as a definition of h, but as a possible condition fixing the state of an atomic electron. For any force law other than the inverse-cube, equation (6) and the force balance uniquely determine both r and ω. It is consequently noteworthy that in Bohr's earliest extant treatment of atomic models, probably prepared in July 1912, he employed a

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[38] Bohr, *Studier,* 34, 117.

[39] Bohr Manuscripts (BMSS) in the Archive for History of Quantum Physics.

[40] The best known of these treatments, that of A. E. Haas ("Über die elektrodynamische Bedeutung des Planckschen Strahlungsgesetzes und über eine neue Bestimmung des elektrischen Elementarquantums und der Dimensionen des Wasserstoffatoms," *Sitzb. Wien. Ak., 119:2a* [1910], 119–144; "Der Zusammenhang des Planckschen elementaren Wirkungsquantums mit den Grundgrössen der Elektronentheorie," *Jahrb. Rad. und Elek., 7* [1910], 261–268), sought to express h in terms of e, m, and a, the radius of the Thomson diffuse-sphere atom. The question whether to take h or a set of mechanical quantities as fundamental was by no means clear in 1911. At the Solvay Congress of that year, in response to Sommerfeld, who had said he preferred "a general hypothesis about h to particular models of atoms," Lorentz remarked (*La théorie du rayonnement et les quanta. Rapports et discussions de la réunion tenue à Bruxelles du 30 octobre au 3 novembre 1911* [Paris, 1912], 124), "M. Sommerfeld does not deny that there is a relation between the magnitude of the constant h and atomic dimensions (positive Thomson spheres). One can express this in two ways: the constant h is determined by these dimensions (Haas), or else the dimensions one attributes to atoms depend on the magnitude of h. I don't see any great difference." Bohr apparently knew nothing of Haas's work at this time (Interviews I, 10).

[41] The problem of fixing atomic structure solely in terms of the fundamental constants characterizing the components was not new. It figures prominently, for example, in Larmor's *Aether and Matter* (Cambridge, 1900), 189–193, which Bohr read with pleasure during his stay in Cambridge (Interviews II, 8).

quantum condition identical in form to equation (6) and that it did then serve to fix both r and ω.[42]

Despite the disappointment of Thomson's indifference, Bohr spent the first of his two semesters at Cambridge busily, profitably, and, on balance, happily. He had arrived with letters of introduction to friends and colleagues of his former teachers. He visited Littlewood and Hardy; he dined at Thomson's house; he journeyed to Oxford to call on Dreyer, to Manchester to see Lorrain Smith, a physiologist trained by his father, and to Birmingham to talk electron theory with S. B. McLaren. He gave small entertainments in his rooms, and he joined a football club.[43] In addition, of course, Bohr took seriously his role as a student, faithfully attending the lectures of Jeans and Larmor on various aspects of electricity, and following two courses, one advanced and one elementary, given by Thomson. Bohr was very enthusiastic about both, the second because of its "most beautiful experiments," the former because in it Thomson developed his latest ideas.[44] As for his own work, Bohr spent many hours trying to produce a discharge of cathode rays with the help of positive rays, this being the little experimental task Thomson had set him. It went very slowly. Bohr did not know where the problem was to lead; the professor was not easy to consult; and the Cavendish laboratory, crowded and disordered,[45] was always trying for a new-comer.

Meanwhile Bohr worked as he could on the electron theory of metals. He labored in the old vein, criticizing the calculations of others and firing off long letters pointing out new mistakes he had encountered.[46] In addition, he tried, with Thomson's help, to interest the Cambridge Philosophical Society in printing his thesis. A fellow student was asked to revise the translation, and Bohr impatiently awaited the decision of the Society's publication committee. Articles were appearing on every side by authors unaware of his results; the longer he waited the more likely that his own contributions would be rediscovered, and the English version rendered superfluous. As it hap-

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[42] We discuss this document at length in Section III.

[43] NB to Harald Bohr, 29 Sept and 23 Oct 1911; NB to Ellen Bohr (his mother), 31 Oct and 6 Dec 1911 (BPC). Bohr was an excellent soccer player, and Harald was an Olympic star; Rozental, *Niels Bohr,* 23–24.

[44] NB to Harald Bohr, 23 Oct 1911 (BPC).

[45] *Ibid.;* Rosenfeld and Rüdinger, *op. cit.* (note 1), 41; Interviews II, 3, 7–8.

[46] Letters to M. Reinganum, 9 Nov and 17 Dec 1911, and to C. Oseen, 1 Dec 1911 (BSC).

pened his patience was sorely tried, but to no purpose. The Society's publication committee did not act until May 1912, and they then declined to publish the thesis, at least *in toto,* because of its length.[47]

During his second Cambridge term Bohr spent less time in formal academic work. Though he continued to attend lectures, and to criticize developments of the theory of metals, he abandoned the laboratory and directed more of his time to private reading and study.[48] The problem of bound electrons doubtlessly figured prominently among his meditations, as his thesis, by its very generality, had brought him to a position from which he could advance only by making special assumptions about their motions and arrangements. We do not know precisely what directions his thought took in these first months of 1912. But we do know what he planned to ponder. Writing to his friend C. W. Oseen on 1 December 1911, Bohr concluded a very long letter devoted to special problems in electron theory with the words: "I am at the moment very enthusiastic about the quantum theory (I mean its experimental side), but I am still not sure this is not due to my ignorance. I can say the same, in a far higher degree, about my relation to the theory of magnetons. I very much look forward to trying to get all these things straight next term."[49]

The magneton to which Bohr referred had been introduced only a few months previously by Pierre Weiss as an explanation, or representation, of careful measurements he had made of the magnetic properties of certain metals.[50] The susceptibilities of these metals, whether para- or ferromagnetic, suggested the existence of a fundamental unit or atom of magnetism. A molecule, regardless of its species, would accordingly possess either no magnetic moment or one equal to an integral number of magnetons. It is evident why Bohr would have found Weiss's work of absorbing interest. If one referred the magnetic properties of matter to orbiting electrons, as Bohr did, the existence of a fundamental unit of magnetism implied that the elements of the orbits, particularly the electrons' angular momenta, were fixed. The magnetic moment **M** of a circulating electron is

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[47] NB to Harald Bohr, 23 Oct 1911; Camb. Phil. Soc. to NB, 7 May 1912 (BPC).

[48] BMSS; Rosenfeld and Rüdinger, *op. cit.* (note 1); NB to Harald Bohr, 2 Feb 1912 (BPC); N. Bohr, "Note on the Electron Theory of Thermoelectric Phenomena," *Phil. Mag., 23* (1912), 984–986, a critique of a paper by O. W. Richardson. The note is dated 5 Feb 1912.

[49] BSC.

[50] P. Weiss, "Über die rationalen Verhältnisse der magnetischen Momente der Moleküle und das Magneton," *Phys. Zs., 12* (1911), 935–952.

$(-e/2mc)\mathbf{L}$, where **L** represents angular momentum; if **M** is a determinate quantity, so then is **L**. Such a restriction on the electronic motions is just what Bohr sought: his thesis, one remembers, had shown that a collection of molecules which faithfully followed Boltzmann's statistics displayed no diamagnetism, and implied that the solution lay in somehow constraining the behavior of the bound electrons. The restriction implied by the magneton might resolve the diamagnetic dilemma! We do not know how far Bohr proceeded along these lines in the first months of 1912. We can, however, infer the expectations he might then have entertained from a short section on magnetism written for, but omitted from, Part II of the trilogy of 1913.[51] Bohr there wrote that if his principle of the universal constancy of angular momentum, assumed to hold without, also held with a magnetic field, then diamagnetism would indeed be a general property of matter.[52]

The connection of the magneton and the quantum, at which Bohr hints in his letter to Oseen, was straightforward. The angular momentum L of an orbiting electron is $1/\pi$ times the ratio of its kinetic energy T to its orbital frequency ν. A procedure for fixing the angular momentum therefore lay close to hand: one needed only to imitate Planck and set T/ν equal to h or a multiple thereof. Since the circulating electron possesses a magnetic moment $M = -(e/2mc)L$,

$$M = -(e/2mc)\frac{1}{\pi}\cdot\frac{T}{\nu} = -(e/2mc)\cdot(h/\pi). \tag{7}$$

Bohr could either have produced this association for himself or have

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[51] Many drafts of this section, amounting to over fifty pages, remain in the Bohr MSS. Prof. Rosenfeld has published the most finished of these in Rosenfeld, *op. cit.* (note 1), 75–77.

[52] Bohr here perhaps intended an argument similar to the following. As will appear below (Section VI), in the model of 1913 Bohr confined the electrons of a given atom to a plane and assigned the same value of the angular momentum, say p, to each of them. For simplicity, assume **H** acts along their common axis of rotation. By hypothesis p remains unchanged under **H** and the vector sum of the momenta is zero. The radii of the orbits must therefore change if the Larmor precession is to occur, and this makes possible a change in total kinetic energy ΔT. Consider two electrons describing the same circular orbit in opposite senses with velocity v. One will accelerate (that whose **p** parallels **H**) and the other slow down by the same amount Δv. The combined ΔT for the two is $(m/2)[(v + \Delta v)^2 + (v - \Delta v)^2 - 2v^2] = m(\Delta v)^2$. A simple calculation shows that, ignoring terms of order H^2, $\Delta v = (p^2/Zmec)H$, where Z is the effective nuclear charge acting on the two electrons. Hence $\Delta T \propto +H^2$. The positive sign indicates a diamagnetic effect, but how it is to be understood in absence of a net atomic angular momentum is not evident. Perhaps it was for this reason that Bohr deleted this section. Writing Harald on 3 Aug 1913 (BPC), Bohr said: "I had thought about including some remarks about it [magnetism] in the proof to Part II: however I'm giving it up and will wait until I have had time to think more about it." (The forgoing reconstruction corresponds to Bohr's deleted section on magnetism in [1] fixing the angular momenta and [2] arguing from the positive quadratic form of the resultant energy increment.)

discovered it in the literature; it was in fact made by several people in the fall of 1911.

At the end of September, for example, in a discussion at the Karlsruhe meeting of the *Gesellschaft der deutschen Naturforscher und Ärzte* following Weiss's first major address on the magneton, Abraham, Gans, and Einstein (as reported by Weiss) all observed that the magneton should involve "the famous *h*."[53] Gans even supplied equation (7). In his model, electrons were attached to the ends of weightless spokes of length r, the spokes forming a rimless wheel rotating with angular velocity ω. Gans equated the kinetic energy of rotation, $\Sigma mr^2\omega^2/2$, with an integral multiple of $h(\omega/2\pi)$, "in accordance," he thought, "with Planck's theory."[54] With this assumption,

$$mr^2\omega/2 = p \cdot h/2\pi, \tag{8}$$

p being an integer; and since $M = \Sigma er^2\omega/2c$, equation (8) yields (7) as the smallest possible magneton, corresponding to $p = 1$. But this minimum magneton is unfortunately an order of magnitude too large. If one took Weiss's results seriously, however, one might consider that some submultiple of h, rather than h itself, entered into equation (6) or (7). Contemporary theory certainly did not discourage such a consideration: in the literature of the time one sometimes finds h/π or $h/2\pi$ used as the elementary quantity. In the "Rutherford Memorandum" of July 1912, which is discussed at length below, Bohr leaves the magnitude of the submultiple open.

Bohr knew Weiss's address and the following discussion at least by 1913, as both are mentioned in the deleted section on magnetism. We may be confident, however, that he knew them much earlier. They appeared in print on 15 November 1911, in a double number of the *Physikalische Zeitschrift* devoted to the Karlsruhe meeting. Exactly two weeks later Bohr wrote of his hope of straightening out the quantum and the magneton during his second term at Cambridge. It seems likely that his program reflected a reading of Weiss and Gans, and that while pursuing it he replaced the right side of Thomson's quantum relation, $mv^2/2 = h\nu$, with the less definite "$K\nu$" of the Rutherford Memorandum. Certainly questions of this sort were very much on his mind before he left Cambridge for Manchester in March 1912.

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[53] *Phys. Zs.*, *12* (1911), 952.

[54] Gans's was not the only possible formulation of Planck's theory. See below, 244, n.85.

Manchester

Bohr may first have met Rutherford at the beginning of November 1911, in the home of Lorrain Smith, the former student of his father's who had become a professor of physiology at the University of Manchester. Rutherford would then have just returned from the Solvay Congress, which adjourned on 3 November; and its deliberations, Bohr later recalled, were the subject of his initial conversations with the man who was to influence his career so decisively.[55] In December Rutherford spoke at the annual Cavendish Dinner, a very informal affair arranged by the advanced students in the laboratory. Bohr was much taken with the talk and, if he were not already, with the man as well. Rutherford was vigorous, extroverted, modern, brilliant, and, though only fourteen years Bohr's senior, already an inspiring international success. No entirely reliable information about the subject of Rutherford's talk has survived.[56] But its substance was of secondary importance, as it was more Rutherford's personality than his message that prompted Bohr to consider the possibility of spending part of his post-graduate year at Manchester. He quickly set up a meeting with Rutherford at the home of Lorrain Smith. Tentative arrangements were probably then worked out for Bohr's removal to Manchester the following spring, arrangements confirmed after discussion with Harald, who visited him in Cambridge in January 1912.[57]

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[55] N. Bohr, "Reminiscences of the Founder of Nuclear Science and of Some Developments Based on his Work," *Proc. Phys. Soc., 78* (1961), 1083–1115; NB to Ellen Bohr, 31 Oct 1911, announcing a planned visit to Smith at Manchester "on Friday," which was 3 November. A meeting with Rutherford later that weekend is thus just possible.

[56] Bohr ("Reminiscences," 1084) recalled that Rutherford had spoken of Wilson's newly-invented cloud chamber. Wilson's experiments would not have been novel to Rutherford's audience, however, as the cloud-chamber was developed at Cambridge. Cf. C. T. R. Wilson, "On an Expansion Apparatus for Making Visible the Tracks of Ionizing Particles in Gases and Some Results Obtained by its Use," *Proc. Roy. Soc., A, 87* (1912), 277–292.

[57] Rosenfeld and Rüdinger, *op. cit.* (note 1), 43–44; Bohr, "Reminiscences," 1083–1084, and Interviews II, 8. The chronology is not entirely secure, for Bohr's "Reminiscences," which Rosenfeld and Rüdinger follow, place the Cavendish Dinner before the Solvay Congress, and imply that the subsequent negotiations at Smith's house occurred early in November. The Dinner, however, took place in December as usual (cf., Rutherford to W. H. Bragg, 20 Dec 1911, as quoted in A. S. Eve, *Rutherford* [New York and Cambridge, 1939], 208, a reference we owe to Prof. Rosenfeld). One is left with either another Cambridge event featuring Rutherford in October, or a second visit to Smith in December. The latter is more probable: we doubt that Bohr would have seriously considered leaving Cambridge after only a month's experience of it. Moreover, Rutherford did not formally accept Bohr as a student until the end of January 1912, a puzzling delay if the negotiations occurred in early November (NB to Harald and Ellen Bohr, 28 Jan 1912 [BPC]).

This decision proved critically important for the development of modern physics, and some writers have not unnaturally interpreted it as a conscious choice between the "bitter disappointment" of Cambridge and the bright promise of Manchester, between the outdated Victorian physics of the unreachable Thomson and the bold ideas of the open and earthy Rutherford.[58] This is to read history backwards, however. If disappointed in his hopes for collaboration with Thomson, Bohr was not miserable at Cambridge. He loved the city, admired the professors, and made so many friends there it took him several days to bid them all good-bye.[59] Nor was the Cavendish passé. It led the world, for example, in studying the passage of β particles through matter, a subject which may be considered a special case of Bohr's particular interest, the electron theory of metals.[60] None of his friends could understand why he wanted to leave.[61] As for Thomson, he remained for Bohr "a tremendously great man," a teacher from whom he had learned "an enormous amount," a person he liked very much.[62] Nor was Manchester an irresistable siren. Bohr took time over his decision, stayed a second term at Cambridge, and thought seriously of spending Easter in Copenhagen.[63] In fact Bohr migrated to Manchester primarily to learn something about radioactivity, the specialty of his most recent scientific hero, Rutherford. No profound break was intended or required. It was not remarkable for a foreign student with his own fellowship to seek experience in more than one laboratory during a post-graduate year abroad. For Bohr it was not Cambridge *or* Manchester, but Cambridge *and* Manchester.

Bohr arrived in Manchester in the middle of March 1912, and immediately set about mastering what he had come to learn, the experimental side of radioactivity. He began by repeating elementary experiments on the absorption of α and β rays, introductory exercises which he took very seriously, as the careful and thorough record of them surviving among his papers testifies.[64] After working in this way

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[58] E.g., Ruth Moore, *Niels Bohr. The Man, his Science and the World they Changed* (New York, 1966), 31–39; cf. Rosenfeld, *op. cit.* (note 1), xv.

[59] NB to Harald Bohr, 7 March 1912 (BPC).

[60] The chief β-ray men at the Cavendish in 1911–1912 were Thomson, Crowther, and W. Wilson (for whose work see J. L. Heilbron, "The Scattering of α and β Particles and Rutherford's Atom," *Arch. Hist. Exact Sci., 4* [1968], 247–307), C. T. R. Wilson, and R. Whiddington.

[61] NB to Margrethe Nørland, March (?) 1912, quoted by Rosenfeld and Rüdinger, *op. cit.* (note 1), 45.

[62] *Ibid.*

[63] NB to Harald Bohr, 7 March 1912 (BPC).

[64] BMSS.

for about six weeks, from 16 March to 1 May, his initiation was deemed complete, and he began an experimental investigation of his own.

Few details about this investigation, which proved no more fruitful than the positive-ray work at Cambridge, have survived. We know only that Rutherford set the problem and specified the method, that it involved radium, and that it did not arouse Bohr's enthusiasm.[65] It did, however, have the advantage of throwing Bohr into regular contact with Rutherford, who routinely visited his students and assistants in their laboratories. And, of course, it provided the occasion for the new-comer to associate with his fellows—with men like G. Hevesy and C. G. Darwin—whose work was to have a critically important effect upon his own.

The uninspiring experimental investigation, though pursued conscientiously, did not occupy all Bohr's professional time. As in Cambridge, he continued his critical examination of the electron theory and worried about printing his thesis in English. The problem of publication had become acute at the beginning of May, with the final refusal of the Cambridge Philosophical Society to print it *in extenso.* Bohr at first considered acceding to their demand to reduce it by half, but decided against doing his carefully-wrought arguments such violence.[66] Toward the end of May, and through the middle of June, his frustration reached the point that he thought seriously of bringing out the translation at his own expense.[67] In those weeks the delay in publication particularly oppressed him because he believed he had hit upon ideas which might resolve some of the difficulties the thesis had uncovered. The value of his work, as he wrote Harald, would then "be a little different from what it now seems";[68] what had before appeared a purely critical, and therefore a somewhat negative study, might now serve as the extended introduction to the positive innovations the criticism anticipated.

Two letters written Harald on successive days, 27 and 28 May,[69] permit us to discern the spirit of the innovator, if not the substance of the innovations. In the earlier letter Bohr told his brother that his new ideas would do nothing less than "answer all the chief objections which

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[65] NB to Harald Bohr, 27 May 1912 (BPC).

[66] NB to Camb. Phil. Soc., 8 May 1912 (copy); to Harald Bohr, 19 May 1912 (BPC).

[67] NB to Harald Bohr, 27 May and 12 June 1912 (BPC).

[68] NB to Harald Bohr, 27 May 1912 (BPC).

[69] BPC.

can be raised (and have been raised lately) against an electron theory of the kind I have treated." He was not altogether certain, of course; Harald knew "how easily I fall into error"; and he had no opportunity in Manchester, where "no one at all is interested in such things," [70] to test and refine his ideas in conversation. Maturer reflection, however, only slightly moderated his enthusiasm, and the second letter to Harald, on 28 May, is filled with plans for the ultimate improvement of the electron theory. His own innovations seem to explain "various difficulties of a general character," e.g., the Thomson effect and the specific heats of metals at low temperatures; a recent suggestion of Stark's offers hints towards an explanation of electrical conductivity.[71] Stark's proposal is not free from error; Bohr plans to "write a little about it," beginning his positive reforms in the old critical manner.[72] "Then," he says, "I must let a little time go by, and reach some certainty [komme lidt til Ro] about these different things. How far I can get this year I have no idea; it depends on so many outside circumstances, and also on what others find (or have found) to write about on the matter. I just feel that I must again begin to work into these subjects."

These passages are of very great interest. They reveal, we believe, that even after two and one-half months at Manchester Bohr's interests had by no means shifted to matters of common concern to Rutherford's group. In particular, he displayed no interest whatsoever in the problems of radioactivity or the new nuclear atom. The electron theory of metals, which had brought him to Cambridge, continued to be his primary commitment, a commitment which, if anything, was stronger in the last days of May 1912 than it had been at any previous time during his stay at Manchester. There lay his expertise and his most original and promising ideas.

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[70] Rosenfeld, *op. cit.* (note 1), xvi, misleadingly prints this passage as if it referred to the attitude of Rutherford's group towards atomic models. In context it plainly refers to their attitude towards general questions in the electron theory of metals: "er det [that Bohr's new ideas clear up general difficulties in the electron theory] Tilfaeldet, vil ja vaerdien af mit Arbejde [Bohr's thesis] vaere eǹ lidt anden, end den nu anses for. Kaere Harald, Du ved jo, hvor let jeg kan tage Fejl; og det er maaske ogsaa dumt at sige saadan noget saa tidlig; men jeg havde saadan Lyst til at kunne tale med Dig i Aften, for jeg har jo slet ingen her, der virkelig interesser sig for saadan noget."

[71] J. Stark, "Folgerungen aus einer Valenzhypothese II. Metallische Leitung der Elektrizität," *Jahrb. Rad. u. Elek.*, *9* (1912), 188–203. Stark suggests that the valence forces constraining the electrons in a metal lattice permit them to move freely under an external force only in certain directions, so that the kinetic theory of gases is inapplicable to their motions; and that they are displaced together, almost like a lattice, along the directions permitted by the forces.

[72] A sheet of comments on and objections to Stark's ideas is preserved in the Bohr MSS.

III. ABSORPTION, ISOTOPES, AND THE FIRST BOHR ATOM: MANCHESTER, JUNE AND JULY 1912

Two months later, however, by the time of his departure from Manchester for Copenhagen in late July, Bohr had shelved these problems indefinitely. In the event, he never returned to them, with the result that few people today realize how substantial a contribution to physics his thesis might have made if published, as Bohr had hoped, in a generally accessible language. Instead of the electron theory of metals, on which his research had focussed since at least 1909, Bohr was fully involved, by the mid-summer of 1912, with the main research problems of Rutherford's laboratory.

The earliest remaining hint of this transition is found in a letter to Harald dated 12 June 1912.[73]

> It doesn't go so badly with me at the moment; a couple of days ago I had a little idea for understanding the absorption of α particles (the story is this: a young mathematician here, C. G. Darwin (grandson of the right Darwin) has just published a theory about it, and I thought that not only was it not quite correct mathematically (a rather small thing, however), but also very unsatisfactory in its basic conception), and I have worked out a little theory about it, which even if it is not much in itself, can perhaps shed a little light on some things concerning the structure of atoms.[74] I am thinking of publishing a little paper about it very soon. . . . In recent years [Professor Rutherford] has been working out a theory of atomic structure, which seems to be quite a bit more solidly based than anything we've had before. And not that my work is of the same importance or kind, yet my result does not agree so badly with his (you understand that I only mean that the basis of my little calculation can be brought into agreement with his ideas). . . .

Clearly, when this letter was written, Bohr had at last engaged a local problem, α-absorption. Furthermore, he was for the first time

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[73] BPC. Rosenfeld (*op. cit.* [note 1], xvii–xviii) has reprinted the first part of this most interesting and important letter.

[74] Darwin's paper, "A Theory of the Absorption and Scattering of the α Rays," appeared in the *Phil. Mag.*, *23*, 901–920, in the number for June 1912. Since this issue probably did not reach Bohr before 12 June (the accession date of the British Museum's copy is 23 June), he probably read the article in manuscript or proof. But both the date of the letter to Harald and Bohr's phrase "has just published" suggest that Bohr was unaware of Darwin's work until the time of its publication. That fact illustrates the extent of Bohr's initial involvement with Rutherford's group, particularly since he and Darwin were the only mathematical physicists on the premises.

employing a structural model of the atom, Rutherford's, in his own research. Yet this was only the beginning of a transition, not a sudden conversion. The passage of charged particles through matter was a problem very closely related to the central concerns of electron theory.[75] Bohr was entirely prepared for it by past experience, and he approached it in his typical manner, the criticism of someone else's work, without for a moment setting aside the problems that had dominated his thought until June. Indeed, he returns to those problems towards the end of the letter excerpted above: "I still think that (if [my new ideas on electron theory] are right) they will perhaps be important; but I haven't time to think of publishing them in the short time I yet have here, and I have my work in the laboratory. As regards my thesis, as I said I'm making my last effort to get it published here, and if it fails I'll have to publish it myself. . . ." Initially, therefore, the absorption problem was but a minor digression. Perhaps it would not have occurred at all if Bohr had not, as he told Harald, been forced from the laboratory for a few days while awaiting the delivery of some radium.

One week later, however, the nature and depth of Bohr's involvement had entirely changed. Writing Harald on 19 June he speaks of atoms with all the enthusiasm previously reserved for electron theory, a topic he no longer mentions.

> It could be that I've perhaps found out a little bit about the structure of atoms. You must not tell anyone anything about it; otherwise I certainly could not write you this soon. If I'm right, it would not be an indication of the nature of a possibility* [the asterisk leads to a marginal note: "i.e., impossibility"] (like J. J. Thomson's theory) but perhaps a little piece of reality. It has all grown out of a little piece of information [oplysning] I obtained from the absorption of α particles (the little theory I wrote you about in my last). You understand that I still could be wrong, for it's not yet completely worked out (I believe it's not, however); nor do I believe that Rutherford thinks it's completely mad [helt vildt]; but he is the right kind of man and would

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[75] The close parallel between electron theory and the problems of absorption and scattering would, of course, exist only for the group, still minuscule in 1912, which conceived the dimensions of the α particle to be very small compared with those of an atom. That view, which was scarcely to be found outside of Manchester, is the only consequential debt to Rutherford's model apparent in either Darwin's paper or the published version of Bohr's. Both authors show that the contribution of the nucleus to the problems which concern them is negligible and thereafter distribute electrons uniformly through the atom. For changing views of the nature of α particles, see Heilbron, "Scattering . . . and Rutherford's Atom" (note 60).

> never say that he was convinced of something that was not entirely worked out. You can imagine how anxious I am to finish quickly and I've stopped going to the laboratory for a couple of days to do so (that's also a secret). This must do for a short greeting from your Niels, who would give so much to talk with you.[76]

From this time on absorption and the atom occupied more and more of Bohr's time. The calculations took far longer than his first optimistic estimate, and the laboratory work was entirely abandoned in their favor. So, as it turned out, was the electron theory of metals, for the direct pursuit of the Bohr atom had now begun. What can Bohr have learned from Darwin's paper by 12 June and what can the decisive event of the following week have been? Certainty in these matters is impossible, but we find much in the following account compelling.

Darwin's primary objective had been to investigate Rutherford's model by applying it to the computation of the velocity loss of an α particle moving through air or a thin sheet of metal. His results for the shape of the absorption curve agreed quite well with experiment, and he was also able to compute values for n, the number of electrons per atom, close to those required by Rutherford's theory. To make his computations manageable, however, Darwin had introduced two related assumptions of which Bohr was extremely critical. The first was that an α particle would not be impeded unless it actually penetrated the atom; the second that the intra-atomic forces on an electron could be neglected during the short time of its interaction with a rapidly moving α particle. The latter assumption required the former, for, as Bohr pointed out in his critique, any computation which did include the interaction between atomic electrons and non-penetrating α particles would yield an infinite result for the transferred energy unless the forces exerted by the rest of the atom on the electron were taken into account.

With his characteristically brilliant sense for legitimate approximation, Bohr rejected Darwin's first assumption at once. Outside an atom, he agreed, the *net* force on a passing particle due to the nucleus and electrons must be very nearly zero. But that net force is relevant principally to scattering computations, in which the transfer of energy from particle to atom may reasonably be neglected. Absorption computations, however, demand the consideration of energy transfer; the

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[76] BPC. For a likely interpretation of the puzzling note, "i.e., impossibility," see below, 245–247. We have here reproduced the entire text of this important letter.

nucleus, because of its weight, scarcely contributes; and the relevant forces are those between particle and electrons alone. For purposes of absorption computations, therefore, the atom has no surface beyond which the relevant forces cancel. To avoid, without arbitrariness, an infinite product in the computations, the force binding the electron into the atom must be taken into account.[77]

Bohr's initial contribution to the problem, presumably facilitated by acquaintance with a recent paper of J. J. Thomson on ionization,[78] was to recognize that the effect of this force depended critically (and computably) on the relation between the period of the electron's motion and the collision time. The interaction between a moving charged particle and a bound electron takes the form of a pulse, and its effect on the electron is very sensitively dependent on the ratio of the pulse length to the electron's natural period. In effect, as Bohr put it in a passage that displays the preparation provided by his thesis, "the theory of the decrease of velocity of moving electrified particles on passing through matter . . . bears a great analogy to the ordinary electromagnetic theory of dispersion; the different times of vibration for the different wave-lengths considered in the theory of dispersion is here replaced by the different times of collision of particles of different velocities and at different distances from the electrons. . . ." [79] It follows that knowledge of the frequencies of the electrons in an atom should permit a computation of absorption far more accurate than Darwin's.

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[77] These criticisms are a paraphrase from pp. 11–12 of the published paper, N. Bohr, "On the Theory of the Decrease of Velocity of Moving Electrified Particles on passing through Matter," *Phil. Mag.*, *25* (1913), 10–31, communicated by Rutherford from Manchester in August 1912. We presume that they represent the views Bohr developed in June.

[78] J. J. Thomson, "Ionization by Moving Electrified Particles," *Phil. Mag.*, *23* (1912), 449–457, a paper which Bohr cites in "Moving Electrified Particles," 11 and 12.

[79] Bohr, *op. cit.*, 13. The parallel between the absorption problem and dispersion appears clearly in Bohr's treatment. He supposes that an elastically bound electron of resonant frequency ν is exposed to a perturbing force $\phi(t)$ per unit mass, with $\phi(-\infty) = 0$. The electron's equation of motion is, then, $\ddot{x} + (2\pi\nu)^2 x = \phi(t)$. If the electron is at rest before the force is applied, $x(-\infty) = \dot{x}(-\infty) = 0$, and the solution of the equation of motion is, for any ϕ,

$$x = \frac{1}{2\pi\nu}\int_{-\infty}^{t} \sin\,[2\pi\nu(t - z)]\phi(z)\,dz.$$

If $\phi(t)$ is the force exerted by a negligibly deflected α particle which passes the electron at a distance p at time $t = 0$ and with velocity v, then its component perpendicular to the particle's motion is given by $m\phi_{\perp}(t) = 2pe^2/(p^2 + v^2t^2)^{3/2}$, with m the electron's mass. A similar equation gives $\phi_{\parallel}$. For the dispersion problem, the same solution holds, but with $\phi = 0$ until some time t_0, and $\phi = (eE/m)\sin(2\pi\nu' t + \beta)$ for $t > t_0$, where E is the amplitude of the applied radiation, ν' its frequency, and β its phase.

Conversely, knowledge of the velocity loss on passage through matter should enable one "to get more information about the higher frequencies in the atoms, and from this some more information about the internal structure of the atoms." [80] Presumably this is what Bohr had in mind when he wrote Harald that "the basis of my little calculation can be brought into agreement with [Professor Rutherford's] ideas." Or, perhaps, it was the possibility of getting from absorption measurements additional information about *bound electrons,* information required for the elucidation of the two fundamental problems isolated in his thesis, that led Bohr from his criticism of Darwin to the development of an absorption theory of his own.

This far, we believe, Bohr had gone by 12 June. Reconstruction of the crucial developments of the ensuing week is necessarily more speculative, but they are likely to have taken the following form. Unlike the Thomson atom, in which the effective charge attracting an electron towards the atom's center increases with the radius of the electron's orbit, the Rutherford atom is *mechanically* unstable.[81] Whenever two or more electrons equally spaced on a ring rotate about the nucleus, there is at least one mode of oscillation produced by displacement of the electrons in the plane of the ring that will grow until the atom is ripped apart. (The atomic problem differs from that of, say, Saturn's rings because the electrons repel, while planetary particles attract, each other.) This difficulty had been discussed at length in 1904 and 1905 in connection with Nagaoka's Saturnian model (it

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[80] *Ibid.*

[81] We italicize "mechanically" because of the persistent implication in the literature on Rutherford's atom and on Bohr's development of it that *radiative* instability was what set Rutherford's model apart. Rosenfeld even writes (*op. cit.* [note 1], xv) that Bohr, "with his dialectical turn of mind, . . . greeted Rutherford's nuclear model of the atom just because its radiative instability, inescapably following from classical electrodynamics, created such an acute contradiction to chemical and physical evidence about the stability of atomic and molecular structures." There are, however, two decisive objections to giving radiative instability a special role in either the reception of Rutherford's model or in Bohr's attitude towards it, objections to which mechanical instability is immune. In the first place, radiative instability is a characteristic of any model which employs electrons in motion, as all contemporary models did. Hence radiative, unlike mechanical, instability does not distinguish Rutherford's atom from Thomson's, though the former, by supposing a one-electron atom, admitted the least stable case. Second, the problem of radiative instability was well known and seems to have caused little concern. Radiation losses rapidly decreased to manageable proportions as the number of electrons in a ring increased. Thomson was even able to make positive use of such losses in accounting for radioactive decay, and his viewpoint was for a time shared by Rutherford. (Cf., Heilbron, "Scattering . . . and Rutherford's Atom," *op. cit.* [note 60], 256–257.) We are not suggesting, of course, that the problem of radiative instability was unimportant either to Bohr or to the development of quantum theory; we stress only that, unlike mechanical instability, it played no special role in Bohr's choice and initial development of Rutherford's atom.

provided one principal reason for the model's abandonment), but there is little to suggest that Bohr or anyone else at Manchester was aware of it before the fall of 1912. Neither Rutherford, nor Darwin, nor Bohr cite this earlier literature; before Bohr took up problems of electronic structure, the Manchester group had been content to treat the electrons as uniformly distributed through the atomic sphere.[82] Bohr, however, could not long have remained unaware of mechanical instability once he began to compute the displacement of electrons from their orbit by interaction with passing charged particles.

In fact, among Bohr's scientific manuscripts are some forty sheets which appear to record his first encounter with the problem of stability. They are collected in a file titled "Dispersion and Absorption of Alpha Rays," and they divide into three parts, each with its own descriptive coversheet.[83] The first deals with velocity changes caused by "an Atom consisting of an Electron which moves about a fixed Point under the Influence of a Force that varies inversely as the Square of the Distance"; the second generalizes to an arbitrary force; and the third considers the case of atoms "with several Electrons in a Ring (provisionally only 2)." The first two parts reach a conclusion, while the cover sheet of the third announces that it is "Temporarily Abandoned, since the Computation breaks down over the System's Instability, [and] cannot be continued without Applying some other Hypothesis." Unfortunately, none of these sheets is internally dated. They must,

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[82] For the main early discussions of the instability of Saturnian atoms see, G. A. Schott, "On the Kinetics of a System of Particles illustrating the Line and Band Spectrum," *Phil. Mag., 8* (1904), 384–387; "A Dynamical System illustrating the Spectrum Lines . . . ," *Nature, 69* (1904), 437. On 11 March 1911 Bragg wrote Rutherford mentioning that Nagaoka had once developed a Saturnian atom and identified the article with the phrases, "Time about 5 or 6 years ago when Schott and others were on the subject: probably in the Phil. Mag." (cf., Heilbron, "Scattering . . . and Rutherford's Atom," *op. cit.* [note 60], 300 n.). Rutherford either knew the article or looked it up, for he cited it on the last page of his classic paper, "The Scattering of α and β Particles by Matter and the Structure of the Atom," *Phil. Mag., 21* (1911), 669–688. His text shows that he had not studied Schott and was unaware of instability: "[Nagaoka] showed that such a system was stable if the attractive force was large."

[83] BMSS; The coversheets are in Mrs. Bohr's hand but must have been written to her husband's dictation. The calculations appear to deal only with displacements in the plane of the orbit and could not, therefore, have taught Bohr that the atom can be made stable against perpendicular displacements. (For the importance of this distinction see 280–281, *infra.*) That these were very early computations is suggested, among other things, by the fact that they are even more closely modelled on classical dispersion theory than Bohr's published paper. For example, instead of using a pulse for the perturbing force ϕ (cf., note 79, *supra*), Bohr uses a sine wave, sometimes with an exponential damping factor. He thereby avoids integrals of the form $\int_{-\infty}^{\infty} dz \cos(\nu z)/(z^2 + 1)^{3/2}$, which occur in the pulse problem but not in dispersion. Since these integrals, for which Bohr developed a series solution in the published absorption paper, figure in the letter to Harald of 12 June 1912, it is almost certain that the manuscript computations were prepared before that date.

however, represent a very early stage of Bohr's concern with the absorption problem, for they embody an approach of which only mathematical traces remain in the published paper, submitted from Manchester during August. In the latter, Bohr ignores orbits entirely, presumably in order to eliminate the stability problem until prepared to confront it directly; the electrons in an atom are treated as simple harmonic oscillators, just as in classical dispersion theory.[84] We think it likely, therefore, that Bohr had completed the manuscript calculations before 12 June, the date of his first letter to Harald about Darwin's calculations and Rutherford's atom.[84a]

When that letter was written, the "other Hypothesis" demanded by the multi-electron case was not, we presume, yet at hand. We conjecture that it was just this hypothesis, together with some first fruit sufficient to account for Bohr's enthusiasm and conviction, which intervened and were discussed with Rutherford during the week prior to 19 June. The hypothesis was, of course, stabilization of the orbit by extra-mechanical fiat, through the introduction of Planck's quantum. An electron was to remain in stable orbit if and only if its kinetic energy, T, were related to its orbital frequency by the equation $T/\nu = K$, with K a constant closely related to Planck's h. About the likely first fruit of such stabilization by fiat, we reserve our conjecture until discussing the manuscript in which, together with the quantum condition, it is made explicit.

Much in Bohr's previous career leads up to this first quantization of Rutherford's atom. Convinced since the completion of his thesis that

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[84] Though Bohr, in the published paper, never considers orbits and makes no use of his "other Hypothesis," for which see immediately below, he does twice promise a sequel which will deal with orbital dynamics in a way that only the new hypothesis would permit. In particular ("Moving Electrified Particles," *op. cit.* [note 77], 27, 23), he promises to consider "the relation between the frequencies and the dimensions of the orbits of the electrons in the interior of the atoms" and also to examine the difference between the frequencies of vibrations perpendicular and parallel to the plane of the orbit. Both of these topics are considered in Parts II and III of the trilogy published in 1913.

[84a] While this article was in press, Professor Rosenfeld kindly informed us of some of the content of letters Bohr wrote his fiancée, Margrethe Nørlund, during May, June, and July 1912. That correspondence, which has not been available to us, forces a slight alteration in the dating we had inferred from the letters to Harald: the first mention of Darwin's problem and of Bohr's interest in it must be pushed back a week, to 4 June 1912. But the correspondence with Margrethe fully confirms that the essential event in Bohr's conversion to the problem of atomic structure occurred between 12 and 19 June. A letter of 15 June mentions the discovery of a special clue that Bohr is following with alternate hope and despair, a clue which two days later (according to a letter of 17 June) he thinks has opened a prospect which might lead to something true. We should note, however, that Professor Rosenfeld, who has been so helpful in this as in other matters, does not fully share our views as to the suddenness or the lateness of the transition in Bohr's research interests.

classical mechanics must break down in the interior of the atom, he cannot have been surprised by, and may well have welcomed, mechanical instability. Both Planck's work on blackbody radiation and his own on magnetism had suggested, furthermore, that the new mechanics, whatever its form, would differ from the old in excluding a large proportion of the electron orbits permitted by classical theory. Even the quantitative formulation of Bohr's hypothesis lay close to hand in the theory of the magneton, in Thomson's model for the photoeffect, and elsewhere.[85] No wonder Bohr felt, as these elements of his previous experience coalesced about Rutherford's atom, that he had "found out a little bit about the structure of atoms . . . , perhaps a little piece of reality."

That possible "piece of reality" is what Bohr described for Rutherford in a memorandum prepared for discussion before his departure for Copenhagen.[86] Conceivably it was the basis for the discussions that occurred in the week after 12 June, for the requisite calculations are not arduous, and they contain an important error which suggests they

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[85] *Supra,* 227, 232. There are other sources, for by 1912 *ad hoc* equations connecting the ratio of an energy to frequency with Planck's constant were becoming more usual. At the Solvay Congress in 1911 Lorentz suggested that the energy of a rotator be set equal to $nh\nu$, and Bohr could have known the procedure through the Solvay *Rapports* (*op. cit.* [note 40], 447), which were published in January 1912 (*Bibliog. de la France, 102* [1913], No. 887). Bjerrum, whom Bohr knew (though perhaps not at this time), independently applied the condition to a rotating diatomic molecule in 1912 (*Nernst-Festschrift,* 1912, 90–98), the same year in which Nicholson developed it for electron rings (*infra,* 259). In "Moving Electrified Particles," *op. cit.* [note 77], 27, Bohr uses the same device without comment to estimate the frequency of the interior electrons of oxygen. If there is a puzzle about Bohr's quantum condition, it is not his choice of the ratio of energy to frequency but the lack of an integral multiplier.

In addition to offering him possible Planck-like relations between T and ν, the accumulating contemporary literature on quantum theory—particularly the Solvay *Rapports* and perhaps also an important paper published by Poincaré in January 1912—may have been helpful to Bohr in a less specific way. Before the first Solvay Congress very few people shared the conviction Bohr had expressed in his thesis about the inevitability of a quantum-like break with classical mechanics. The Congress and Poincaré's response to it did much to spread the view that Bohr had arrived at for himself. (Cf., Russell McCormmach, "Henri Poincaré and the Quantum Theory," *Isis, 58* [1967], 37–55.) At the very least Bohr must have been reassured. Perhaps more important, Rutherford had been at the Congress and discussed it with Bohr when the two first met (Interviews II, 8; *supra,* 233). The discussions there might have reinforced Rutherford's sympathy towards the quantum, which he had already regarded favorably because of the remarkable agreement between Planck's value for the charge of the electron and the apparently anomalous value he and Geiger had obtained by counting α particles (cf., Rutherford's "Note" in the Planck-Heft of *Naturwissenschaften, 17* [1929], 483).

[86] BMSS. This crucial document (henceforth to be called the Rutherford Memorandum or the Memorandum), most of which has been reprinted by Rosenfeld (*op. cit.* [note 1], xxi–xxviii) is filed in an envelope labelled by Bohr, "First draft of the considerations contained in the paper 'On the Constitution of atoms and molecules' (written up to show these considerations to Prof. Rutherford)/(June and July 1912)." The memorandum is in English. In quoting from it, below, we have rectified Bohr's spelling and punctuation for ease in reading, but retained his characteristic turns of phrase.

were done in haste. More likely, though, the Rutherford memorandum dates from later in June or from July, for it is rich in illustrative examples which clearly display both the extent of Bohr's achievement while in Manchester and the concerns which dominated his research during the seven months after his departure.

At the start of the Memorandum Bohr points out that in Rutherford's model there can be no equilibrium configuration without motion of the electrons. "We shall therefore," he continues, "first consider the conditions of stability of a ring of n electrons rotating around a point-shaped positive charge of magnitude ne."[87] What follows without a break is almost certainly the discovery which accounts for the enthusiasm of Bohr's letter of 19 June and which rendered the Thomson model, for the first time, "an impossibility."

> By an analysis analogous to the one used by Sir J. J. Thomson, . . . 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.
>
> It is however immediately seen that there is an essential difference between the stability of rings containing a different number of electrons, as it can be shown that the energy of an electron in the ring (the sum of the kinetic energy and the potential energy relative to the kern [nucleus] and the other electrons) is negative if $n \leqq 7$, but positive if $n > 7$, and that therefore an electron of a ring containing more than seven electrons is able to leave the atom. It is therefore a very likely assumption that an atom consisting of a single ring cannot contain more than seven electrons. 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 is assumed to depend on the stability of the outermost ring, the "valency electrons") by help of the atom-model in question. . . .
>
> * 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.

The ideas explicit and implicit in this striking passage mark, we believe, a critical point in Bohr's development. Bohr has discovered a second decisive contrast (the first being large-angle scattering) between

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[87] *Ibid.*, xxii.

the Thomson and Rutherford models, and the comparison is for him conclusive. This discovery is no less important historically because it rests on a mistake in calculation[88] and never recurs in Bohr's later writings. What had he in mind?

In Thomson's model, as in Bohr's version of Rutherford's, electrons were arranged in rotating, concentric, coplanar rings. In both models, also, additional chemical elements were constructed by adding electrons one-by-one to the outermost ring (simultaneously adjusting the positive charge to keep the atom neutral) until the addition of one more electron would, by mutual repulsion, rip the ring apart. At this point, Thomson restabilized the ring by adding an additional electron to the interior of the atom, again adjusting the positive space-charge for neutrality; thereafter he again added electrons to the outside ring until it once more approached instability. Interior electrons were themselves arranged in concentric rings subject to the condition that each ring be as full as possible before additional electrons were placed on the ring next inside it.[89] With Rutherford's model, however, Bohr found that adding electrons *within* a ring slightly reduced stability. Once the point of instability had been reached, he therefore began a new *external* ring, adding electrons one-by-one until it too verged on instability.

Though Thomson had been able to display interesting parallels between his results and the structure of the periodic table, there were overwhelming advantages to Bohr's procedure. First, Thomson's con-

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[88] That the argument cannot be right is indicated by its conflict with an elementary theorem which Bohr himself proves on the last page of the Memorandum: "In a system of electrical charged corpuscles which possess an axis of symmetry (common axis of rotation) the total potential energy will always be equal to the total kinetic energy multiplied by -2" (Rosenfeld, xxi n.). It follows that if T is the kinetic energy of the system, then the total energy $= T + V = T - 2T = -T \leqq 0$, since kinetic energy is never negative. If the electrons are symmetrically distributed in a ring, the energy is equally divided between them, and none can have a positive total energy. No argument like Bohr's will explain the existence of periods in the periodic table. It is odd—surely evidence of haste and probably also of the need for a particular answer—that Bohr should have missed the contradiction between his key result and a theorem he himself introduces five pages after it in the Memorandum.

The computational error can be found on p. A 3b of the Memorandum (one of the two sheets which Rosenfeld, who supplied the numbering, omits). When evaluating the potential energy of one electron due to the others in the ring, Bohr sums the quantity e^2/d_s over the ring, where d_s is the distance between the Zth and the sth electron. In doing so, he forgets that e^2/d_s is the potential energy of the interaction between a *pair* of electrons and that only half of it may properly be attributed to the Zth electron. His result, which does cause the total energy to change sign between $Z = 7$ and $Z = 8$, is therefore twice too large.

[89] The *locus classicus* for these aspects of Thomson's atom and for those which follow is, J. J. Thomson, *Corpuscular Theory of Matter,* 103–120.

struction yielded periods of steadily increasing length: 5, 11, 15, 17, 21, 24; Bohr's erroneous computation gave at least roughly regular periods of length seven. Second, Thomson explained the similar properties of the elements of a given column in the periodic table by pointing to the identity (not always quite maintained) in the construction of their *interior* rings, the number of electrons in the outermost ring differing for each member of the family. In the Bohr-Rutherford model, on the other hand, all atoms in the same column had the same number of electrons in the outermost ring, the ring whose electrons, being most loosely bound, would enter most readily into chemical and optical interactions. Finally, the number of electrons required for Bohr's construction of a given element were compatible with the values of nuclear charge which Rutherford had determined from large-angle scattering. Thomson rarely committed himself to parallels between particular electronic structures and particular elements, but when he did the numbers were invariably far too high, so that oxygen, for example, received sixty-five electrons rather than the eight required by the Rutherford model.[90] Apparently it was these impressive contrasts that made Bohr so sure he was following the right path.

Having, he thought, established this much at the start of the Memorandum, Bohr turned immediately to the quantum condition.

> In the investigation of the configuration of the electrons in the atoms we immediately meet with the difficulty (connected with the mentioned instability) that a ring, if only the strength of the central charge and the number of electrons in the ring are given, can rotate with an infinitely great number of different times of rotation, according to the assumed different radii of the ring; and there seems to be nothing (on account of the instability) to allow from mechanical considerations to discriminate between the different radii and times of vibration.[91] In the further investigation we shall therefore introduce and make use of a hypothesis from which we can determinate the quantities in question. The hypothesis is: that there, for any stable

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[90] Even in 1907 these values for n were significantly higher than those which Thomson estimated from experiments on secondary X-rays and electron scattering. By 1912 they were still further out of line, though Thomson continued to think that Rutherford's values for n were too low, perhaps by a factor of 2 (cf. Heilbron, "Scattering . . . and Rutherford's Atom," *op. cit.* [note 60]). Anyone puzzled by the popularity of Thomson's atom despite these and other difficulties should remember that most people followed its author in expecting only the crudest sort of quantitative agreement. The assumptions of coplanar distribution and of positive space charge had both been introduced solely to facilitate computation (cf., *supra,* 226).

[91] In *The Corpuscular Theory of Matter,* 158–162, Thomson had discussed a mechanical means, based upon calculations of the astronomer Sir George Darwin, of restricting the orbits.

> 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 of rotation. [Bohr clearly intends frequency, not time 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.
>
> * This seems to be nothing else than what was to be expected, as it seems to be rigorously proved that the mechanics is not able to explain the experimental facts in problems dealing with single atoms. In analogy to what is known for other problems it seems however to be legitimate to use the mechanics in the investigation of the behavior of a system if we only look apart from questions of stability (or of final statistical equilibria).[92]

That footnote, with its echoes both verbal and intellectual, reminds us how firmly the Rutherford Memorandum is rooted in Bohr's thesis. But he has travelled a long way from the electron theory of metals. He has, that is, chosen an atom model, justified its use, and selected a quantum condition to ensure its stability. In the Memorandum he immediately proceeds to investigate its power in application. We here examine his discussion of the hydrogen molecule, the one example for which the Memorandum provides an explicit quantitative treatment.[93]

Bohr assumes, in keeping with the requirements of Rutherford's model, that the hydrogen atom possesses only one electron, a view accepted at Manchester but not widely elsewhere. The molecule, Bohr thought, must therefore be arranged as in the figure below: two electrons, each with charge $-e$ and mass m, rotate with frequency ν at the ends of the diameter of a ring of radius a; the ring itself is centered on an axis of length $2d$ connecting the two nuclei, each with charge $+e$; the plane of the ring bisects the inter-nuclear axis perpendicularly. For equilibrium of the nuclei, their mutual repulsion must just balance the axial component of the attraction due to the two electrons. That is,

$$\frac{e^2}{(2d)^2} = \frac{2e^2 d}{(a^2 + d^2)^{3/2}},$$

an equation satisfied if $a = d\sqrt{3}$. For equilibrium of the electrons, the

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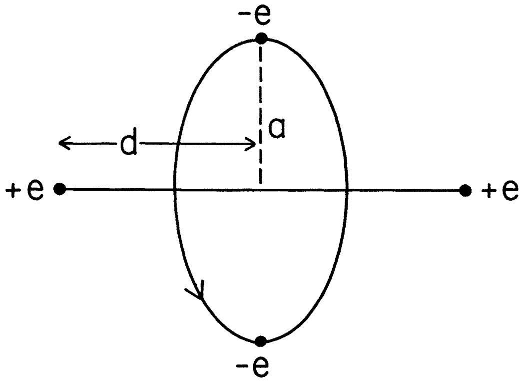
[92] Rosenfeld, xxiii.

[93] Rosenfeld, xxv–xxvii.



net radial force to which each is subject—i.e., the radial attraction of the two nuclei less the mutual repulsion between the electrons—must balance the centrifugal force due to the motion of the ring. The net attractive force on each electron is, therefore,

$$\frac{2e^2a}{(a^2+d^2)^{3/2}} - \frac{e^2}{(2a)^2} = \frac{e^2}{a^2}\left\{\frac{2}{[1+(d/a)^2]^{3/2}} - \frac{1}{4}\right\} = \frac{e^2}{a^2}X,$$

with $X = 1.049$. (Bohr discusses the problem more generally, showing first that the net radial force for any ring may be written as $(e^2/a^2)X$ and then that $X = 1$ for the hydrogen atom, 1.049 for the hydrogen molecule, 1.75 for the helium atom, etc.) For equilibrium therefore

$$\frac{e^2}{a^2}X = ma(2\pi\nu)^2, \tag{9}$$

so that the frequency is given in terms of the radius and vice versa.

This is as far as ordinary mechanics can go. To continue Bohr turns to the quantum, introducing the "*special* Hypothesis $E = K\nu$,"[94] with E the kinetic energy of an electron. Equation (9) permits the kinetic and potential energy to be related, so that W, the negative of the total energy or the work required to remove an electron from the ring may be written:

$$W = -\left[\frac{1}{2}ma^2(2\pi\nu)^2 - \frac{e^2}{a}X\right] = \frac{e^2}{2a}X. \tag{10}$$

Manipulated with (9) and $W = E = K\nu$, equation (10) yields the three new equations:

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[94] *Ibid.,* xxvii, italics in the original.

$$W = \frac{\pi^2 me^4 X^2}{2K^2}, \tag{11}$$

$$a = \frac{K^2}{\pi^2 me^2 X}, \tag{12}$$

$$\nu = \frac{\pi^2 me^4 X^2}{2K^3}. \tag{13}$$

Assuming e and m known from experiment, these equations determine the energy, frequency, and radius of the hydrogen molecule (or of any other for which X has been computed) in terms of the universal constant K.

In the Memorandum, Bohr writes none of the last three formulas explicitly, but all of them, or equivalent forms, are implicit in his computations. (The use of [11] and [13] is illustrated below; [12] is implicated in the investigation of atomic radius.) He gives explicitly only a numerical equivalent for (11), writing that the negative total energy of a ring of n electrons is "nX^2A where A approximately is equal to $1.3 \cdot 10^{-11}$ erg."[95] That formula is then applied to the computation of the heat released when two atoms of hydrogen combine to form a molecule, yielding order of magnitude agreement with experiment. It is a remarkable computation, scarcely precedented in the literature of atomic theory.

Bohr's computation depends, however, upon the choice of K, and his Memorandum supplies neither an explicit value nor a source for this universal constant.[96] Given Bohr's reasons for adopting the "*special* Hypothesis," one would expect the value of K to equal Planck's h or one of its simple sub-multiples, but none seems reconcilable with the value Bohr attributes to A. Very likely he first tried computations using $K = h$, h/π, etc., decided they did not agree adequately with experiment, and determined, at least for the time being, to use an empirical value instead. Rosenfeld has suggested the source of the value, and his ingenious hypothesis is unlikely to be bettered.[97] Comparing $W = X^2A$ (Bohr's form for the absolute value of the energy per electron in a ring) with equation (11), yields $A = \pi^2 me^4/2K^2$. Setting $A = 1.3 \cdot 10^{-11}$, as Bohr did in the Memorandum, and assuming, as Bohr did in his absorption paper, that $e = 4.65 \cdot 10^{-10}$ esu and $e/m = 5.31 \cdot 10^{17}$ esu/g, K becomes

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[95] *Ibid.*

[96] Rosenfeld (*op. cit.* xxi) conjectures that a page of the Memorandum may be missing. If so, the determination of K may once have been part of Bohr's manuscript.

[97] Rosenfeld, xxx–xxxi.

$4.0 \cdot 10^{-27}$ erg-sec or approximately 0.6 h.[98] This is just the value one obtains if K is computed from equation (13) with the preceding values for e and e/m, and with the frequency set at $\nu = 3.5 \cdot 10^{15}$ sec^{-1} and X at 1.049. The value of ν, as Rosenfeld points out, is the experimental figure for the resonance frequency of molecular hydrogen which Bohr employs in Part III of the trilogy. He also uses it, which makes Rosenfeld's suggestion even more plausible, in the absorption paper which he prepared at the same time as the Rutherford Memorandum.[99]

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[98] Bohr, "Moving Electrified Particles," *op. cit.* (note 77), 23. Rosenfeld's calculation employs values taken from Part I of the trilogy, a slightly less likely source, but the single minor difference in value (4.7 for 4.65 in the figure for electronic charge) has no effect on the outcome of his argument.

[99] *Ibid.* Note that Bohr's value is for angular velocity and must be divided by 2π to give the figure cited above. (The values for the resonance frequencies of He and H_2 available to Bohr were determined indirectly by matching the experimental curve $\mu(\nu)$, μ being the index of refraction, to the classical formula $\mu^2 - 1 = Ne^2/\pi(\nu_0^2 - \nu^2)$. Here N is the number of dispersion electrons/cm^3 and ν_0 is the resonance frequency in question.)

More depends upon this reconstruction than is immediately apparent. Bohr's transition from the atom model of the Rutherford Memorandum to the one for which he is now known involves, among other things, equating K with $h/2$. We shall suggest in Section IV, again following Rosenfeld, that his motive for the change was simply to make his model produce the Balmer formula, including the value of Rydberg's constant. It follows that his first argument to justify the factor of ½, an argument which turns out to contain the germ of the Correspondence Principle, was in its origins a *post hoc* rationalization. One would therefore like to be quite certain that Bohr did not have other, earlier and more theoretical reasons for selecting a value of K.

One piece of evidence can be read to suggest that he did. In a typewritten letter to Hevesy dated 7 February 1913, before he had recognized the possible relevance to his model of the Balmer formula, Bohr states that his theory assumes "that the energy emitted as radiation by this binding [of an electron previously at rest relative to the nucleus] is equal to Planck's constant* multiplied by the frequency of rotation of the electron considered in its final orbit." The asterisk leads to a handwritten footnote, present in the copy sent to Hevesy but not in Bohr's carbon, which reads, "The constant entering into the calculations is not exactly equal to Planck's constant, but differs from it by a numerical factor *as was to be expected from theoretical considerations*" (BSC; Rosenfeld, xxxii–xxxiii, italics added). We now take the italicized phrase to mean only that the obvious differences between the Rutherford model and Planck's oscillators, e.g., the anharmonic structure of the former, lead one to expect a value for K different from h but otherwise unspecified. It can, however, be read to mean that Bohr's theory led him to a particular value for K, presumably $h/2$, and we initially understood it in that way.

As a result we have looked for alternate values of the physical constants current in 1912, values which might reconcile Bohr's choice of A, above, with the equation $K = h/2$. Bohr's value for e/m had, however, been standard to within a fraction of a percent since at least 1909. For Planck's constant he uses the original value, one confirmed by all subsequent measurements to within 2 percent. The electronic charge, e, was far more uncertain in 1912, but Bohr's value, $4.65 \cdot 10^{-10}$ esu, had been gospel at Manchester since the measurements of Rutherford and Geiger in 1908. Its main competitors elsewhere, Regener's value of 1909 and Millikan's of 1911, were higher, which would increase the discrepancy between K and $h/2$. To eliminate it, the electron's charge must be $4.3 \cdot 10^{-10}$ esu, and the only relatively recent measurements to give so low a value were those of Perrin, an unlikely source for Bohr, partly because the method involved was so indirect. In any case, Perrin's value of e would make $A = 1.2 \cdot 10^{-11}$ erg. We thus find Rosenfeld's reconstruction of the source of Bohr's value inescapable. (A particularly useful and convenient critical survey of the values of e and e/m current from 1897 to 1914 is included in J. S. Townsend, *Electricity in Gases* [Oxford, 1915], Chaps. VII, XII. For assistance in the search for alternate constants we are indebted to Mr. E. M. Parkinson.)

Though the hydrogen-molecule computation is the only one carried through fully in the Memorandum, the manuscript shows clearly that Bohr had already thought deeply about a considerable number of other problems. He provides, for example, models for the electronic structure of O_2, O_3, H_2O, CH_4, C_2H_2, He, and [He_2]. By comparing the energy of He with that of [He_2], he shows that the lattter, unlike H_2, cannot exist free in nature (whence the square brackets), a result that is likely to have given him particular pleasure and encouragement, for it was only with simple, single-ring atoms and molecules that he could anticipate exact results from computation. Bohr also employed his theory to estimate the dissociation temperature of H_2, and to explain why O_2 displays no infrared absorption bands and why it dissociates into two neutral atoms rather than into ions of opposite sign. Finally, he suggested that his theory could explain "the periodic law of the atomic volumes of the elements," Bragg's law relating stopping power for α rays to atomic weight, and Whiddington's law relating atomic weight to the excitation energy of characteristic X radiation.[100] Few of these results receive more than brief mention in the Memorandum. Bohr can scarcely have undertaken more than preliminary computations during late June and July, particularly since he was simultaneously deeply engaged with the absorption paper. These are the problems to which he devoted himself after his return to Copenhagen. His solutions to them provide the substance of Parts II and III of the trilogy.

The absorption paper and the quantized model are the two facets of Bohr's Manchester research which ultimately reached print under his name, but they are not the only areas in which he had made sub-

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[100] The periodic law of atomic volume states that atomic volume (atomic weight/density), though increasing slowly with atomic weight from row to row of the periodic table, is fundamentally a periodic function dependent on position in the table. It has a recurrent high peak with the alkali metals in the first column of the table and falls rapidly to a minimum approximately half way between them. The law originated with Lothar Meyer ("Die Natur der chemischen Elemente als Funktion ihrer Atomgewichte," *Ann. d. Chem. u. Pharm.*, 1870, Suppl. *7*, 354–364) and by the close of the century had become a standard topic for discussion in books on physical chemistry. For one of the many volumes from which Bohr might have known it see, W. Nernst, *Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics,* trans. R. A. Lehfeldt from 4th German ed. (London, 1904), 189–192.

Bragg's law stated that the stopping power of different metals for α rays was proportional to the square root of their atomic weights. (Cf., W. H. Bragg, "On the α Particles of Radium, and their Loss of Range in passing through various Atoms and Molecules," *Phil. Mag.*, *10* [1905], 318–340.) Whiddington's law related v, the minimum velocity an electron required to excite characteristic X rays, to the atomic weight of the target material through the equation, $v = A \cdot 10^8$ cm/sec. (Cf., A. Whiddington, "The Production of Characteristic Röntgen Radiations," *Proc. Roy. Soc. A*, *85* [1911], 323–332.) For Bohr's discussion of the first and third of these topics see Section VI, *infra.*

stantial advances before returning home. His own later recollections, supplemented, if sketchily, by letters written during 1913, show that he had also reached a clear understanding of the way in which nuclear charge, i.e., atomic number, governs the chemical properties of the elements. In the process, he had recognized, too, that radioactivity and weight must be entirely nuclear phenomena, had invented for himself the concept of isotopes, and had developed, at least in part, the radioactive displacement laws.[101] A half century after these events, Bohr suggested he had become involved with this constellation of problems during "the first weeks in Manchester," [102] and his account implies that he was much concerned with them throughout his stay. That dating, unlike the description of Bohr's achievement, seems to us extremely improbable. Such an involvement should have left traces in Bohr's rich correspondence, and there is, as we have already noted, none to be found before 12 June. We believe it far more likely that Bohr's innovations regarding the role of the nucleus, like his ideas on electronic structure, were consequences of the chain of thought initiated by Darwin's paper on absorption. Excepting recollections from the last years of Bohr's life, there is no reason to suppose that he had taken more than the most casual interest in Rutherford's model before June 1912.

Whatever their date, Bohr's nuclear innovations were important both for him and for others at Manchester. Apparently they followed quickly from a chance remark of his friend George Hevesy, who informed him that the number of known radioelements already considerably exceeded the available space in the periodic table. "Everything," Bohr later said, "then fell into line." [103] For that to have been the case, he must simultaneously have learned (or already have been aware) of one other striking feature of the surplus population, the existence of elements with different atomic weights and radioactive properties but with apparently identical chemical characteristics. Examples of such "chemically inseparable" elements were turning up

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[101] The main contemporary testimony about this aspect of Bohr's work in Manchester is from letters: particularly, NB to Hevesy, 7 Feb 1913 (BSC); and Hevesy to Rutherford, 14 Oct 1913 (quoted in Rosenfeld and Rüdinger, *op. cit.* [note 1], 48). Fuller evidence from a date still fairly close to the event is provided in G. von Hevesy, "Bohrsche Theorie und Radioaktivität," *Naturwissenschaften, 11* (1923), 604–605. Most of the information about this episode comes, however, from two much later autobiographical sources and is correspondingly suspect as to details though not in general tenor: Bohr's "Reminiscences," *op. cit.* (note 55), 1084–1086, and Interviews I, 3–7; II, 11–16; and III, 6, 10. Only these late sources contain any implications about the point during Bohr's stay in Manchester when his ideas about the role of the nucleus emerged.

[102] Interviews II, 12–13.

[103] *Ibid.,* I, 7; II, 11–12, 16; Bohr, "Reminiscences," 1085.

frequently by 1912, and Hevesy himself had been wrestling with one pair of them, radium D and lead.[104]

Thomson's atom, which Bohr knew well, was powerless to deal with phenomena of this sort. Its chemical properties depended on all of its electrons, superficial and deep, and the total number of these atomic electrons determined the atom's weight by fixing the amount of the massive neutralizing positive charge. Bohr saw, however, that Rutherford's model permitted a quite different response to the challenges posed by Hevesy's illuminating remark. It provided the basis for a rigorous distinction between radioactive and chemical, or between nuclear and electronic, phenomena. The nuclear charge, Ze, determined the number of atomic electrons, n, and hence the atom's chemistry; while the atomic weight, A, which governed radioactivity, was essentially the mass of the nucleus, a quantity theoretically independent of n. The periodic table must, that is, be regulated by Z, not by A. Atomic weight was, as Bohr later put it, "a complete accident"[105] which might vary among atoms possessing identical chemical properties.

To this general viewpoint, Rutherford's theory of large-angle scattering added essential quantitative and qualitative detail. It required that helium have exactly two electrons and strongly suggested that hydrogen possesses only one. The experiments of Geiger and Marsden, interpreted on that theory, implied in addition that the Z's, and therefore the n's, of the metals closely approximated $A/2$. An obvious, simple, though hazardous extrapolation made the Z's of all the elements equal to their serial position in the periodic table. That novel view is one that Bohr had probably assimilated at the time he designed the atomic models in the Rutherford Memorandum and wrote his absorption paper. When, for example, he says in the latter, "According to Rutherford's theory of atoms we should expect 16 electrons in an oxygen molecule,"[106] he is likely to be referring to his own interpretation of Rutherford's theory, not to a consequence that its author had yet altogether accepted.

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[104] Bohr, "Reminiscences," 1085; G. von Hevesy, "Die Valenz der Radioelemente," *Phys. Zs.*, *14* (1913), 49–62.

[105] Interviews II, 12.

[106] Bohr, "Moving Electrified Particles," *op. cit.* (note 77), 26. Note, however, that in an early manuscript Rutherford, too, attributes eight electrons to the oxygen atom, presumably using simply the approximation $n = A/2$ (Heilbron, "Scattering . . . and Rutherford's Atom," *op. cit.* [note 60], 305.)

In a series of interviews held just before his death, Bohr described the source of his conviction about Rutherford's model with the words, "one knew the number of electrons in the atom, one knew the isotopes."[107] On the following day he added, "This problem of the isotopes was actually the reason that I felt we have now got some knowledge of the atom."[108] Though we do not believe that atomic number and isotopy were either the only or the very first of Bohr's reasons for taking up Rutherford's model,[109] they did provide him with essential early evidence that his research had taken the right turn, that everything would now "fall into line." As much as anything else, those discoveries must be what sustained him through the difficult and distracting year in which he attempted to work out the consequences of the quantized atomic model of which he had caught a first glimpse in June.

IV. EXCITED STATES AND SPECTRA: COPENHAGEN, AUGUST 1912 THROUGH FEBRUARY 1913

Late in July, Bohr left Manchester for Copenhagen where he was married on 1 August. The couple spent their honeymoon in England, rather than Norway as originally planned, so that Bohr could put the

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[107] Interviews I, 7.

[108] *Ibid.,* II, 16. In this connection Bohr's last comments on Moseley's work are of great interest: "And Moseley's thing, that is presented in a wrong manner, you see, because then we knew the hydrogen, we knew the helium. We knew the whole beginning [of the periodic table] . . . ." (*Ibid.,* I, 7). From Bohr's viewpoint, Moseley had confirmed an obvious extrapolation of Rutherford's model and scattering theory, and he should have said so. (See J. L. Heilbron, "The work of H. G. J. Moseley," *Isis, 57* [1966], 336–364, for Bohr's possible role in the planning of Moseley's investigation. Moseley did acknowledge that his purpose was to test the doctrine of atomic number which, however, he attributed to van den Broek.)

[109] Our conviction that Bohr's late memories of events in Manchester over-emphasize the role of his ideas about isotopy and atomic number is reinforced by our experience during the interviews from which much of the above is taken. When those interviews were conducted, the Rutherford Memorandum had not yet been discovered in Bohr's files. One of us had conjectured, however, from hints in his correspondence and in Part I of the trilogy, that Bohr had developed a detailed, non-spectroscopic, quantized version of Rutherford's atom some time before he saw the relevance of the Balmer formula. In early interviews, therefore, we repeatedly asked him for information about his work on atom models during the months before he first related the models to spectra. Bohr found such questions merely "silly" and insisted that, in the absence of the Balmer formula, he could have done no significant work on models. He consistently denied, that is, the very possibility of the sort of research which the Rutherford Memorandum ultimately documented. We conjecture that his emphasis on the role of his nuclear discoveries helped to fill the gap in memory left by the erasure of his work at Manchester (and Copenhagen, cf., *infra*) on electronic structure. Tricks of memory like this were, we should add, typical in our experience as interviewers. Bohr was by no means the only scientist unable to recall, or even to conceive as possible, participation in work which subsequent developments had removed from the corpus of proper physics.

finishing touches on the absorption paper, which he then delivered in person to Rutherford. Next they returned to Copenhagen, where Bohr undertook the duties of Assistant to the new Professor of Physics, Martin Knudsen, and also delivered a series of lectures on the foundations of thermodynamics.[110] The work on atomic and molecular models necessarily slowed down, but it was not abandoned.

In the final version of his absorption paper Bohr had promised readers a sequel, one which would treat the problems of electronic structure and orbital dynamics raised by Rutherford's atom.[111] It was to be a development of the Rutherford Memorandum, and Bohr expected in August that he could complete it quickly. As early as 4 November 1912 he wrote to Rutherford apologising for the time he was taking "to finish my paper on the atoms and send it to you."[112] Academic duties had, Bohr explained, combined with "serious trouble arising from the instability of the [atomic] systems in question" to delay the work's completion. He hoped, however, "to be able to finish the paper in a few weeks."

That estimate, too, proved excessively optimistic. Competing demands on Bohr's time continued to delay him, and he therefore asked Knudsen to relieve him of his duties, retired to the country with his wife, and "wrote a very long paper on all these things."[113] No physical trace of that manuscript remains, but its contents can be identified with assurance. Letters to Rutherford on 4 November 1912 and 31 January 1913 describe problems on which Bohr was at work, and a long letter to Hevesy on 7 February provides an extensive list of the resulting achievements.[114] The topics touched on in those letters are, in full: atomic volume and its variation with valence; the periodicity of the system of the elements; the conditions of atomic combination; excitation energies of characteristic X rays; dispersion; magnetism; and radioactivity. Those subjects are, of course, the ones on which Bohr had worked in Manchester. They are, furthermore, precisely the ones, and also the only ones, which he was to discuss in Parts II and III (including the unpublished section on magnetism) of the famous

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[110] NB to Rutherford, 4 Nov 1912 (BSC); Rosenfeld and Rüdinger, *op. cit.* (note 1), 50–51.

[111] Cf., note 84, *supra.*

[112] BSC.

[113] Interviews III, 11; cf., *ibid.,* II, 13.

[114] BSC. The letter to Hevesy is reproduced in full by Rosenfeld, xxxii–xxxiv.

trilogy.[115] Almost certainly, therefore, those two portions of the trilogy were put together—with minor revisions to take account of what had intervened—from the "very long paper" Bohr had dictated in the country, the earlier draft vanishing through partial incorporation into the new one. As late as 7 February 1913, Bohr's research program, of which Parts II and III are the direct product, remained that of the Rutherford Memorandum.

A month later, however, that program had changed decisively, and the first fruits of the transformation were already embodied in a draft manuscript intended for publication. Part I of Bohr's trilogy was mailed to Rutherford on 6 March 1913,[116] and its subject was, for Bohr, entirely new: atomic spectra, particularly the line spectrum of hydrogen. Nothing in the correspondence or in Parts II and III suggests that he had worked on any such topic before February. In a letter to Rutherford dated 31 January 1913, he had, in fact, explicitly excluded the "calculation of frequencies corresponding to the lines of the visible spectrum" from the subject matter he took as his own. His program for model building, like that of Thomson which it closely followed, relied mainly on chemical, scarcely on optical, evidence. The complexity of spectra and the conspicuous failure of those who had tried to relate them quantitatively to models warned atom builders off the subject. Not that spectra were thought irrelevant—most physicists in 1912 would have agreed that they must directly relate to the most basic principles of atomic structure—but the evidence provided by spectra seemed inscrutable. Though Bohr, by 6 March, had proved that widespread attitude mistaken, it had been implicit in his research program until 7 February.[117] What can have happened in the interval to change his mind?

The February transformation of Bohr's research program was pre-

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[115] N. Bohr, "On the Constitution of Atoms and Molecules [Part I, untitled]," *Phil. Mag., 26* (1913), 1–25; "Part II. Systems containing only a Single Nucleus," *ibid.,* 476–502; "Part III. Systems containing Several Nuclei," *ibid.,* 857–875. For the section on magnetism, cf., note 51, *supra.*

[116] NB to Rutherford, 6 Mar 1913 (BSC).

[117] In fact, Bohr's attitude towards the relevance of spectra may have been more negative than that of most of his contemporaries. Much later (*Interviews* I, 7) he said: "The spectra was a very difficult problem. . . . One thought that this is marvelous, but it is not possible to make progress there. Just as if you have the wing of a butterfly, then certainly it is very regular with the colors and so on, but nobody thought that one could get the basis of biology from the coloring of the wing of a butterfly."

pared during the two preceding months, beginning with his discovery, probably in December 1912, of a series of papers by J. W. Nicholson.[118] The articles of particular importance to Bohr dealt with the application of a quantized Saturnian model, much like his own, to the spectrum of the solar corona. Though they had appeared during June 1912 in the *Monthly Notices of the Royal Astronomical Society*,[119] Bohr did not encounter them until late in the year, for the journal is not one he would ordinarily have read. Perhaps someone who knew his interests called them to his attention, or he may have been led to them by the published report of Nicholson's remarks to the British Association meeting in September 1912.[120] In any case, Bohr's first known reference to Nicholson's atomic theory occurs in a Christmas card he and Mrs. Bohr sent to Harald on 23 December 1912,[121] and late in life Bohr indicated that he had been unaware of Nicholson's theory until about that time.[122] Even when he did discover it, assimilation cannot have been easy, for Bohr had known Nicholson before and been profoundly unimpressed. A letter to his close friend Oseen, written from Cambridge on 1 December 1911, mentions an "entirely preposterous" [ganske sindsvag] paper of Nicholson's on the electron theory of metals. Bohr's comments on the piece of work end with the words: "I also had a discussion with Nicholson [then at Cambridge]; he was extremely kind but I scarcely agree with him about much." [123] This was the man in whose work Bohr, a year later, recognized a severe challenge.

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[118] Much of the following discussion of the effect on Bohr of his encounter with Nicholson is an elaboration of suggestions in Heilbron, *History of Atomic Structure,* 276–278, and McCormmach, "Atomic Theory of... Nicholson," 175–177 (both cited in note 1). Partial support for their analyses is provided by Bohr in Interviews III, 11. Asked if the notion of stationary states had first come to him only after he saw the relevance of the Balmer formula, Bohr replied: "Yes. (There you have it.) But still this is difficult because first of all the work of Nicholson is such (confusion). There I thought perhaps it is that he deals with other states...." (The phrases in parentheses were unclear on the tape.)

[119] J. W. Nicholson, "The Constitution of the Solar Corona. II," *Month. Not. Roy. Astr. Soc., 72* (1912), 677–692; "The Constitution of the Solar Corona. III," *ibid.,* 729–739. They belong to a series of papers, the earliest of which appeared in November 1911. They are, however, the first articles in which Nicholson introduced Planck's quantum in discussions of an atom model and are thus the ones that would particularly have concerned Bohr.

[120] *Nature, 90* (1912), 424. This is the issue for 12 December 1912, and Bohr's first reference to Nicholson is dated 23 December.

[121] Rosenfeld, xxxvi.

[122] Interviews III, 4. Bohr here suggests that his letter of 31 January 1913 was written in the heat of first knowledge of Nicholson, but he had written on the subject to Harald five weeks before.

[123] NB to C. W. Oseen, 1 December 1911 (BSC). Nicholson's paper is "On the Number of Electrons concerned in Metallic Conduction," *Phil. Mag., 22* (1911), 245–266. Though Rutherford

To discover the nature of the challenge, consider briefly what Nicholson had done.[124] Using mechanical techniques like Bohr's, he had derived the energy of a ring of n electrons rotating about a nucleus of charge ke, and he had written the result in terms of the two related parameters, ring radius and frequency, a and ν. (Nicholson considered the potential energy "of aetherial strain," not total energy, so that his formula must be divided by 2 for comparison with Bohr's.) Then, with $n = k = 5$, corresponding to "neutral protofluorine," a hypothetical element present in hot coronal gases, he had chosen the orbital frequency ν so that the transverse vibration frequencies of the disturbed electrons about their equilibrium orbit would correspond to the maximum number of observed coronal lines. The determination of frequency also fixes, via the balance of centrifugal and centripetal force, the ring radius, and Nicholson could therefore compute the ratio of energy to frequency. He thus obtained,

$$mna^2(2\pi\nu)^2 \cdot 1/\nu = 154.94 \cdot 10^{-27},$$

a value which he pointed out was very nearly $25h$. The difference, he said, could easily be accounted for by uncertainties in the values of e and e/m. Performing similar computations for the singly and doubly charged ions of protofluorine gave, for the ratio of energy to frequency, $22h$ and $18h$, respectively. "These [multipliers of h]," Nicholson stated, "are the first three members of the harmonic sequence 25, 22, 18, 13, 7, 0, which would, if it continued valid, give no units to the positive nucleus alone, as would be expected."

These manipulations might have been dismissed as mere numerology if they had not resulted in impressive agreement with experiment. But they did. Nicholson's protofluorine atom accounted for fourteen previously observed but unidentified lines of the solar corona with an accuracy generally better than 4 parts in 1000. His nebulium atom, with nuclear charge $4e$, accounted for ten previously unexplained lines in nebular spectra, and his computations led, with an accuracy of one part in 10,000, to the discovery of a previously un-

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regarded Nicholson as a promising young man, he agreed with Bohr that Nicholson could produce nonsense: "I do not know if you read Nicholson's paper and the awful hash he made of the α ray problem. I never saw so many howlers in two pages of a scientific article." Rutherford to W. H. Bragg, 23 Dec 1912 (Rutherford Correspondence, Cambridge University Library). We are indebted to Paul Forman for a copy of this letter.

[124] Cf., "Solar Corona II," *op. cit.* (note 119), 678–680, for the information cited and quoted in this paragraph.

noticed line.[125] It is no wonder that Bohr and other physicists were greatly impressed.[126]

Bohr was also troubled. His important letter of 31 January to Rutherford is primarily devoted to Nicholson's theory. "Nicholson deals, as I," he wrote, "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." Nicholson did not, it is true, categorically identify any of his ring structures with terrestrial elements. But the four elementary ones, by compounding which Nicholson thought he could construct the periodic table, had atomic weights of the same order as hydrogen; one of them either was hydrogen or was closely related to it.[127] It was therefore disconcerting that the radii, frequencies, and energies which Nicholson computed for his rings were very different from those Bohr had found. Presumably that is what Bohr had in mind when he reported to Rutherford that Nicholson's theory "gives apparently results which are in striking disagreement with those I have obtained; and I therefore thought at first that the one or the other necessarily was altogether wrong." Unfortunately, no clearcut criterion of choice was available. Bohr's theory had greater scope,[128] and it fit better with Rutherford's scattering theory, but Nicholson had produced spectroscopic evidence of unprecedented precision. There was real cause for concern.

Bohr's concern was productive and short-lived. Though his confrontation with Nicholson did not at once lead him to embrace spectroscopic problems as his own, it did produce an important change in his understanding both of his model and of its physical basis. During December and January 1912–1913, his atom acquired excited states, and the relation between Bohr's theory and Planck's became temporarily clearer.

The first explicit sign of the change is found in a Christmas greet-

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[125] Cf., J. W. Nicholson, "On the New Nebular Line at $\lambda 4353$," *Month. Not. Roy. Astr. Soc.*, *72* (1912), 693, and McCormmach, "Atomic Theory of . . . Nicholson," 167–169.

[126] McCormmach, *op. cit.*, 183–184.

[127] *Ibid.*, 165–166, and Nicholson, "Solar Corona II," 682.

[128] But cf., J. W. Nicholson, "A Structural Theory of the Chemical Elements," *Phil. Mag.*, *22* (1911), 864–889, appearing in a journal that Bohr read. Furthermore, this article might well have interested him, for its aims were not unlike his own. Very likely he noticed the article when it appeared, but dismissed it in the light of his previous experience with Nicholson.

ing from the Bohrs to Harald,[129] and its nature is greatly elaborated in the letter of 31 January to Rutherford. Describing his progress, Bohr there wrote:

> I am now much more clear of the foundation of my considerations, and I think that I also now better understand the relation and the difference between my calculations and, for instance, such calculations as those published in recent papers of Nicholson of [about] the spectra of stellar nebulae and the solar corona. . . .
>
> [Nicholson's theory closely resembles mine, yet our results appear at first to be irreconcilable.] The state of the systems considered in my calculation are however—between states in conformity with the relation in question [a prescribed ratio of energy to frequency]—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 system 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, [on the] contrary, of a less stable character; they are states passed during the formation of the atoms, and are the states in which the energy corresponding to the lines in the spectrum characteristic for the element in question is radiated out. From this point of view systems of a state [such] as that considered by Nicholson are only present in sensible amount in places in which atoms are continually broken up and formed again; *i.e.,* in places such as excited vacuum tubes or stellar nebulae.

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[129] Rosenfeld, xxxvi, lv. The remark is contained in a footnote which suggests, both in tone and condensation, that the brothers had already discussed fully both Bohr's concern and its source. The footnote reads, "P.S. Although it does not belong on a Christmas card, one of us would like to say that he thinks Nicholson's theory is not incompatible with his own. In fact his [Bohr's] calculations would be valid for the final, chemical state of the atoms, whereas Nicholson would deal with the atoms' sending out radiation, when the electrons are in the process of losing energy before they have occupied their final positions. The radiation would thus proceed by pulses (which much speaks well for) and Nicholson would be considering the atoms while their energy is still so large that they emit light in the visible spectrum. Later light is emitted in the ultraviolet, until at last all the energy which can be radiated away is lost. . . ." Cf. the following passage from Nicholson's "Solar Corona III," 730: "An atom with only two electrons . . . has a comparatively rapid rate of radiation. If it loses its energy by definite amounts, instead of in a continuous manner, it should show a series of spectrum lines corresponding to each of the stages. Moreover, its incapacity for radiating in a continuous way would secure sharpness of the lines." Russell McCormmach has called our attention to the likelihood that "Solar Corona III" was particularly important for the development of Bohr's intermediate radiation theory.

The central differences between his theory and Nicholson's were, Bohr now felt, essentially resolved. Like Planck's theory, Nicholson's permitted electron systems to possess a variety of different, though simply interrelated, values of the energy-frequency ratio. Derivation of the law of blackbody radiation demanded oscillators having the whole spectrum of energies, $W = \tau h\nu$, with τ any integer. Nicholson's ring systems were governed by an analogous law, but he investigated them only at the high energies and large values of τ to be anticipated among the particles of hot celestial gases. Bohr's interest had been in systems like Nicholson's, but he had considered them only in their lowest energy, or permanent, states. If his model were endowed with a whole series of levels, $E = \tau K\nu$, or, more generally $W = f(\tau)K\nu$, with f some function to be discovered, its permitted states should include those dealt with by Nicholson. No wonder that Bohr, having noted this deeper analogy with Planck's oscillators, felt that he was "now much clearer of the foundation" of his considerations.

The step to excited states and to a fuller use of Planck's conception of the quantized oscillator moved Bohr close to the final version of his atom.[130] The debt to Nicholson revealed in the preceding letter to Rutherford is quite sufficient to justify Jeans's remark in 1914 that,

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[130] Bohr's study of Nicholson may also have been fruitful in two other ways. First, it may well be from Nicholson that Bohr first learned of the difference in stability between vibrations parallel and perpendicular to the plane of the orbit, a difference of which Bohr made significant use in the published paper (cf., Section VI, *infra*). Second, Bohr could have noticed that a quantitative parallel to Nicholson's theory would emerge if his constant K were set equal to $h/2$, a step which would have facilitated his recognition of the quantitative match between his equation (11) for the energy and the Balmer formula.

Besides the harmonic sequence quoted above Nicholson provides a series for the absolute potential energy per electron. The equivalent series for kinetic energy is 2½, 2¾, 3, 3¼, 3½, so that the energy of each permissible state differs from its predecessor by $h\nu/4$. For Nicholson, of course, each term in the series had reference to a differently ionized atom of protofluorine; the series does not yield successive energy levels of a neutral Bohr atom. Nevertheless, Nicholson had found something for which Bohr was looking, a simple numerical factor relating electron energy in a ring atom to that in one of Planck's linear oscillators. If Bohr's theory were to parallel both Planck's and Nicholson's, then his K should be some simple function of $h/4$, the Nicholson quantum unit.

Empirically Bohr's K was already very nearly two such units. In the Rutherford Memorandum it had been $0.6h$, and an equally accessible empirical source (the resonance frequency of He, also cited by Bohr in the absorption paper) would have made it $0.4h$, a fact Bohr is likely to have noted. An exploration of the quantitative fit between Bohr's theory and Nicholson's could therefore have made the equation $K = h/2$ seem very attractive. Bohr does not in fact seem to have made a final decision about the value of K at this time. Had he done so, he would presumably have specified ½ rather than "a numerical factor" in the letter of 7 February 1913 to Hevesy (cf., note 99, *supra*). But no decision is required. The preceding exercise, if Bohr had put himself through it, would have further eased the assimilation of the Balmer formula.

whatever the ultimate fate of Nicholson's theory, "it has probably already succeeded in paving the way for the ultimate explanation of the phenomenon of the line spectrum." [131] But, as the letter to Rutherford also indicates, the largest and most radical steps to the Bohr atom were still to come. At the end of January 1913 Bohr still envisaged a radiation mechanism that was in two respects quasi-classical. First, spectral radiation must be preceded by ionization: atoms must be "broken up" before they can begin to radiate; spectral lines are produced "during the [re]formation of the atoms." Second, each optical frequency radiated corresponds to a mechanical resonance frequency of the atom or ion. Though the radiation is emitted in pulses, after (or during) which the electron ring settles into a lower energy state, the frequencies of the emitted lines are the transverse vibration frequencies of the perturbed electrons in one or another of the permitted excited states. By a mechanism which Bohr never had occasion to work out fully, an electron falling into its final orbit in the previously ionized atom causes the electrons in the high energy orbits to vibrate at their resonance frequencies, acting rather like a finger drawn across the strings of a harp.

That a spectral line of a given frequency must be produced by a charge vibrating at the same frequency was a consequence of electromagnetic theory which even Planck and Einstein had not thought to challenge. Though the nature of the atomic vibrators remained obscure, no contemporary would seriously have doubted their existence. Far more controversial was the correlation of ionization with spectral emission, but, as a natural product of research with gas discharge tubes, it too was widely held at this time. Spectra were emitted only under circumstances which, like high temperature or electric discharge, did produce ionization. The very multiplicity of lines in even the simplest spectra seemed to demand the existence of a larger number of vibrating systems than could be present in any normal atom, whatever its structure.[132] Johannes Stark, to whose influential *Prinzipien der Atomdynamik*[133] Bohr later turned to learn about spectral regulari-

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[131] J. H. Jeans, *Report on Radiation and the Quantum Theory* (London, 1914), 50; quoted by McCormmach, "Atomic Theory of... Nicholson," 184.

[132] For a contemporary review of the considerable literature on this subject, one which Bohr may well have known, see, F. Horton, "On the Origin of Spectra," *Phil. Mag.*, 22 (1911), 214–219. For a fuller and more historical sketch see, Heilbron, *History of... Atomic Structure, op. cit.* (note 1), 176–185.

[133] J. Stark, *Prinzipien der Atomdynamik*, 3 vols. (Leipzig, 1910–1915).

ties, had argued forcefully for the association of ionization with spectra since 1902; Thomson lent his authority to that view in 1907 and developed additional arguments in its favor from that date to 1912.[134] Bohr had probably assimilated a similar position long before he applied it to his own and Nicholson's model. It was, in any case, deeply enough implanted so that he retained and used it for a time after he had recognized the relevance of the Balmer formula and revised his model to suit. Part I of the trilogy employs two different models for spectral emission: one is the now familiar process of transitions between stationary states; the other is the ionization and recombination process discussed above. The latter was, of course, incompatible with Bohr's principal innovations in Part I, and it was eliminated from all his subsequent discussions of the atom. Nevertheless, it is more than a mere out-of-date residue, overlooked as a result of hasty composition. On the contrary, it underlies Bohr's first published derivation of the Balmer formula.

Before Bohr could undertake to derive the Balmer formula, however, he had to "discover" its existence.[135] That must have occurred shortly after he wrote Hevesy on 7 February, or the manuscript which resulted could not have been sent to Rutherford so soon. Because of his concern with Nicholson, Bohr became interested in optical spectra for the first time during the early weeks of 1913.[136] On such topics H. M. Hansen, recently returned from Göttingen, was the local expert, and Bohr may well have sought him out for a reaction to his recent thoughts on radiation. In any case, it was Hansen who told him that

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[134] For Stark's views, see, *ibid.* 2 (1911), 131–144. For Thomson's early statement, see, *Corpuscular Theory of Matter,* 156–160; and for an important later statement in an article Bohr used and cited, see the section on "Radiation Produced by the Recombination of Ions," 454–462, in the paper cited in note 78, *supra.*

[135] We use the word "discover" because Bohr himself repeatedly said that he had not known the Balmer formula until led to it by Hansen early in 1913 (Interviews I, 8; III, 11; Rosenfeld, xxxix–xl). But that account is unlikely to be quite right. Certainly Bohr did not take note of the Balmer formula until early in 1913; very probably he then had to look it up and did so because of Hansen's intervention. But he is likely to have seen the formula more than once before, failing to register it through disinterest. Bohr was a broadly educated physicist, and the formula was not obscure. Moreover, Bohr's teacher at Copenhagen, Christiansen, was a particular admirer of Rydberg's and had made a thorough study of his work (cf., Sister St. John Nepomucene, "Rydberg: the Man and the Constant," *Chymia, 6* (1960), 127–145, an article of which the relevance was kindly called to our attention by Professor Rosenfeld). Among other places where Bohr could easily have seen the Balmer formula, a particularly likely one is the report in *Nature* (note 120 *supra*) which may also have introduced him to Nicholson's work.

[136] Nicholson develops a formula for series spectra in "Solar Corona III." Though it was not a formula of the Rydberg type, it may well have increased Bohr's interest in the topic.

many spectroscopic lines fell into strikingly simple series, and Bohr went to look up the formulas in Stark's book. Later he said repeatedly, "As soon as I saw Balmer's formula, the whole thing was immediately clear to me."[137]

To a gifted mind like Bohr's, given also its special preparation, the Balmer formula could well have been the source of such insight. Stark gives the Balmer formula in the form $\bar{\nu} = N_0/4 - N_0/m^2$, in which $\bar{\nu}$ is the reciprocal wavelength and N_0 is a universal constant, 109675 cm^{-1}.[138] For comparison with his own formula (13) for frequency, Bohr would have multiplied N_0 by the speed of light, $3 \cdot 10^{10}$ cm/sec. The Balmer formula would then read $\nu = 3.29025 \cdot 10^{15} (1/4 - 1/m^2)$, with ν the frequency in cycles per second. In this formula the running index m, which may take any integral value greater than 2, should be related to and might be identical with the index τ which selects higher states in Bohr's radiative version of his atom. Unfortunately, τK, or $f(\tau)K$, appears cubed in the denominator of the radiative version of equation (13), and the Balmer formula calls for a square. It does, however, appear as a square in the energy formula (11), and by 1913, it was very nearly a matter of course for someone concerned with the quantum to divide an energy by h and look for the frequency that results.[139]

If Bohr's thoughts had developed in this way, everything at once would have become truly clear. Set $X = 1$ for the case of atomic hydrogen; substitute $\tau h/2$ for $f(\tau)K$ in the post-Nicholson version of equation (11), a step for which Bohr was by now well prepared; and divide once more by h to convert energy to a frequency. The result is the running term of the Balmer formula in the form $2\pi^2 me^4/h^3\tau^2$. Inserting Bohr's usual values for e and e/m, and the value $6.5 \cdot 10^{-27}$ erg-sec for h (the value Bohr uses in Part I), the constant in the Balmer formula works out to $3.1 \cdot 10^{15}$, within 7 percent of the spectroscopic value, an

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[137] Rosenfeld, xxxix; and cf., Interviews III, 11.

[138] Stark, *op. cit.* (note 133), 2, 44–45. The formula was often written in terms of wavelength rather than wave number; in that form, which Stark also gives, its relevance to Bohr's atom is less apparent.

[139] Cf., *supra.* 244, n.85. One more example is worth recording, because it occurred at this time and was ultimately important to the development of the Bohr atom. Early in 1914 Franck and Hertz announced that they had divided what they took to be the ionization energy of mercury by h and then found the corresponding line emanating from their ionization apparatus. ("Über die Erregung der Quecksilberresonanzlinie 253.6 $\mu\mu$ durch Elektronenstösse," *Verh. deutsch. phys. Ges.* [1914], 512–517.)

extraordinarily close agreement in view of the state of the constants.[140] The first term of Balmer's formula is simply the running term with $\tau = 2$. The frequencies of the lines in the Balmer series are therefore the differences between the energies in two stationary states divided by Planck's constant. In view of the Combination Principle, the same must, as Bohr says in Part I, be true of series spectra in general. Optical and mechanical frequencies have at last been divorced, perhaps the greatest and most original of Bohr's breaks with existing tradition.

V. BOHR'S ATOM AND THE QUANTUM THEORY: FEBRUARY TO DECEMBER 1913

What Bohr had seen, shortly after 7 February 1913, was a relationship between his one-electron hydrogen model and the Balmer formula. If the latter were multiplied by h and the resulting terms interpreted as energy levels, then his post-Nicholson model, with $\tau h/2$ written for $f(\tau)K$, would yield those levels precisely. That relationship was, however, altogether *ad hoc* with respect to the determination both of energy levels and of radiated frequency. Neither the atomic, nor the spectral, nor the quantum theory of the day could justify the necessary interpretations and substitutions. Though the central step to a radiative atom model had already been taken, Bohr had still to forge a quantum theory of atom mechanics and of radiation which would permit something like a derivation of the Balmer formula. Without such a reformulation his treatment of spectra would inevitably appear—as it did, in any case, to many readers—merely an ingenious play with numbers and formulas. In the event, reformulating quantum theory to keep pace with a developing understanding of atomic spectra occupied many scientists throughout the years from 1913 to 1926. But a remarkable number of the conceptually fundamental steps were inaugurated by Bohr during 1913, mostly in February of that year. We possess, unfortunately, little explicit information about how they were made. The published papers and two letters to Rutherford provide

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[140] Bohr demonstrates an even closer agreement in Part II, 487/39n. (Because references to the published paper will henceforth be frequent, we adopt an abridged notation for use in both footnotes and text. In "487/39n" the first number refers to the original publication in *Phil. Mag.*, *26* [1913], and the second to the reprint in Rosenfeld, *op. cit.* [note 1]. When citing Part I, only a single number is given since the pagination of the two sources is identical.) He there adopts Millikan's value for e and a recent value for e/h obtained by Warburg and his collaborators. With these constants the theoretical value of the Rydberg becomes $3.26 \cdot 10^{15}$ sec^{-1}, within one percent of the experimental value.

the only clues to the development of Bohr's thought after the first week in February.

In its essentials the draft sent to Rutherford on 6 March must have closely resembled the paper published in July, but there were a few changes. Fifteen days after mailing the first manuscript, Bohr wrote Rutherford again, enclosing a second copy in which he had "found it necessary to introduce some small alterations and additions."[141] Bohr mentions what are likely to have been the only significant changes. Both are additions: all or most of Section 4, "Absorption of Radiation," and a few paragraphs in Section 5 intended to reconcile his results with Nicholson's. Shortly after mailing that letter, Bohr travelled to Manchester to persuade Rutherford that his manuscript could not be reduced in length without grievous loss.[142] Probably further revisions were introduced during their discussions, but, given the nature of Rutherford's concerns, they are not likely to have been more than verbal. The same is true of the alterations Bohr mentions in a letter of 10 May, accompanying the return of corrected proof to Rutherford: "I have altered very little in it, and not introduced anything new. I have, however, attempted to give the main hypothesis a form which appears to be in the same time more correct and more clear."[143] Excepting the additions on absorption and on Nicholson's theory, the paper published in July was probably close in all but phraseology to the draft sent Rutherford on 6 March. The point is worth emphasizing, for the speed with which the draft was prepared may help to account for some revealing oddities in the published version.

As published, Part I contains two incompatible derivations of the energy levels in the Balmer formula, and a third is given in a talk Bohr delivered to the Danish Physical Society on 20 December 1913.[144] Examined *seriatim* the three display a fascinating developmental pattern which is at least partly autobiographical. A strong analogy between Bohr's atom and Planck's oscillator is basic to the first, muted in the second, and absent (in fact, explicitly rejected) from the third. The first depends, in addition, on the radiation-through-recombination

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[141] NB to Rutherford, 21 March 1913 (BSC).

[142] Rosenfeld and Rüdinger, *op. cit.* (note 1), 54.

[143] BSC. The revision which Bohr introduced to clarify his hypothesis probably occurs on p. 7 of the published paper.

[144] An English translation of this lecture is the first essay in Bohr's *Theory of Spectra and Atomic Constitution* (Cambridge, Eng., 1922), 1–19. It had previously appeared in *Fysisk Tidsskrift, 12* (1914), 97–114. Our future references to this lecture are to the English text, but we have compared the relevant passages with the Danish original.

model which Bohr had developed when first reconciling his results with Nicholson's but which his new view of the Balmer formula might already have rendered obsolete. What emerges increasingly in the second and third derivations, gradually usurping the roles played in the first by the analogy to Planck and by the old radiation theory, is another one of Bohr's fundamental contributions to quantum theory. In a somewhat more developed form, it would later be known as the Correspondence Principle.

At the start of the first derivation Bohr restricts attention to a single electron of charge $-e$ and mass m circulating about a nucleus of charge E. If there is no energy radiated, he continues, the electron will describe stationary elliptical orbits of major axis $2a$ with a mechanical frequency ω. (In the one-electron case there is no problem of mechanical instability.) If, furthermore, W is the energy required to remove the electron from its orbit to infinity, then the preceding quantities are related by the equations:

$$\omega = \sqrt{\frac{2}{m}} \cdot \frac{W^{3/2}}{\pi e E}, \quad 2a = \frac{eE}{W}. \tag{14}$$

Maxwell's theory demands, however, that a system of this sort radiate energy and that the electron spiral rapidly into the nucleus. A paradox results, for atoms are known to possess characteristic dimensions many times larger than those of their nuclei. Planck's theory may, Bohr suggests, provide a way to resolve the dilemma:

> Now the essential point of Planck's theory of radiation is that the energy radiation from an atomic system does not take place in the continuous way assumed in the ordinary electrodynamics, but that it, on the contrary, takes place in distinctly separated emissions, the amount of energy radiated out from an atomic vibrator of frequency ν in a single emission being equal to $\tau h\nu$, where τ is an entire number, and h is a universal constant.[145]

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[145] At this point Bohr cites three recent papers by Planck (*Ann. d. Phys.*, *31* [1910], 758–768; *ibid.*, *37* [1912], 642–656; and *Verh. deutsch. phys. Ges.* [1911], 138–148). Hirosige and Nisio (*op. cit.* [note 2]) argue that Planck's revision of the quantum theory in these papers had special importance for the development of Bohr's theory of the atom. Perhaps the second and third (the first is a condensed sketch of Planck's original theory and thus irrelevant) did play a role in Bohr's localization of "the essential point of Planck's theory" in the quantization of emitted energy, and they may also have reinforced his conviction of the association between ionization and radiation. But these ideas were not novel when Planck took them up; Bohr could have found them in many other places. What was novel in the two versions of the quantum theory that Planck developed in 1911 and 1912 was the notion of continuous absorption, and this

> Returning now to the simple case of an electron and a positive nucleus considered above, let us assume that the electron at the beginning of the interaction with the nucleus was at a great distance apart from the nucleus, and had no sensible velocity relative to the latter. Let us further assume that the electron after the interaction has taken place has settled down in a stationary orbit around the nucleus . . . [and] that, during the binding of the electron, a homogeneous radiation is emitted of a frequency ν, equal to half the frequency of revolution of the electron in its final orbit; then, from Planck's theory, we might expect that the amount of energy emitted by the process considered is equal to $\tau h\nu$, where h is Planck's constant and τ an entire number. If we assume that the radiation emitted is homogeneous, the second assumption concerning the frequency of the radiation suggests itself, since the frequency of revolution of the electron at the beginning of the emission is 0 (Part I, 4–5).

These assumptions permit the immediate derivation of the hydrogen energy levels. An electron initially at rest outside the atom can be bound only into an orbit satisfying the condition,

$$W_\tau = \tau h \frac{\omega_\tau}{2}, \tag{15}$$

an equation which, together with (14), yields the energy levels,

$$W_\tau = \frac{2\pi^2 m e^2 E^2}{h^2 \tau^2} = \frac{2\pi^2 m e^4}{h^2 \tau^2}, \tag{16}$$

the right-hand formula being derived from its predecessor by setting $E = e$ for the case of hydrogen, e remaining the absolute value of the electron's charge.

From equation (16) Bohr might have reached the Balmer formula in one easy step, obtaining a frequency by dividing h into the difference between two energy levels, one with $\tau = 2$. The formula which results provides, among other things, a theoretical value for Rydberg's

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Bohr must necessarily have rejected. In both of Planck's revised theories vibrators could possess all classically permitted energies (quantization was restricted to the emission process), a conception incompatible with Bohr's use of the quantum to select and stabilize particular stationary states. We therefore believe that Bohr cited these papers primarily because they were up to date and that he is unlikely to have drawn anything from them he could not have taken as well, or even better, from Planck's original formulation or from other parts of the contemporary literature. When Nicholson introduced a quantum condition very like Bohr's, he did cite one of Planck's *original* papers, actually a more appropriate choice ("Solar Corona II," *op. cit.* [note 119], 677).

constant impressively within 7 percent of the one determined spectroscopically. Bohr, however, could not take this direct route, for it had been barred by his derivation of the quantum condition, equation (15). If the radiation process is one in which a free electron at rest is bound into the τ-th energy level of a bare hydrogen nucleus, emitting in the process τ quanta all of frequency $\omega_\tau/2$, then the atom will not at the same time emit the diverse lines described by the Balmer formula. Before Bohr can derive the latter, he must change his account of the mechanism of radiation. We shall shortly examine the way in which he does so, but must first detour to ask how he happened to place himself in this potentially uncomfortable position. Why, that is, did Bohr initially derive the hydrogen energy levels from a radiation mechanism incompatible with the application of his model to Balmer's formula? Part of the answer has already been given: Part I was prepared at white heat. But there were, in addition, two important substantive reasons for retaining the first derivation of the hydrogen levels, whatever difficulties it might later create.

In order to *derive* the Balmer formula, Bohr needed a quantum condition to determine energy levels. The required condition proves to be equation (15), $W_\tau = \tau h\omega_\tau/2$, and this equation gains whatever plausibility it possesses from its resemblance, emphasized by Bohr, to the quantum condition governing Planck's oscillator. Such an oscillator can emit several quanta at a time but only at a single frequency determined by its mechanical structure. Equation (15) must, by analogy, govern a process in which τ quanta are emitted, each of frequency $\omega_\tau/2$. To reach the Balmer formula Bohr will ultimately change this interpretation, saying instead that equation (15) represents the emission of a single quantum with frequency $\tau\omega_\tau/2$. That interpretation, however, at once destroys the analogy between the Bohr and Planck radiators, and some other justification for (15) is therefore required. In fact, Bohr found none. In the later portions of Part I and for some time after its publication, equation (15) ceased to be a quantum condition and became instead a derived formula. In its derivation, the Balmer formula itself became a premise, and it could not therefore be deduced from first principles. One function, then, of this first derivation of energy levels was to provide a quasi-derivation of the Balmer formula, an objective which Bohr was forced to renounce after the transition to a more appropriate radiation mechanism.

Nevertheless, Bohr would, we presume, have abandoned the first derivation if its conflict with the radiation process required to produce the Balmer formula had been as clear to him as it is in retrospect. The published text of Part I, however, demonstrates that he had not seen the full depth of the difficulty when he submitted revised proof in May. On the one hand, his discussion of the Balmer formula, of Rydberg's series, and, above all, of absorption spectra, shows a complete and subtle conceptual command of the process in which a single quantum of homogeneous radiation is emitted or absorbed in conjunction with the transition of an electron between two specified energy levels. On the other hand Bohr refers repeatedly to "the assumption used in this paper that the emission of line-spectra is due to the re-formation of atoms after one or more of the lightly bound electrons are removed" (Part I, 18). In deriving the Rydberg-Ritz formula, for example, he writes: "Let us assume that the spectrum in question corresponds to the radiation emitted during the binding of an electron" (Part I, 12). And in explaining why the Pickering series is not found in gas discharge tubes filled with helium, he states that "the condition for the appearance of the [Pickering] spectrum is . . . that helium atoms are present in a state in which they have lost both electrons" (Part I, 11).[146] Clearly all these passages refer to the process of spectral emission-through-recombination that Bohr had outlined in the letter of 31 January 1913, the result of assimilating Nicholson's theory to his own. When Part I was prepared he had not yet quite seen that he could not retain both that process and a theory of radiation through transitions. That is another reason why Bohr, who needed it to reach the Balmer formula, could retain his first derivation of energy levels. It fitted closely with an older view of the radiation process which he had not yet altogether abandoned.

One last aspect of Bohr's initial quantum condition, equation (15), requires discussion, namely, the source of the factor of ½. Following Rosenfeld, we suggest that, well prepared as Bohr was to find his old K close to $h/2$, his definitive choice of the value was probably determined by the need to match the constant in his theoretical formula to the one deduced from experiment. In that case, his remark that the frequency $\omega_\tau/2$ is an average of the electron's mechanical frequencies, 0 and ω_τ, in its initial and final states, appears an *ad hoc* ration-

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[146] The Pickering series is described by a formula just like Balmer's but with half-integers rather than integers in the denominators of the energy levels. Before Bohr attributed it to ionized helium, it had been observed only in stellar spectra and in gas tubes containing a mixture of hydrogen and helium. Bohr's success in demonstrating that it derived from helium rather than hydrogen was one of the most persuasive early arguments for his theory. (Cf., Rosenfeld and Rüdinger, *op. cit.* [note 1], 59–60.)

alization, designed to preserve the parallelism between Bohr's radiator and Planck's.[147] Probably that was its origin, but it quickly acquired a far greater significance. In Bohr's second and third derivations of the hydrogen energy levels, this passing remark about an average of mechanical frequencies has, we shall soon discover, been transformed to a first, but already powerful, formulation of the Correspondence Principle.

How then does Bohr manage the transition from his first derivation of the hydrogen levels to the apparently incompatible Balmer formula? He interrupts his argument to discuss the work of Nicholson

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[147] Hirosige and Nisio (note 2) argue that Bohr's idea of averaging frequencies was suggested by Planck's averaging of oscillator energies in the later formulations of his theory. But Planck's technique of averaging *actual* oscillator energies is entirely straightforward and can scarcely have been a source of novel insights. Besides, Bohr's argument for frequency would parallel Planck's for energy only if the electron, during binding, had radiated all frequencies between 0 and ω_r. He would then be determining the average of the *actual* frequencies radiated, and the factor of ½ would present no problems. It did present problems to contemporaries, particularly at Göttingen (Interviews I, 5), and no parallel to Planck's modified theory was, to our knowledge, educed in its defense.

A passage in Bohr's lecture to the Danish Physical Society (*op. cit.* [note 144], 13–14) can be read as supplying still another explanation of the factor of ½.

> By introducing the expression, which has been found for R [Rydberg's constant], we get for the nth state $W_n = \frac{1}{2} nh\omega_n$. This equation is entirely analogous to Planck's assumption concerning the energy of a resonator. W in our system is readily shown to be equal to the average value of the kinetic energy of the electron during a single revolution. The energy of a resonator was shown by Planck you may remember to be always equal to $nh\nu$. Further the average value of the kinetic energy of Planck's resonator is equal to its potential energy, so that the average value of the kinetic energy of the resonator, according to Planck, is equal to $\frac{1}{2} nh\omega$. This analogy suggests another manner of presenting the theory, and *it was just in this way that I was originally led into these considerations.* When we consider how differently the equation is employed here and in Planck's theory it appears to me misleading to use this analogy as a foundation, and in the account I have given I have tried to free myself as much as possible from it. (Italics added.)

The italicized clause seems to say that Bohr adopted the factor of ½ in equation (15) because he recognized early in his research that the parallel to Planck should be drawn through kinetic energy rather than total energy and the average kinetic energy of Planck's oscillator was $nh \cdot \nu/2$. It need, however, mean only that Bohr was "originally led into these considerations" by a general analogy to Planck's theory, the particular parallel being incompletely specified.

Strong arguments favor the latter interpretation. First, footnotes 99 and 130 provide evidence that Bohr had not settled on the factor of ½ before 7 February 1913 (or had at least found no theoretical justification for it). Second, if Bohr had developed the preceding derivation of (15) by the spring of 1913, he would surely have mentioned it in Part I, perhaps as an alternate to the less plausible averaging of mechanical frequencies. (He did, in fact, use it in a subsequent recapitulation of his theory: "On the Quantum Theory of Radiation and the Structure of the Atom," *Phil. Mag., 30* [1915], 394–415, esp. 396.) Finally, the argument that the quantization of kinetic rather than total energy requires, at least in the case of a rotating dipole, setting $T = nh\nu/2$ was first published during 1913 by Paul Ehrenfest ("Bemerkung betreffs der spezifischen Wärme zweiatomiger Gase," *Verh. deutsch. phys. Ges.* [1913], 451–457; "A Mechanical Theorem of Boltzmann and its Relation to the Theory of Energy Quanta," *Proc. Amsterdam Acad., 16* [1913], 591–597). Bohr may well have heard of Ehrenfest's argument before the lecture, or at least before its publication. Possibly the paragraph above was intended to record his reasons for ignoring it in discussing the atom.

on which his own has so far been partially dependent.[148] In the discussion he isolates and rejects an implausible assumption that he and Nicholson have to this point shared. The way to a new radiation mechanism and to the Balmer formula is then open to him.

Bohr first briefly describes Nicholson's model, points out that its agreement with observation provides strong arguments in its favor, and then notes that "serious objections . . . may be raised against the theory" (Part I, 6–7). Minor objections include the theory's failure to yield formulas like Balmer's and Rydberg's as well as the problem of mechanical instability to which Bohr promises to return. The central criticism, however, is of a different sort, one "intimately connected with the problem of the homogeneity of the radiation emitted":

> In Nicholson's calculations the frequency of lines in a line-spectrum is identified with the frequency of vibration of a mechanical system in a distinctly indicated state of equilibrium. 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 energy, cannot emit a finite amount of a homogeneous radiation; for, as soon as the emission of radiation is started, the energy and also the frequency of the system are altered (Part I, 7).

In part Bohr is saying that one must, as he already has, abandon the connection between mechanical and radiated frequency. The latter, he immediately points out, is to be computed from Planck's theory, the emitted energy being divided by h. But Bohr seems also to be saying—or else his next step is incomprehensible—that during a nonclassical transition between stationary states only a single quantum may be emitted. The frequencies of successive quanta would otherwise be different, and the radiation would not be homogeneous.

That point Bohr makes explicit only five pages later, at the start of his second derivation of the energy levels, but he has meanwhile used it. Immediately after the preceding critique of Nicholson, he determines the frequency emitted in a transition from state τ_1 to τ_2 by the equation $W_{\tau_2} - W_{\tau_1} = h\nu$. The Balmer formula, including the theoretical value of Rydberg's constant, follows at once. The latter provides strong evidence for Bohr's theory, and he immediately reinforces it by attributing the Pickering series to ionized helium and by

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[148] This discussion of Nicholson is *not* the one that Bohr added to his manuscript after its first submission (*infra*, 281). We shall examine that addition later.

a persuasive argument explaining why the identical multiplicative constant appears in the formulas of all spectral series (Part I, 10–12). Only after this powerful evidence has been educed does Bohr put the foundations of his theory in order with a new derivation of the hydrogen energy levels.

He prefaces his second derivation with a paragraph rejecting the assumption which was fundamental to the first:

> We have assumed that the different stationary states correspond to an emission of a different number of energy-quanta. Considering systems in which the frequency is a function of the energy, this assumption, however, may be regarded as implausible; for as soon as one quantum is sent out the frequency is altered. We shall now see that we can leave [out] the assumption used and still retain . . . [equation (15)] and thereby the formal analogy with Planck's theory (Part I, 12).

The alternative interpretation of (15) makes the energy radiated when an electron is bound from rest consist of a single quantum with frequency $\tau\omega_\tau/2$ rather than of τ quanta with frequency $\omega_\tau/2$. One sees why Bohr now describes the analogy with Planck's theory as "formal."

The derivation itself is very different from its predecessor. Bohr first assumes that the quantum condition determining energy levels must take the form $W_\tau = f(\tau)h\omega_\tau$, with f an unknown function. By a process exactly parallel to that which took him from equation (15) to (16), he finds,

$$W_\tau = \frac{\pi^2 me^4}{2h^2f^2(\tau)} \quad \text{and} \quad \omega_\tau = \frac{\pi^2 me^4}{2h^3f^3(\tau)}. \tag{17}$$

No formula like Balmer's will result, he points out, unless $f(\tau) = c\tau$ with c a constant to be determined.

It is in the determination of c that the Correspondence Principle first emerges clearly in Bohr's work. Setting $f(\tau) = c\tau$, he applies equation (17) to the determination of the optical frequency emitted in a transition between neighboring states, from $\tau = N$ to $\tau = N - 1$. The radiated frequency is,

$$\nu = \frac{\pi^2 me^2E^2}{2c^2h^3}\left\{\frac{1}{(N-1)^2} - \frac{1}{N^2}\right\} = \frac{\pi^2 me^2E^2}{2c^2h^3}\cdot\frac{2N-1}{N^2(N-1)^2}, \tag{18}$$

and the corresponding mechanical frequencies are,

$$\omega_N = \frac{\pi^2 me^2E^2}{2c^3h^3N^3} \quad \text{and} \quad \omega_{N-1} = \frac{\pi^2 me^2E^2}{2c^3h^3(N-1)^3}.$$

"If N is great," Bohr continues, "the ratio between the frequency before and after the emission will be very nearly 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. This condition will only be satisfied if $c = ½$" (Part I, 13). Thus, equation (15), the Balmer levels, and the Balmer formula are produced again.

Bohr also notes briefly a further, and historically even more pregnant, parallel between classical electrodynamics and the emerging quantum theory. If one considers a transition between states N and $N - n$, with n small compared to N, one again finds $c = ½$ provided that $\nu = n\omega_N$. (The second factor on the right side of equation [18] becomes in this case $[2nN - n^2]/N^2[N - n]^2$.) This occurrence of an n-th harmonic of the orbital frequency ω_N provides Bohr with a further analogy between classical and quantum results. He points out that "with the ordinary electro-dynamics . . . an electron rotating round a nucleus in an elliptical orbit will emit radiation which according to Fourier's theorem can be resolved in homogeneous components, the frequencies of which are $n\omega$, if ω is the frequency of revolution of the electron" (Part I, 14). That is the interpretation which Bohr would later invert to arrive at his consequential selection rules: an atom will emit all and only those frequencies which correspond to Fourier components of its permissible classical orbits.

However fragmentary their initial formulations, these insights were of decisive importance for the subsequent development of the old quantum theory.[149] From Bohr's first paper on "Atoms and Molecules" through Heisenberg's first publication on matrix mechanics, many of the considerable triumphs of the quantum were associated with the discovery of new and more precise ways of employing classical mechanics and electrodynamics to determine the appropriate quantum formulation of special problems. More than any particular correspondences, that program of exploring ways of relating classical and quantum computations was the core of the Correspondence Principle. As it appears in Part I of Bohr's trilogy, the Principle is in embryo,

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[149] For a perceptive study of the development of Bohr's conception of the Correspondence Principle, see K. M. Meyer-Abich, *Korrespondenz, Individualität, und Komplementarität,* Boethius, Texte und Abhandlungen zur Geschichte der Exakten Wissenschaften (Wiesbaden, 1965). In an appendix Meyer-Abich also provides a useful schematic sketch of the structure of what we have here called Bohr's three derivations of the hydrogen energy levels. His monograph is, however, mainly concerned to discover what Bohr took Correspondence to be. A comprehensive account of the role of the Correspondence Principle in the technical development of the old quantum theory remains to be written.

and its parentage is still clear. Planck's blackbody-radiation formula was known to reduce to the classical Rayleigh-Jeans law in the low-frequency limit, and Bohr anticipates that radiation from his atom will approach the classical limit in the same way. But Bohr, unlike Planck, employs the classical result to determine the appropriate quantum mechanical treatment of his atom. Besides, as Bohr develops the limiting case, it is apparent that classical and quantum computations coincide only in their results: *the models and the mechanisms of radiation remain distinct.* Planck's oscillator, in contrast, could with relative ease be viewed as itself behaving classically in the low frequency limit. Both as a heuristic tool and as a mark of the chasm separating classical from quantum physics, the Correspondence Principle thus transcended the limiting principle that had emerged when h was allowed to approach zero in the blackbody distribution law. Used with imagination and skill, as it was by Bohr and his Copenhagen colleagues during the years before 1926, it proved consequential in ways that its parent principle was not.

Shortly before Christmas, 1913, Bohr presented a revised version of this second derivation in a lecture to the Danish Physical Society. By that time radiation had for him become entirely a transition process, and he no longer referred at all to radiation during the binding of an electron initially at rest. As a result, his third derivation of 1913 caps the line of development inaugurated by its predecessors. In Bohr's lecture, the essence of Planck's contribution is reduced to the fundamental assumption,

$$h\nu = W_1 - W_2, \tag{19}$$

and he emphasizes that "it is possible to derive Planck's law of radiation from this assumption alone," without reference to a Planck resonator or to any mechanical frequency of oscillation.[150] A comparison of (19) with the Balmer formula yields $W = Rh/\tau^2$ for the permitted energy levels of the hydrogen atom, where R is the Rydberg constant (more accurately, the usual Rydberg constant divided by the velocity of light, since spectral formulas are generally written for wave number rather than, as here, for frequency). By reference to (14) the mechanical frequencies of the orbital electrons are found to be,

$$\omega_\tau{}^2 = \frac{2R^3h^3}{\pi^2 me^4\tau^6}. \tag{20}$$

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[150] *Op. cit.* (note 144), 11.

Bohr now compares that mechanical frequency with the frequency ν radiated in a transition from the state τ to the state $\tau - 1$. For large values of τ,

$$\nu = R\left\{\frac{1}{(\tau - 1)^2} - \frac{1}{\tau^2}\right\} = \frac{2R}{\tau^3}. \tag{21}$$

The Correspondence Principle demands that the mechanical frequency (20) and the radiated frequency (21) be equal for large τ, a condition which will be fulfilled only if,

$$R = \frac{2\pi^2 me^4}{h^3}.$$

Once again Bohr has derived a theoretical value for the constant in the Balmer formula.

That, however, is all that Bohr now derives. The very clarity of his third derivation highlights an element that has been gradually lost with the rejection of the detailed analogy to a Planck oscillator. That analogy provided the first derivation with an explicit quantum condition, $W_\tau = \tau h\omega_\tau/2$, and that condition permitted a derivation, if an imperfect one, of the Balmer formula as well as of the Rydberg constant. In the second derivation a looser analogy to Planck permitted only the more general quantum condition, $W_\tau = f(\tau)h\omega_\tau$; reference to the Balmer formula was required to determine the form of $f(\tau)$; and the formula itself was only in part derived. By the time of the third derivation Bohr was convinced that it was "misleading to use this analogy [to the Planck oscillator] as a foundation,"[151] and he had therefore to proceed without any quantum condition at all. He took the Balmer formula, interpreted from the start as a statement about energy levels, as his point of departure, and could deduce only the value of the multiplicative constant, the Rydberg coefficient. Before the Balmer formula could be derived again, Bohr would need a new quantum condition or at least a new justification for the old one.

Not until 1915 was a satisfactory new formulation developed, and then it was not Bohr who supplied it. He had, however, already reinterpreted his own initial quantum condition in ways that provided two sorts of significant guidance to his successors. In both Bohr's first and second derivations of the hydrogen energy levels, the quantity W_τ, when it appeared in a quantum condition like (15), stood for the

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[151] *Ibid.*, 14.

"amount of energy emitted" during the binding of an electron into the τ-th stationary state (Part I, 5, 12–13). W_τ was also, of course, the negative of the energy of the electron in that state, but the quantum condition was, in the first instance, a condition on emitted energy rather than on the mechanical variables determining the τ-th orbit. Bohr, however, was necessarily aware of the possibility of the latter interpretation, which in any case was not new. A quantum limitation on the values of mechanical variables was the condition he had sought in order to resolve the problem of magnetism, and he had used just such a condition in developing his atom model until February 1913, the time at which the radiation of line spectra first came to concern him. In Part I of the trilogy, though he first developed a condition on emitted radiation, he made explicit the possibility of an alternate mechanical interpretation, and he put the point in an especially consequential way, one that he noted had also been developed by Nicholson:[152]

> While there obviously can be no question of a mechanical foundation of the calculations given in this paper, it is, however, possible to give a very simple interpretation of the result of the calculation [of stationary states] by help of symbols taken from the ordinary mechanics. Denoting the angular momentum of the electron round the nucleus by M, we have immediately for a circular orbit $\pi M = T/\omega$, where ω is the frequency of revolution and T the kinetic energy of the electron; for a circular orbit $T = W$ . . . and from [15] we consequently get
>
> $$M = \tau M_0$$
>
> where
>
> $$M_0 = \frac{h}{2\pi} = 1.04 \times 10^{-27}.$$
>
> If we therefore assume that the orbit of the electron in the stationary state is circular, the result of the calculation can be expressed by the simple condition: that 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 (Part I, 15).

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[152] Like Bohr, Nicholson had initially set the ratio of energy to frequency equal to a multiple of Planck's constant ("Solar Corona," *op. cit.* [note 119], 679). He immediately noted, however, that that ratio was proportional to angular momentum and that the introduction of the quantum might therefore "mean that the angular momentum of an atom can only rise or fall by discrete amounts when electrons leave or return. It is readily seen that this view presents less difficulty to the mind than the more usual interpretation, which is believed to involve an atomic constitution of energy itself."

From the time this passage was written, Bohr consistently deployed quantum conditions that restricted mechanical variables rather than emitted energy. At the end of Part I of the trilogy, for example, he announced the hypothesis which he would use when treating multi-electron systems in Parts II and III (Part I, 24–25; both the quotation marks and italics are Bohr's):

> *"In any molecular system consisting of positive nuclei and electrons in which the nuclei are at rest relative to each other and the electrons move in circular orbits, the angular momentum of every electron round the center of its orbit will in the pemanent state of the system be equal to $h/2\pi$, where h is Planck's constant."*

That condition on the mechanical variable, angular momentum, was, Bohr thought, applicable only to atoms in their permanent state. (His derivation of the angular momentum condition from [15] was restricted to circular orbits in which the electrons' kinetic energy is constant. In excited states, where orbits might be elliptical [Part I, 21–22], no angular-momentum formulation could be assumed to apply.[153]) When dealing with radiation problems, Bohr therefore continued to employ the more general quantum condition (15), but after Part I of the trilogy he consistently read it as a restriction on the values of mechanical variables. In his lecture to the Physical Society late in 1913 W is always the energy of an orbital electron, never an emitted energy. The analogy to Planck (which Bohr mentions to illustrate his point but then rejects as not fundamental) is to the mechanical energy possessed by an oscillator, not to the energy it emits.[154] The same approach is used in Bohr's subsequent publications on radiation problems up to the development of the phase-integral quantum conditions in 1915.[155]

Those new quantum conditions, which proved vital to the further development of the old quantum theory, were like Bohr's in two important respects. They limited, not emitted energy, but the permitted values of mechanical variables. More significant, they were momentum conditions, a generalization of the form that Bohr had developed for the circular orbits of the permament state. Clearly their emergence in

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[153] For elliptical orbits, of course, the average value of kinetic energy equals W, and the angular momentum can be equated to the ratio of average energy to frequency. But there is a considerable conceptual difference between quantizing a constant of the motion, as Planck had done, and quantizing the average value of a variable.

[154] Cf., note 147, *supra.*

[155] Cf., N. Bohr, "On the Effect of Electric and Magnetic Fields on Spectral Lines," *Phil. Mag.*, *27* (1914), 506–524; "On the Quantum Theory of Radiation and the Structure of the Atom," *ibid.*, *30* (1915), 394–415.

1915 depended in major ways on the work Bohr had published two years before. The men who developed the phase-integral conditions were all quite consciously seeking a quantum formulation that could cover the two quite different problems—one-dimensional linear oscillator and two-dimensional planetary system—to which the quantum had previously been applied so successfully.[156] All of them, that is, forged their conditions in an attempt to reconcile Planck and Bohr, discovering and making explicit what the two had in common. Sommerfeld, who prepared the most influential version of the phase-integral conditions, actually credited Bohr with having quantized angular momentum in his derivation of the Balmer formula, a historical slip which is nonetheless revealing of Bohr's role in the evolution of the new mode of quantization.[157]

Bohr's reinterpretation of his quantum condition was also implicated in another aspect of the development of the old quantum theory, the treatment of dispersion. When he dealt with rings containing more than a single electron, Bohr had, for the first time in print, to confront the problem of mechanical instability. His solution was, in its essentials, the same quantum fiat offered in the Rutherford Memorandum: "The stability of a ring of electrons rotating round a nucleus is [in the atom's permament state] secured through the above condition of the constancy of the angular momentum" (Part I, 23). In discussing this version of the stability condition, however, Bohr made explicit a feature of classical orbital mechanics of which he had been unaware at the time the Rutherford Memorandum was written. Citing Nicholson's calculations, Bohr pointed out that it is only for displacements in the plane of the ring that the atom is incurably unstable. Electrons displaced perpendicular to the orbital plane will, unless the ring is already overloaded, vibrate parallel to the atomic axis until their vibrational energy is dissipated through radiation.[158]

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[156] The complex history of the evolution of generally applicable quantum conditions demands separate treatment, which one of us (T. S. K.) is undertaking. The generalizations above are based on the work of Sommerfeld, Wilson, and Ishiwara, who are generally commonly credited with independent inventions of the phase-integral conditions during 1915 (cf., Max Jammer, *The Conceptual Development of Quantum Mechanics* [New York, 1966], 91–93). A fuller account of the sources of these new conditions would also emphasize the role of Planck's phase-space reformulation of quantum statistics, e.g., at the Solvay Congress in 1911 (cf., note 85, *supra*).

[157] A. Sommerfeld, "Zur Theorie der Balmerschen Serie," *Sitzungsb. Bayer. Akad. zu München*, 1915, 425–458, esp. 428, 431. That Bohr derived the Balmer formula by quantizing angular momentum is now a recurrent myth. On the functions of such myths, cf., Thomas S. Kuhn, *The Structure of Scientific Revolutions* (Chicago, 1962), 138–139.

[158] Bohr probably learned this important distinction between parallel and perpendicular displacements from Nicholson, whom he mentions when he first introduces it. There are many other

The orbital plane is also, however, the locus of the electron displacements or transitions which permit atoms to form themselves by electron capture. Those phenomena are just the ones which could not, Bohr had found, be treated classically. It was they which demanded the introduction of a quantum condition. That condition, viewed as a restriction on mechanical variables, need apply, however, only to displacements parallel to the orbital plane. Displacements perpendicular to the orbit, since they presented none of the quantum paradoxes, could remain the preserve of classical theory. For Bohr that distinction between the two types of displacement was the clue to an explanation of the striking success of Nicholson's theory. In a passage presumably added to Part I in the new draft mailed to Rutherford on 21 March, he suggested that Nicholson had not been dealing with a case of genuine emission but rather with scattering of the sun's light by the widely spaced atoms in the solar corona. Electrons vibrating perpendicular to the plane of their ring would at once emit the energy they absorbed, and there need be no change in the ring's size or mechanical frequency. Unlike spectral emission, dispersion need not be a quantum phenomenon (Part I, 23–24; cf., Part II, 482/34).

Except for the restriction to perpendicular vibrations, that explanation of dispersion is the same one Bohr had used in the Rutherford Memorandum when relating orbital frequency to the measured frequencies of anomalous dispersion. In Parts II and III of the trilogy he used it again to compute theoretical dispersion frequencies for comparison with experiment, and his procedure was soon taken up by other physicists.[159] Not until a few years later did Bohr or anyone else recognize that a classical treatment of dispersion could not possibly be right. On such a treatment the frequencies of anomalous dispersion must necessarily occur at the mechanical resonance frequencies of the electrons in the rings. Experimentally, however, they were found at the same frequencies as lines in the emission spectrum, and the latter, Bohr had just shown, occurred at frequencies different from those dic-

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places he could have learned it (cf., note 82, *supra*) but he mentions none of them when discussing stability problems. He could also have worked it out for himself, but he had certainly not done so by August 1912 and probably not by the following November (cf., note 161 *infra*).

[159] P. Debye, "Die Konstitution des Wasserstoff-Moleküls," *Sitzungsb. d. Bayer. Akad. zu München*, 1915, 1–26; A. Sommerfeld, "Die allgemeine Dispersionsformel nach dem Bohrschen Modell," in *Arbeiten aus den Gebieten der Physik, Mathematik, Chemie—Festschrift Julius Elster und Hans Geitel* (Braunschweig, 1915), 549–584; and "Die Drudesche Dispersionstheorie vom Standpunkte des Bohrschen Modelles und die Konstitution von H_2, O_2, und N_2," *Ann. d. Phys.*, *53* (1917), 497–550.

tated by classical mechanics. Dispersion is necessarily a quantum phenomenon if emission is, a fact that Bohr had recognized by 1916.[160]

That being the case, it is particularly interesting that in Parts II and III Bohr had already begun to develop a quantum theory of dispersion side by side with the classical theory. In his absorption paper he had noted that, if dispersion electrons were treated as linear oscillators, the number of dispersion electrons in helium proved to be 1.2 rather than 2, a conflict with Rutherford's theory. In a footnote he promised to deal with the source of the discrepancy in a sequel, and on 4 November 1912 he reported to Rutherford that he had somewhat improved the agreement by substituting an inverse-square force for the elastic type he had used before.[161] But the problem had not been solved, for in Part II (489–490/41–42) Bohr found that the transverse vibration frequency $\nu_{\perp}$ of his two-electron model was $20.3 \cdot 10^{15}$ sec^{-1}, more than three times the experimental figure, $5.9 \cdot 10^{15}$. To remove the discrepancy he computed a frequency $\nu_{\parallel}$ which, he thought, might plausibly correspond to a resonance vibration in the plane of the orbit. Since, classically, such a vibration would rip the atom apart, Bohr set $\nu_{\parallel} = I/h$, I being the energy needed to remove one of the helium electrons from the atom. The result, $\nu_{\parallel} = 6.6 \cdot 10^{15}$ sec^{-1}, agreed reasonably

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[160] N. Bohr, "Die Anwendung der Quantentheorie auf periodische Systeme," in *Abhandlungen über Atombau aus den Jahren 1913–16,* trans. H. Stintzing (Braunschweig, 1921), 123–151; cf., iv–v, 138–139. The article had reached corrected proof for the *Phil. Mag.* for April 1916, but was withdrawn when Bohr saw the paper (note 157, *supra*) Sommerfeld had delivered to the Munich Academy.

By about 1920, as the gap between quantum theory and Newtonian mechanics widened, classical stability considerations ceased to seem a part of quantum physics, and physicists tended to forget that they had ever made creative use of them. (Bohr, for example, talked in the interviews [I, 7] as though his approach to the quantized atom had always been incompatible with a quasi-classical treatment of dispersion.) We suspect that this shift in perspective is one source of the myth (cf., note 91, *supra*) that radiative, rather than mechanical, instability was a special characteristic of Rutherford's atom and played a major role in Bohr's development of it. Even Bohr (Interviews II, 13) spoke of radiative instability as central to his earliest work on Rutherford's model. Apparently he remembered wrestling with stability considerations but misplaced what, in 1912 and 1913, had been the most relevant sort of stability.

[161] Bohr, "Moving Electrified Particles," *op. cit.* (note 77), 23 n. The extent of the discrepancy is not, however, indicated there but in the trilogy, Part II, 490/42. The letter of 4 November 1912 to Rutherford is in BSC.

Bohr cannot have known about the distinction between parallel and perpendicular displacements when he wrote the footnote to the absorption paper, for he suggests that the difficulty in the computation of the number of electrons in helium may have to do with the difference in the frequencies of vibrations of electrons displaced parallel and perpendicular to the atomic axis. He could have discovered it by the time he wrote Rutherford, for he says that he has been delayed by difficulties due to the instability of the two-electron system, but has made progress. If, however, he had learned that parallel displacements were unsalvageable, perpendicular not, he would likely have said so.

well with experiment. Dispersion in helium was, he concluded, primarily due to vibrations in the orbital plane, and was thus governed by the quantum. Perpendicular displacements, he later suggested (Part II, 865/63), occurred in helium at a frequency too high to make a significant contribution. In Part III (864/62) Bohr performed a similar set of calculations, classical and quantum, for the dispersion frequency of the hydrogen molecule. The fact that the frequencies obtained for parallel and perpendicular displacement were almost identical explained, he thought, why classical theory had given so much better results when applied to H_2 than to He.

These computations were, of course, but primitive first steps towards a quantum theory of dispersion, and it was a long time before the next ones were taken. In the event, dispersion turned out to present one of the central difficulties that undermined the old quantum theory and provided clues towards a new one.[162] But, at least conceptually, those next steps, as taken in Copenhagen, were closely linked to these first efforts of Bohr's. Like any revolutionary contribution to science, his "Constitution of Atoms and Molecules" provided a program for research as well as a concrete research achievement.

VI. THE PRINCIPLES OF ATOMIC STRUCTURE

Parts II and III of "On the Constitution of Atoms and Molecules," published in the *Philosophical Magazine* for September and November 1913, present Bohr's solution to the problem of the principles of atomic structure, the question that had led him to Part I. Though published later, these portions of the trilogy were prior to the first: they are the elaborations of the matter and method of the Rutherford Memorandum on which Bohr labored so vigorously after his return to Copenhagen in the fall of 1912. The chief aim of Part II is to assign definite ring configurations to the various chemical atoms; that of Part III is to urge Bohr's novel view of molecular binding by a girdle of electrons circulating about the axis formed by the united nuclei. Part II also touches on X radiation and radioactivity, making public for the first time that qualitative picture of the nuclear atom, regulated by the principles of isotopy and atomic number, which still survives in introductory physics courses. But most of Parts II and III are given up to

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[162] T. S. Kuhn, "The Crisis of the Old Quantum Theory, 1922–1925," to appear.

material much less familiar: elegant mechanical considerations about the behavior of interacting rings of electrons, dexterous applications of stability conditions to radically unstable systems, and arguments almost numerological about the structure of the elements.

Part II derived little benefit from the exact results of its predecessor, a fact which should occasion no surprise. Not only was the second part essentially completed before the first, but the primary concern of the latter, the excited states of one-electron systems, barely brushed that of the former, the normal configurations of poly-electronic atoms. In only one respect did the treatment of the hydrogen spectrum enable Bohr, in Part II, to go beyond the formulations of the Rutherford Memorandum. In place of the indefinite quantity K representing the ratio of kinetic energy to orbital frequency for each electron in its ground state, he could substitute the exact law of the universal constancy of the angular momentum: "in the permanent state of an atom, the angular momentum of every electron around the center of its orbit is equal to the universal value $h/2\pi$" (Part II, 477/29). But even this improvement was largely formal.

In Part II, as in the Memorandum, the electrons are arranged in coaxial, coplanar rings, a distribution Bohr justified on the slippery ground of stability. He supposed a ring system stable if its electrons, which of course all satisfy the principle of the constancy of the angular momentum, are so distributed that their total energy is less than that of any neighboring configuration satisfying the same principle of angular momentum (Part II, 477/29). This condition, as he neatly showed, insures the ground state stability against *all* displacements in the plane of the rings (Part II, 480/32). As for displacements normal to the rings, Bohr subjected them to the ordinary mechanics (Part II, 481–482/33–34), a refinement of the procedure in the Memorandum most likely adopted during his study of Nicholson's papers. These conditions make possible the investigation of the stability of certain three-dimensional configurations, for example of coaxial but not coplanar rings, or of mutually inclined rings passing through the nucleus. Bohr implied that he had examined some of these possibilities, and that the outcome vindicated the earlier restriction of the electrons to a single plane. "Calculation indicates," he said, "that only in the case of systems containing a great number of electrons will the plane of the rings separate; in the case of systems containing a moderate number of electrons, all the rings will be situated in a single plane through the nucleus" (Part II, 483/35). Bohr adopted a two-dimensional model not, as had Thomson, as an artificial alternative to a mathematically intractable spatial atom, but as a supposed consequence of his principles of atomic structure.

In his assignment of ring arrangements Bohr was of course guided by the doctrine of atomic number, which immediately specified the *total* number of non-nuclear electrons associated with each chemical atom. He had then to decide how many rings a given element required, and how its electrons were distributed among them. The stability conditions and the principle of angular momentum are insufficient to resolve the problem, as they are compatible with various distributions, and regrettably tend to favor those which conflict with the chemical evidence. The most helpful condition is that on the transverse displacements, for it does provide a relation between n, the number of electrons in a single-ring atom, and Ne, the nuclear charge just necessary to retain them against such displacements. The most interesting feature of this relation is that $N < n$ for $n \leqq 7$, and that $N > n$ for $n > 7$ (Part II, 482/34). Hence the largest possible neutral, single-ring atom contains only seven electrons, precisely the result Bohr had obtained in the Memorandum by an entirely different, erroneous procedure.[163] For the rest, the calculation yields the information that N increases rapidly with n; a central charge of ten, for example, is necessary to bind a ring of eight, and one of seventy-two to bind a ring of sixteen. Bohr concluded that the innermost ring of the atoms of the lighter elements contains small numbers of electrons (Part II, 482/34).

To fix the ring populations precisely, however, Bohr was obliged to use his intuition more often than his principles. He invoked the chemical properties of the elements, and, more directly, the well-known "curve of atomic volumes," which, as Bohr had recognized in the Memorandum, agreed well with his principles and gave an important clue to the number of rings each atom possessed. The curve, one recalls, is periodic, the "atomic radius" decreasing regularly from the alkalis to the inert gases, and increasing abruptly from the latter to the former.[164] According to Bohr's principles, the jump is associated with the beginning of a new ring, and the decrease with the addition

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[163] *Supra,* 245–246.

[164] Rosenfeld, xxiii, and cf., note 100, *supra.*

of further electrons to it.[165] The place where the jump occurs cannot, however, be determined by those principles; and thus Bohr's assignment of ring numbers remained phenomenological, a direct translation into the terms of his model of the empirical curve of atomic volumes.[166]

The structure of hydrogen of course presented no new problems. Helium's two electrons Bohr assigned to a common ring, an arrangement which coincidentally yielded an ionization potential in close agreement with contemporary measurements (Part II, 488–490/40–42).[167] The third element in the periodic table, lithium, presented a severe problem. Since the energy of its three electrons is least when they occupy a common ring, Bohr's principles required that lithium possess the structure 3(3), where the notation $N(n_1, n_2, \ldots)$ gives the ring distribution of the Nth element, n_1 referring to the innermost ring; while the atomic-volume curve and the chemical properties of that element, which suggested that the lithium atom held one electron very loosely, pointed to the structure 3(2, 1). Bohr chose the double-ring arrangement (Part II, 490–492/42–44). Similarly, he selected 4(2, 2) for beryllium, although the single-ring system 4(4) has the lower energy. Continuing in this way, always guided by chemical data and atomic size, he arrived at the following suggestions for the electronic configurations of the lighter atoms (Part II, 49/497):

1(1)
2(2)
3(2,1)
4(2,2)
5(2,3)
6(2,4)
7(4,3)
8(4,2,2)
9(4,4,1)
10(8,2)
11(8,2,1)
12(8,2,2)
13(8,2,3)
14(8,2,4)
15(8,4,3)
16(8,4,2,2)
17(8,4,4,1)
18(8,8,2)
19(8,8,2,1)
20(8,8,2,2)
21(8,8,2,3)
22(8,8,2,4)
23(8,8,4,3)
24(8,8,4,2,2).

Particularly noteworthy is the confluence of inner rings between elements 9 and 10, and between 17 and 18, giving neon the structure

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[165] Consider a neutral atom with nuclear charge Ne and an external ring of n electrons, and imagine that each internal ring acts on an electron outside it as if it (the internal ring) formed a continuous ribbon of current. The effective charge acting on an external electron is then $(N - s_n - \alpha)e$, where s_n represents the effect of the mutual repulsion of the outer-ring electrons and α, a complicated function, expresses the effect of the inner "continuously charged" rings. The radius of the outer ring, according to Bohr's theory, is $a_0/(N - s_n - \alpha)$, a_0 being the radius of the hydrogen atom in its ground state. As $(N + 1 - s_{n+1} - \alpha)$ is always greater than $(N - s_n - \alpha)$, the atom becomes smaller as electrons are added to its outermost ring.

[166] In the Rutherford Memorandum (Rosenfeld, xxiii), Bohr claimed that his quantization rule "explained" the atomic-volume curve. This is true in the sense of the previous note, but not in respect to predicting the periodicity, the most characteristic aspect of the curve.

[167] "Coincidentally" because the "ionization potential," as measured by Franck and Hertz, was in fact the first excitation potential. Cf., Heilbron, *History of... Atomic Structure, op. cit.* (note 1), 313–319.

10(8,2), precisely the reverse of that later accepted, and argon the assignment 18(8,8,2). The importance of the number eight in the electronic arrangements of the light elements is of course obvious from the periodicity of Mendeleev's table. Its connection with the inner rings, however, required a special argument, which we recapitulate as an illustration of Bohr's adroit exploitation of the ordinary mechanics in the service of his unmechanical model.

Imagine that the inner of two concentric and equally populated rings is slowly moved normally to their common plane by appropriate external forces. Electrostatic repulsion between the electrons pushes the outer ring out of the plane in the opposite direction. The inner ring expands, since the centripetal force on it decreases; the outer contracts, for the inverse reason. An equilibrium position might then be reached in which the rings attain the same size, with the electrons in one situated just opposite the intervals between the electrons of the other. If now the extraneous forces relax, the rings will coalesce in their original plane, providing, of course, that the central charge is large enough to protect the combined ring against disruptive oscillations perpendicular to its plane. Bohr concluded that there is a marked tendency for two adjacent rings to combine when each contains the same number of electrons. The formation of inner rings containing two, four, eight . . . electrons is thus likely, larger numbers being favored as the central charge increases. At some point in the periodic table two inner rings of four electrons should flow together into one ring of eight. Bohr set this point at neon because of the periodicity of the chemical elements; and neon, happily, is the first element whose central charge is large enough to bind eight electrons into a single ring stable against displacements normal to itself. As for the confluence of the two eight-rings of argon, it cannot occur until late in the periodic table, for, as we have said, a ring of sixteen requires a central charge of seventy-two. Bohr did not discuss the higher elements in detail. What he did say, however, proved prescient, for he observed that the properties of the iron group and of the rare earths suggested that the members of these families differed among themselves only in the arrangement of their inner electrons (Part II, 493–496/45–48).

The last few pages of Part II record Bohr's explanation of radioactivity and his elucidation of Whiddington's law (498–502/50–54). The latter provided a most fitting finale. It had been on Bohr's mind from the days of the Rutherford Memorandum, where it figured, along with the periodic law of atomic volumes, among the experimental facts marshalled to support the relation $T = K\nu$. Then he had supplied no details. Now, having fixed the value of K, he was able to use Whiddington's intriguing relation to bring the principle of angular momentum, deduced in Part I from a consideration of the hydrogen spectrum, into semi-quantitative agreement with the relation $Z \doteq A/2$, the chief result of Rutherford's scattering theory and a main attraction of the nuclear atom. He had only to assume, as many physicists did in 1913, that the prerequisite for characteristic radiation was the removal of an electron from the innermost electron ring.[168] Whiddington had found that the velocity w just necessary to excite characteristic radiation in an element of atomic weight A is $w = A \cdot 10^8$ cm/sec; the orbital velocity v of one of the innermost electrons, assuming it feels the full force of the nuclear charge Ze, is

$$v = (2\pi e^2/h)Z = 2.1 \cdot 10^8 Z \text{ cm/sec.}$$

Now the energy required to remove an electron describing a circular orbit under an inverse-square force is the electron's kinetic energy. Hence one would expect v to equal w. This indeed follows from the preceding relations and the Rutherfordian approximation, $Z \doteq A/2$.

Part III develops the molecular theory of the Memorandum with the help of the stability considerations elaborated in Part II. The models are those Bohr had invented in the summer of 1912: collinear nuclei or positive ions held together by a ring of electrons each regulated by the principle $T = K\nu$.[169] The Memorandum supported this picture with several impressive qualitative arguments, e.g., that a molecule so joined would dissociate into neutral atoms, in conformity with current experiments on oxygen; that two atoms of hydrogen could, while two of helium could not, remain together in such structures;[170] and that symmetric diatomic molecules, like H_2 or O_2, built on Bohr's plan, would show no infra-red absorption bands corresponding to vibrations of the nuclei along their axis.[171]

Part III improves upon the Memorandum via an obvious gener-

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[168] See, e.g., J. J. Thomson, "Ionization by Moving Electrified Particles," *Phil. Mag.*, *23* (1912), 449–457, and Heilbron, "Moseley" (note 108, *supra*), 345.

[169] Rosenfeld, xxiv–xxviii; *supra,* 248–249.

[170] *Ibid.,* xxvi. The condition is that the energy of the molecule be less than the sum of the energies of its separated atoms.

[171] *Ibid.,* xxv: "The absence of absorption bands in the ultra-red for H_2 and O_2 follows . . . from the symmetrical condition of the two kerns (the same ratio of charge to mass)."

alization of the earlier quantum condition, namely, the requirement that each of the bonding electrons possess an angular momentum $h/2\pi$ about the molecular axis (Part III, 858/56). Then, Bohr showed, the condition for mechanical stability of the electronic vibrations perpendicular to the bonding ring restricts the number of bonding electrons to two or three, and the charges of the ions to unity (Part III, 861/59). This result admirably supported the molecular model for hydrogen, on which Bohr based most of his discussion (pp. 863–871/61–69). He described the formation of molecules much as he had the confluence of electron rings in Part II. He produced the consequential argument about disperson which we noticed earlier.[172] And he computed, as in the Memorandum, the heat of dissociation of a mole of hydrogen, using $K = h/2$ in place of the earlier $K = .6h$. The outcome was not as satisfactory as Bohr deserved; his result, $6.10 \cdot 10^4$ cal, was less than half the best experimental value, which was later found to be far too large.[173]

Parts II and III of "On the Constitution of Atoms and Molecules" evidently differ from Part I in achievement as well as in content. The theory of the Balmer formula was quantitative and, whether or not one approved of the principles from which Bohr deduced it, the demonstrations did follow from the assumptions. The unique and extremely suggestive specifications of atomic and molecular models, on the other hand, gave largely qualitative results, despite the mathematical ingenuity with which Bohr laboriously pursued their consequences, while the details of the structures did not follow from, and often conflicted with the principles deduced in Part I. Contemporaries were not unaware of this difference. Nicholson, for example, though he thought Bohr's theory of hydrogen and ionized helium "very attractive," regarded as wholly unjustified the extension to higher atoms. He even took the trouble to prove that, assuming Bohr's principles and the validity of the ordinary mechanics in the stationary states, the concentric ring model for lithium, 3(2,1), was impossible.[174]

The successful extension of the approach of Part I to the problems of Parts II and III required a decade, and enlisted the collaboration

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[172] *Supra,* 282. The quantum computation obtains ν from the difference in energy between H_2^+ and the system $H^+ + H$.

[173] Rosenfeld, xxvii, xlvii, 61.

[174] For bibliography see Heilbron, "Moseley," *op. cit.* (note 108), 361, n. 81.

of many physicists. The universal principle of angular momentum, assigning the *same* quantum number, unity, to each electron in the ground state *regardless of its ring,* proved fallacious. New quantum numbers appeared. The concentric, coplanar rings burst asunder, scattering their electrons throughout the atomic volume.[175] Meanwhile Bohr was honing the Correspondence Principle, the most promising product of Part I, into a powerful instrument for probing the atom. In 1922 he returned to the problem of Parts II and III, bringing his sharpened Principle to bear on the new spatial models. Once again he built up the atoms with a deft combination of intuition and deduction, and once again he gave his readers the impression that his models followed directly from his principles.[176] This time, however, his profound insight penetrated nearer the atom's heart. Others quickly provided a narrower discrimination of the atomic subshells, culminating, in 1924, in the Pauli Principle, the closest solution the old quantum theory gave to the problem with which Bohr had begun his momentous journey to the quantized atom.[177]

[175] Cf., J. L. Heilbron, "The Kossel-Sommerfeld Theory and the Ring Atom," *Isis, 58* (1967), 451–485.

[176] N. Bohr, "Der Bau der Atome und die physikalischen und chemischen Eigenschaften der Elemente," *Zs. Phys., 9* (1922), 1–67.

[177] E. C. Stoner, "The Distribution of Electrons Among Atomic Levels," *Phil. Mag., 48* (1924), 719–736; W. Pauli, "Über den Zusammenhang des Abschlusses der Elektronengruppen im Atom mit der Komplexstruktur der Specktren," *Zs. Phys., 31* (1925), 765–783, esp. 773–776.