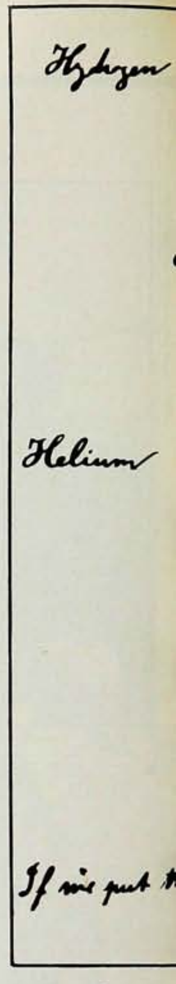


Bohr's first theories of the atom

Bohr's early work on atomic models reveals the method that served him so well: Identify failures of theory and exploit them, even if that means departing from ordinary concepts.

John L. Heilbron

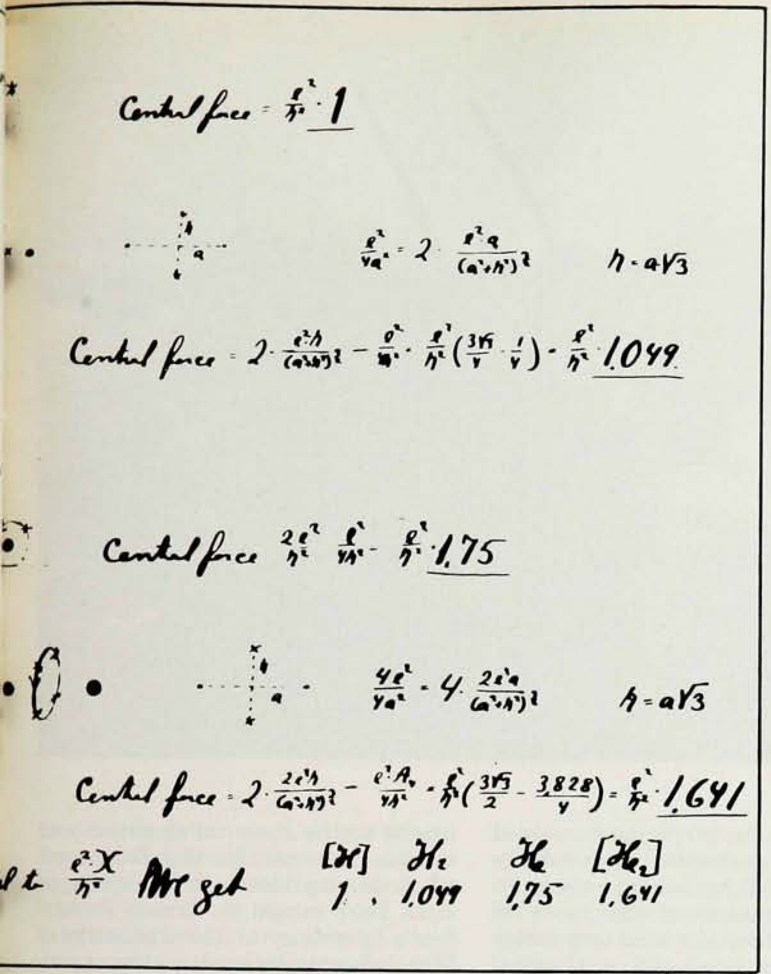
When confronted with a case in which an accepted theory appears to fail, the physicist, like anyone else, has a choice of strategies. The most obvious, which is also that recommended by armchair methodologists, is to invent an entirely new theory; an example might be Johannes Kepler's system of planetary motions. The most likely strategy, because it involves the least reconstruction, is to seek the slightest departure from received ideas that will save the phenomena; an example is John Couch Adams's supposition of the existence of a distant planet to account for irregularities in the motions of Uranus. In both of the examples the strategies worked: Kepler's system, transformed by Newton, became the basis of the world of classical physics; Adams's calculations, and those of his French contemporary Urbain J. J. Leverrier, led to the discovery of Neptune.

They were lucky. Efforts to attribute irregularities in Mercury's motions to an undiscovered planet inside Mercury's orbit failed. No such conservative and minimal adjustment worked, and the little anomaly yielded only to the novel and extravagant theory of general relativity. In contrast, the suggestion by several mathematical physicists of the eighteenth century that a new force, different from Newton's gravity, was necessary to save the motions of the moon proved unnecessary. It is part of the high art of physics to guess correctly whether an apparent failure of theory is an anomaly needing minimal or heroic treatment, or whether it is an anomaly at all.

Perhaps Bohr's greatest strength was his ability to identify, and to exploit, failures in theory. His exercise of this ability amounted to a method. He would collect instances of failure, examine each minutely and retain those that seemed to him to embody the same flaw. He then invented a hypothesis to correct the flaw, keeping, however, the flawed theory to cover not only parts of experience where it worked, but also parts where neither it nor the new hypothesis, with which it was in contradiction, could account for phenomena. This juggling made for creative ambiguity as well as for confusion: Pushing the contradiction might disclose additional anomalies, and perhaps a better, more inclusive hypothesis. A coherent theory might emerge that would remove the need for cooperation with the flawed theory, and the latter would be restricted to a domain for which it fully sufficed. To work in this way one needs not only creative genius, but also a strong stomach for ambiguity, uncertainty and contradiction.

Bohr developed this method in steps, beginning with his work on the electron theory of metals, on which he wrote his doctoral thesis in 1911, and culminating in the invention and deployment of the correspondence principle around 1918. It appears nascent in his atomic theories of 1912–13, and triumphant in the struggle that led to the invention of matrix mechanics. Like most things, however, it had its time and place. During the 1930s it prompted him to spy revolution in novelties that yielded to slight and natural alterations of the prevailing quantum theory. The main subject of this article is Bohr's nascent method.[1] I begin, however, with an account of his doctoral thesis and a survey of the state of atomic theory[2] when he

John Heilbron is professor of history at the University of California, Berkeley, and director of its Office for History of Science and Technology. This essay appears in A. P. French, P. J. Kennedy, eds., *Niels Bohr: A Centenary Volume,* Harvard U.P., Cambridge, Mass.,



Sketches by Niels Bohr of his models for hydrogen and helium. (Niels Bohr Institute, Copenhagen.)

switched his attention to it in 1912.

The electron theory of everything

At the turn of the century several important physicists, building on Joseph John Thomson's evidence of the ubiquity of the electron and Hendrik Antoon Lorentz's theory of electron behavior, tried to explain all physical phenomena as consequences of the interactions of electrons among themselves and with "molecules," or collections of electrons. The first outstanding success of the program came in the theory of metals. Thomson, Lorentz, Paul Drude and others obtained promising agreement with experiment on the assumption that electrons move through metals as do ions through a dilute solution or molecules through a perfect gas.

For example, in 1900 Drude deduced that the ratio of thermal conductivity κ to electrical conductivity σ should be the same for all metals, and directly proportional to the absolute temperature T. His expression agreed with previous empirical generalizations, and with measurement to within a factor of 1.5. Drude then tried his hand at thermoelectric effects, and obtained encouraging indications that a more refined electron theory might account for these also. Lorentz provided such a theory in 1905, treating the free electrons in a metal by the statistical methods worked out for gases. He obtained for the ratio of conductivities κ/σ a value two-thirds of Drude's, which worsened the empirical fit. He advised anyone worried about agreement between the theory and experiment to recalculate the ratio of conductivities using some special hypothesis about the dependence of electron mean free path on velocity.

One whom the disagreement worried was Bohr. In his master's thesis of 1909 he showed that the theoretical value of the ratio of thermal conductivity to electrical conductivity could indeed be raised to the experimental by supposing the mean free path to change with velocity, an assumption he thought equivalent to introducing a force between electrons and metal molecules. The introduction of a central attraction diminishing as the pth power of the distance, the chief innovation of Bohr's doctoral thesis, freed Lorentz's theory from the assumption that electrons interact with metal molecules only when striking them. Bohr brought the ratio of conductivities κ/σ into agreement with experiment by setting the exponent p equal to 3. A few other standard problems in the theory of metals also yielded to him. However, several did not, notably two not treated by Drude or by Lorentz in his theory of 1905: heat radiation and magnetism.

In 1903 Lorentz had formulated a theory applicable to radiation whose vibration period is much longer than the average time interval between successive collisions of an electron with metal molecules. His result under this restriction coincided with the long-wave limit of Planck's radiation formula. However, Planck's formula rested on assumptions very different from those of Drude and Lorentz. Could the agreement be pushed further? In 1907 Thomson thought he had done so. Bohr disagreed. Bohr's lengthy calculations showed that Lorentz's derivation held only at the limit considered. Bohr concluded that Thomson's program was hopeless. "The cause of failure is very likely this: that the electromagnetic theory does not agree with the real conditions in matter."[3]

In considering magnetism, Bohr followed the theory that Paul Langevin had presented in 1905. Langevin had observed that the electric field set up in a substance while an external magnetic field rises or decays, or during reorien-

Ernest Rutherford and Niels Bohr, sitting back to back, on a trip to the Cambridge University rowing regatta, June 1923. Rutherford is on the right. In the spring of 1912 Bohr moved to Rutherford's laboratory at the University of Manchester, to learn about the experimental side of radioactivity. (Niels Bohr Institute photograph, courtesy of the AIP Niels Bohr Library.)

tation of electron orbits, will cause a change in orbital frequency. The change amounts to a current whose magnetic moment μ_{dia} opposes the external field. Langevin concluded that all bodies are diamagnetic. Paramagnetism could arise, therefore, only in substances whose atoms contain moments μ_{para} that can align with the magnetic field and swamp the universal diamagnetism. Langevin noticed that perfect alignment is prevented by thermal agitation, and that in equilibrium the angles at which the moments stand to the field should distribute according to the Maxwell–Boltzmann law. This hypothesis gave a theoretical expression in which the paramagnetic susceptibility is inversely proportional to the absolute temperature, in agreement with Curie's law.

Although Langevin's theory had considerable plausibility, Bohr condemned it as untenable, at least with respect to diamagnetism. If mechanical thermal equilibrium is to prevail, he said, the change of velocity induced during the buildup of the magnetic field must quickly equalize among the electrons in a molecule after the field is established. If so, diamagnetism cannot arise from undamped motions of bound electrons. Bohr also argued that free electrons cannot cause diamagnetism because the field cannot alter their distribution in space or velocity. Thus it appeared that the electron theory of metals could not give an account of a fundamental property of matter in its domain.

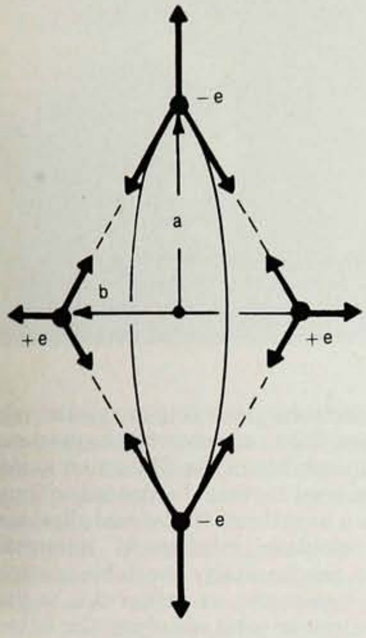
To harvest the fruit of Langevin's theory without the worm, one might declare the sizes and moments of atoms immune from the averaging demanded by statistical mechanics. Such a declaration, which Bohr deemed necessary, implies the existence of what he called "forces in nature of a kind completely different from the usual mechanical sort," forces that might freeze the structure of atoms and molecules so as to legitimize Langevin's approach and fix the sizes of atoms.

Bohr took from his doctoral thesis the conclusion that the electron theory of metals could easily be brought into agreement with experiment in the cases of the conductivity ratio κ/σ and related problems not involving the internal structure of atoms. He also concluded that it could not give a satisfactory account of heat radiation and magnetism without an additional, radical, extramechanical hypothesis. He probably already associated this hypothesis with the nonclassical quantum postulate that Einstein and others had detected as the foundation of Planck's radiation theory. By the spring of 1911, Bohr had pinpointed serious flaws in the prevailing electron theory and had an inkling of the hypothesis needed to repair it. However, he had no precise idea how or where to introduce the hypothesis into the theory.

Bohr spent the academic year 1911–12 in England, engaged in postdoctoral study. He began at Cambridge, where he hoped to discuss problems of the theory with Thomson, to publish his thesis in English and to find a way of attacking magnetism. But Thomson had ceased to work on the theory of metals and was temperamentally averse to the close collaboration and constant conversation that Bohr needed to develop ideas. In the spring of 1912 Bohr moved to Ernest Rutherford's laboratory at the University of Manchester to learn about the experimental side of radioactivity. He soon took an interest in the theory of the nuclear model that Rutherford had then just proposed. Its interest for Bohr lay as much in its imperfections as in its successes. It precisely expressed, and perhaps therefore could model, the results of Bohr's dissertation: In special cases, such as the scattering of alpha particles, the nuclear atom accounted for the phenomena with specific assumptions about the number of charges on the nucleus; but it suffered from radical mechanical instability, which could be overcome only by the sort of rigidification by quantum decree that Bohr had come to recognize as necessary from his study of the electron theory of metals.

Atomic theories around 1910

The prevailing approach to atomic structure when Bohr was finishing his dissertation derived from Thomson's model and the problems that Thomson had studied with its aid. Thomson had dealt with the greatest uncertainty in atomic theory—the nature of the positive constituent of the atom—by supposing that bound electrons circulate in coplanar rings within a sphere that acts as if it were filled uniformly with a resistanceless positive charge. This arrangement has the great advantage of being mechanically stable, unlike the Saturnian model, in which the



Hydrogen molecule. The components of the H_2 molecule were arranged like this according to Bohr's theory of 1913.

electron rings surround a central positive nucleus. The Saturnian model had suggested itself to the first physicists who attempted to picture an atom containing electrons; but it was dropped after the discovery that it is not stable against small displacements of the electrons in the plane of their orbits. Thomson's atom, like the Saturnian, eventually collapses from loss of energy by radiation. However, as Thomson showed, the loss in both cases can be made negligible: The larger the number of electrons equally spaced around a ring, the smaller their total radiation. As for the ultimate collapse, it offered an easy explanation of radioactive disintegration.

At first Thomson supposed that the electrons provided all or most of the mass of the atom. Hence their number n in an atom of atomic weight A would be about $1000A$. To check this hypothesis he devised theories of the scattering of x rays and beta rays by the electrons in his model atoms. Experiments done at the Cavendish Laboratory showed that he had vastly overestimated the electron populations of atoms: The number of electrons n was revealed to be about twice the atomic weight A, not $1000A$. Obtaining a more accurate relation between the number of electrons and the atomic weight became a major goal of Thomson's research program. In 1910 the Cavendish's best result was $n = 3A$. A little later, Rutherford found that $n = A/2$ by analyzing alpha-particle scattering.

A second line in Thomson's program for atomic theory was to explain the periodic properties of the elements. He made periodicity a plausible consequence of electromagnetic forces alone by examining the mechanical stability of a ring of electrons against small displacement from their equilibrium orbit. A single ring of two to seven electrons within a neutralizing positive sphere is stable; the eighth electron must go to the center to achieve stability. The ninth also goes inside, where it and the eighth form a ring of two. Thomson showed that in general the requirement of mechanical stability implies that each total n of atomic electrons has a unique distribution into rings. He also pointed out strong analogies between the properties of certain model atoms and the chemical behavior of elements in the second and third periods of Mendeleev's table.

The third line concerned the building of molecules—the binding together of model atoms. In the vexed case of a diatomic molecule of an elementary gas such as hydrogen or oxygen, Thomson argued that there is a transfer of charge between the initially identical constituents. His illustration of the process is characteristic of his method, which differed fundamentally from Bohr's. Liken each atom to a sealed flask partially filled with water and suspended by a spring. The weak electrical interaction, when the atoms are close together, may be represented by a siphon connecting the flasks. The slightest displacement of one flask relative to the other will cause water to flow through the siphon, increasing the displacement; and the disparity will increase until the air pressure above the water in the lower flask matches the liquid pressure driving the siphon. The flow of water may be taken as a transfer of charge between identical model atoms, and the transfer as chemical binding.

In June 1912, when Bohr went to work full time on the theory of the nuclear atom, his first objective was to obtain solutions, on the basis of this new model, to the problems on which Thomson had made progress: the nature of radioactivity and chemical periodicity, and the binding of molecules. It is noteworthy that in Bohr's agenda of 1912, as in Thomson's a decade earlier, explanation of series spectra does not appear. This neglect contrasts sharply with the concern of the few physicists who around 1910 tried to introduce the quantum into the atom. Two examples deserve attention:

▶ The first, the handiwork of Arthur Eric Haas, a doctoral student at the University of Vienna, concerned a single electron of mass m and charge e oscillating in a neutralizing Thomson sphere of radius a. A simple calculation using Newtonian mechanics shows that the motion is harmonic and that the frequency of oscillation f is independent of the amplitude: $f^2 = e^2/4\pi^2ma^3$. In what he took to be the spirit of quantum theory, Haas set the frequency equal to an energy W divided by Planck's constant h. Because the least arbitrary special value for the amplitude is the radius, Haas equated the two and proposed the equation $hf = e^2/a$. Eliminating the frequency from the preceding equations, Haas had what he called "an electrodynamical interpretation of Planck's quantum

Arnold Sommerfeld (left) and Niels Bohr at a September 1919 physics conference in Lund, Sweden. (AIP Niels Bohr Library, Margrethe Bohr Collection.)

of action," namely, $h = 2\pi e(ma)^{1/2}$. (From this expression it follows that $a = h^2/4\pi^2 e^2 m$, precisely the value later obtained by Bohr, from quite different premises, for the radius of the ground-state orbit in hydrogen. That the radius in both cases must be proportional to h^2/me^2 follows from the dimensions of the atomic constants. It is only a coincidence, but a striking one, that Haas's calculations, based on the Thomson model, resulted in the same numerical value as Bohr's calculations based on the Rutherford model.)

Lorentz took an immediate interest in what he called Haas's "risky hypothesis." In lectures at Göttingen in 1910, he recommended it for having "connected the riddles of the energy elements with the question of the nature and action of positive electricity." In discussions at the Solvay Conference of 1911, called to consider the pressing problems of radiation and the quantum, Lorentz insisted on a link between "the size of the constant h and the dimensions of atoms (positive Thomson spheres)." The Solvay participants discussed several ways other than Haas's for introducing the quantum into the atom, and they considered, without reaching agreement, whether the quantum to be employed was Planck's h or $h/2\pi$ or $h/4$. Their papers and proceedings appeared[4] as a book in 1912. It gave Bohr, who read it, something to think about.

▶ The Solvay book also inspired John W. Nicholson, author of the other early quantized atom we are to consider, to hit on a method of quantization that Bohr came later to adapt. Nicholson had studied single-ring models containing a few electrons; the most interesting of these theoretical atoms, "nebulium," had four electrons. He offered striking evidence in favor of the existence of this "protoelement" in the stars. Small vibrations of electrons perpendicular to the plane of their ring can be stable, unlike vibrations in the plane. Nicholson computed the frequencies $f_\perp$ of the perpendicular vibrations and compared them with the frequencies $\nu_?$ of unassigned lines in nebular spectra. Now, the calculated frequency $f_\perp$ depends upon the charge on the nucleus, the number of electrons in the ring, and the radius of the ring. With a free choice of radius, Nicholson made nine of eleven nebular lines $\nu_?$ agree with as many calculated lines $f_\perp$ for normal and ionized "nebulium." A few months later, astrophysicists found a new $\nu_?$ that agreed perfectly with an unassigned $f_\perp$, and in the meantime recognized that the two "nebular" lines that Nicholson could not accommodate belonged to a terrestrial element.

The counsel from Solvay inspired Nicholson to try to fix the frequency f of the unperturbed rotation of the ring by a quantum rule. He computed the total energy E of each of his model atoms, using the parameters that experience had forced upon him. He then formed the ratio E/f, and learned that in all cases it was a whole number of quanta. After studying the Solvay proceedings, Nicholson required that the *angular momentum* of his models be an integral multiple of $h/2\pi$. That worked, too. He ended with the following picture of a radiating atom: "We are led to suppose [by the quantum theory] that lines of a series may not emanate from the same atom, but from atoms whose internal angular momenta have, by radiation or otherwise, run down by various discrete amounts from some standard value."

Bohr's atomic theories, 1912–1914

Bohr was drawn to the problem of atomic structure by his critical reaction to a paper by Rutherford's mathematical physicist, Charles Galton Darwin (whom his good friend Bohr called "the grandson of the real Darwin"), on the slowing of alpha particles in their passage through matter. Bohr objected that Darwin had neglected resonance effects that enhance energy transfer when the time of flight of the particle past an atom roughly matches the natural period of oscillation of some of its electrons. In trying to calculate the effects, Bohr rediscovered the mechanical instability of the Saturnian model; to proceed further, he needed to introduce a hypothesis that would allow him to calculate mechanical quantities from mechanically unstable models. The hypothesis, or rather fiat, is that any circular orbit satisfying the following condition is stable against mechanical perturbations and radiation loss:

$$T/f = K \qquad (1)$$

Here T and f represent the kinetic energy and frequency of the orbiting electron, and K is analogous to Planck's h. The kinetic energy T replaces the total energy W so as to take account of two major differences between Rutherford's model and a Planck oscillator: In Rutherford's model, the total energy W is negative, and the frequency f depends on the kinetic energy T. Several considerations, other than a loose analogy to Planck's procedure, prompted or justified writing a prescription of stability in the form of equation 1. This formula provided, as Bohr observed, a resolution of the problem of atomic size, and it allowed him at last to express mathematically the conviction to which he had been led by his attempts to save the electron theory of metals.

Bohr's chief line of research from June 1912 to February 1913 aimed at exploiting the condition expressed in equation 1 in the service of the nuclear model and the standard problems addressed in Thomson's theory of atomic structure. In June or July 1912, Bohr began a memorandum drawn up for discussion with Rutherford by reinterpreting Thomson's main accomplishment: the reduction of chemical periodicity to atomic structure. Bohr calculated the total energy W_p of an electron in a single ring of p electrons stabilized by his quasi-quantum fiat, and discovered that the total energy W_p changes from negative at $p = 7$ to positive at $p = 8$. On this reckoning an electron can leave a single ring containing more

than seven others. The eighth electron goes into orbit outside the ring of seven; placing it inside does not make the ring capable of holding more, in contrast to Thomson's model.

Whereas Thomson embroiled all atomic electrons in chemical and optical behavior, arrived at chemical periods of steadily increasing length and offered no neat distinction between the mechanics of ionization and the mechanics of radioactivity, Rutherford's model afforded a firm base for understanding the populations of at least the first two periods and for distinguishing the region implicated in chemistry and spectroscopy (the electronic structure) from the region responsible for radioactivity (the nuclear black box). Bohr thus arrived at the concept of isotopy on his own and recognized immediately, as "in complete accord with my ideas," the electrochemistry of the radioelements as summarized by his friend George de Hevesy in 1912. Much therefore depended on Bohr's demonstration that the total energy W_p of an electron changes sign between $p=7$ and $p=8$. The proposition is, however, altogether wrong: It rests on a numerical error—a doubling of the potential energy—that Bohr soon discovered. No doubt the need to find an alternative to Thomson's theory of periodicity encouraged his productive mistake.

Although Bohr failed to explain chemical periodicity in his first tilt with atomic structure, he retained the result to which his error led him: that an electron added to an atom with a saturated ring or rings goes outside, not inside, the existing structure. With this proposition and Rutherford's finding that the number of electrons is approximately half the atomic weight, Bohr could go far beyond Thomson and suggest the precise number of electrons in any normal atom. Because the nuclear model requires n_{He}, the number of electrons in the helium atom, to be 2, it follows that $n_{\mathrm{H}}=1$, $n_{\mathrm{Li}}=3$ and so on, each neutral atom containing a number of orbiting electrons equal to the number Z of its element in the periodic table, counting from hydrogen as 1. Bohr spent much time in 1912 and 1913 assigning ring structures to light atoms and searching for a principle that would account for the periodicity in the table of elements.

In the problem of diatomic molecules, Bohr worked from calculation and a model—a ring of binding electrons coaxial with the two nuclei—whereas Thomson had made do with analogy. The simplest case is the neutral hydrogen molecule, H_2. The electrons, always diametrically opposite each other, circulate in an orbit of radius a under a net electrical attraction that provides the needed centripetal force. For the nuclei—two protons, each a distance b from the center—to stand in equilibrium under the electric forces alone, we must have $b=a/\sqrt{3}$. For each electron, ordinary mechanics requires that:

$$ma(2\pi f)^2=(e^2/a^2)\,X \qquad (2)$$

Here X is a pure number that is a measure of the centripetal acceleration. For the dumbbell hydrogen molecule just described, this model gives $X=1.049$. (For the hydrogen atom $X=1$, and for singly ionized helium $X=4$.) Combining equations 1 and 2 gives the following results:

$$-W=Xe^2/2a$$

This is equal to the kinetic energy of the orbiting electron, so

$$-\mathrm{W}=\pi^2me^4X^2/2K^2 \qquad (3)$$

The orbital radius is given by

$$a=K^2/\pi^2me^2X \qquad (4)$$

The orbital frequency is

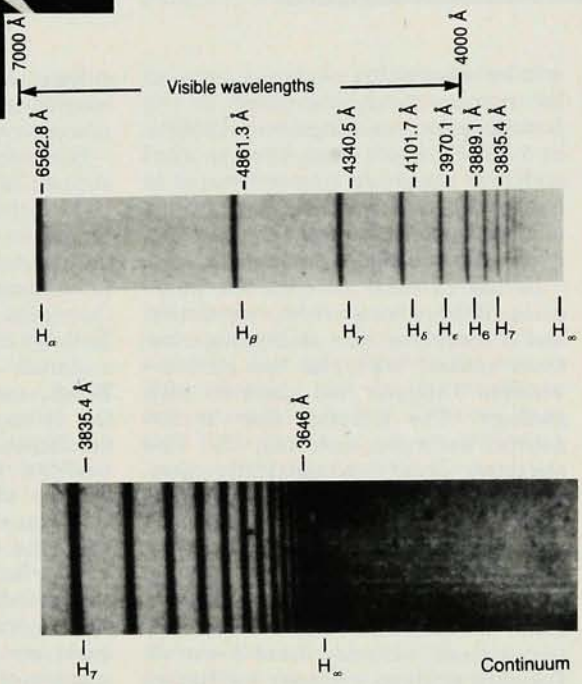
$$f=\pi^2me^4X^2/2K^3 \qquad (5)$$

Even without knowing the constant K, Bohr could deduce from the relative energies before and after dissolution that H_2^+ should dissolve spontaneously into a hydrogen atom and a hydrogen nucleus, and that miscegenated molecules such as HHe do not form. These results were encouraging, and scarcely precedented.

Bohr returned to Copenhagen in the autumn of 1912 to teach, and to wrestle with dispersion and magnetism. He began to worry that he might be anticipated. Others had found pieces to his puzzle: the Solvay symposiasts, the several guessers at isotopy, and in January 1913, in the unlikely person of a Dutch lawyer, Antonie van den Broek, an independent discoverer of the doctrine of atomic number. Van den Broek reasoned from two approximations: Rutherford's result that the number of electrons is approximately half the atomic weight, and the fact that the average change in atomic weight from one element to the next in the periodic table is about 2. From the two approximations he inferred an exact law, $\Delta n=1$: The change in the number of electrons from one element to the next in the periodic table is 1. From Thomson's experiments on positive rays, he took the number of electrons n_{H} in a hydrogen atom to be 1, and from Rutherford's on alpha particles, he set $n_{\mathrm{He}}=2$. Van den Broek declared that "each element must [therefore] have an inner charge equal to $n[e]$—i.e., the nth element must have n intra-atomic charges of the same sign" that determine all its characteristics. "I am afraid I must hurry if [my work] is to be new when it appears," Bohr wrote in February 1913, after reading van den Broek. "The question is indeed such a burning one."

Radiative transition

As the old questions were burning, a new one ignited. By the end of 1912 Bohr had met Nicholson's model of the atom, which, like his, was quantized and nuclear. However, Nicholson's atoms spoke the language of spectra, whereas Bohr's were mute; and nebulium had the same electronic population as the doctrine of atomic number demanded for beryllium. "I therefore thought at first that the one [model] or



Johann Jakob Balmer (1825–1898) and spectra of atomic hydrogen. The upper spectrum shows the visible Balmer lines; the lower spectrum shows Balmer lines in the ultraviolet.

the other was altogether wrong."

The conflict did not last long for Bohr. On New Year's Day 1913, he wrote to his brother: "[My] calculations would be valid for the final, chemical state of the atoms, whereas Nicholson's 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." Having settled with Nicholson, Bohr returned to his own problems. "I do not at all deal with the question of calculation of the frequencies corresponding to the lines in the visible spectrum," he wrote to Rutherford. "I have only tried, on the basis of the simple hypothesis, which I used from the beginning, to discuss the constitution of the atoms and molecules in their 'permanent' state."

Radiation appeared on Bohr's agenda in February 1913, when Hans M. Hansen, Copenhagen's expert on spectroscopy, asked or advised him to explain the Balmer formula for the frequencies ν_n of the lines of the visible spectrum of atomic hydrogen:

$$\nu_n = R\left(\frac{1}{4} - \frac{1}{n^2}\right) \qquad (6)$$

Here R is the Rydberg constant. "As soon as I saw Balmer's formula," Bohr recalled, "the whole thing was immediately clear to me." Clarification may have dawned along the following lines. In Balmer's formula, frequency appears as a difference, which, in accord with the rough contemporary practice, could be connected with an energy difference by multiplying by h. Thus Rh/n^2 would represent an energy, possibly the energy of one of Nicholson's radiating or radiative states. However, Bohr's expression for the kinetic energy $-W_n$ of an orbiting electron, equation 3, contains in its denominator K^2, where K is the same kind of quantity as h; compare this with equation 1. By setting K equal to αhn, where α is a pure numerical factor, equation 3, as applied to the hydrogen atom ($X = 1$), takes on the form Rh/n^2:

$$Rh = \pi^2 me^4/2\alpha^2h^2$$

Using the then most recent values of the constants, Bohr would have found $\alpha = 1/2$, or $K_n = nh/2$. He then had as the condition defining the nonpermanent, or Nicholson, states:

$$(T/f)_n = nh/2 \qquad (7)$$

From this relation he could compute $-W_n$, reverse his argument and obtain the Rydberg constant R of equation 6 as a product of the atomic constants:

$$R = 2\pi^2me^4/h^3$$

To make a theory of this game, Bohr needed a justification of equation 7. He supplied three:

Average orbital frequency. The first part of Bohr's three-part paper on atomic structure published in 1913 opens with an appeal to Planck's radiation theory. In falling from infinity into an excited or Nicholson state—say, the nth—under the attraction of a bare nucleus of charge Ze, an electron will radiate away energy E_n at frequency ν_n, where, "from Planck's theory," $E_n = nh\nu_n$. Bohr offered the following connection between this arbitrary adaptation of Planck and the desired expression $T_n = nhf_n/2$. A planetary electron bound by an inverse-square force has a total energy W_n that is the negative of its kinetic energy: $-W_n = T_n$; the energy required to remove it again to infinity, $-W_n$, equals the amount it lost by radiation during the binding, wherefore $E_n = -W_n = T_n = nh\nu_n$. It remains to show that $\nu_n = f_n/2$, that is, that the radiated frequency is half the final orbital frequency. To do this, Bohr set the radiated frequency equal to the average of the initial orbital frequency f, which is zero, and the final orbital frequency f_n. Here he reached an abyss. On both ordinary and Planck radiation theory, the frequencies in the light from an atomic radiator are just those of the electrons producing it; on Bohr's argument, invented to introduce a factor of two, mechanical and radiated frequencies no longer coincide. Pushing his hybrid theory had revealed an anomaly more serious than any with which he had started.

Having achieved the relation $T_n = nhf_n/2$, Bohr presented the equivalents of equations 3–5 with $K = nh/2$ and $X = Z$:

$$-W_n = \frac{2\pi^2 me^4 Z^2}{n^2h^2}$$

$$f_n = \frac{4\pi^2 me^4 Z^2}{n^2h^2}$$

$$a_n = \frac{e^2}{-2W_n} = \frac{n^2h^2}{4\pi^2 me^2 Z^2}$$

The formulas for the several spectral series of neutral atomic hydrogen ($Z = 1$) follow from energy balance:

$$\nu_{n,p} = \frac{W_n - W_p}{h} = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{p^2} - \frac{1}{n^2}\right)$$

The Balmer formula results from setting $p = 2$, $n = 3,4, \ldots$

Although evidently *ad hoc*, Bohr's "derivation" of his fundamental condition $T_n = nhf_n/2$ had some precedents in the widespread view that series spectra arise during electron capture, and in then-recent reformulations of the quantum postulate by Planck and others. However, the unintelligible outcome of Bohr's calculation, which in the case of the Balmer formula takes the form $\nu_n = f_2 - nf_n/2$ ("the frequency of the nth Balmer line equals the mechanical frequency of the second orbit less $n/2$ times that of the nth"), had no precedent.

Orbital angular momentum. After submitting his *ad hoc* condition on the radiation, $E_n = nh\nu_n$, and its justification, each intended to connect his work closely with Planck's, Bohr discarded both in favor of a condition on the orbits and one-quantum emission, $h\nu = \Delta W$. The restriction is just $(T/f)_n = nh/2$, now stated without argument. As Bohr observed, it is equivalent to Nicholson's condition that the orbital angular momentum be an integral multiple of $h/2\pi$.

Asymptotic agreement. The third derivation, the deepest of all, begins by stipulating asymptotic agreement at large values of n between radiated frequencies as calculated by ordinary mechanics and by Bohr's theory. The rationale for the stipulation is that with large n and big radii, the consequences of the restriction arising from atomic binding should disappear: The agreement concerns the numerical values of spectral frequencies, not their methods of production. Stipulating therefore that $\nu_{n,n-1} \approx f_n \approx f_{n-1}$ for large n, and imposing on the electronic orbits the condition $T_n = \beta(n)hf_n$, $\beta(n)$ an unknown function, Bohr observed that the Balmer formula demands $\beta(n) = \alpha n$, with α a constant. That the constant α is ½ emerges from the asymptotic condition:

$$\nu_{n,n-1} = \frac{\pi^2 me^4}{2h^3}\left[\frac{1}{\alpha^2(n-1)^2} - \frac{1}{\alpha^2 n^2}\right]$$

$$\xrightarrow[n\to\infty]{} \frac{\pi^2 me^4}{\alpha^2 h^3 n^3} \approx f_n \approx \frac{\pi^2 me^4}{2\alpha^3 h^3 n^3}$$

The equations for the frequencies ν and f follow from equations 3–5, with $K = \alpha nh$.

At the end of 1913, in a lecture to the Danish Physical Society, Bohr showed how to derive the Rydberg constant R without imposing any condition on the orbit. From the Balmer formula, read as an energy equation, he took the relation $-W_n = Rh/n^2$; from the usual relations among mechanical quantities of the orbit, $f_n = (-2W_n{}^3/m)^{1/2}/\pi e^2$, whence $f_n{}^2 = 2R^3h^3/\pi^2 me^4 n^6$. Asymptotically,

$$(\nu_{n,n-1})^2 = R^2\left[\frac{1}{(n-1)^2} - \frac{1}{n^2}\right]^2 \approx \frac{4R^2}{n^6}$$

When the last term of this equation is equated to the above value of $f_n{}^2$, the equation $R = 2\pi^2 me^4/h^3$ results once again. By this time Bohr had decided that it was "misleading" to use his original analogy to Planck's oscillator. He had greatly refined the hypothesis with which he repaired the mechanical instability of the nuclear atom.

In one particular, Bohr's mode of spectral analysis enabled him to make a striking prediction. Spectroscopists had detected lines whose frequencies approximately fitted the series formula:

$$\nu_n = R\left[\frac{1}{4} - \frac{1}{(n/2)^2}\right]$$

These lines are known as the Pickering series, and spectroscopists had attributed them to hydrogen on analogy to the Balmer formula. Bohr had no place for half integers, for in his view the running term of the spectral formulas for hydrogen numbered the possible orbits of the single electron; a half quantum would imply an inadmissible half-integral orbit. He accordingly rewrote Pickering's series as $\nu = 4R(1/4^2 - 1/n^2)$, and attributed it not to hydrogen but to ionized helium, which, with a nuclear charge of two, should have an effective Rydberg constant four times that of hydrogen. English spectroscopists confirmed Bohr's conjecture by finding Pickering lines in helium carefully cleansed of hydrogen.

Given the great precision of wavelength measurements, however, the agreement with experiment was not very good; the Pickering formula had never agreed with experiment nearly as well as the Balmer formula did. Bohr cleared up this business in October 1913 in a master stroke that destroyed the Rydberg's universality and made theorists take him seriously. He had neglected, he said, the small motion of the heavy nucleus in estimating the electron's energy in the stationary states. Repairing this omission in the way taught in elementary mechanics, which amounts to replacing the electron mass m by a reduced mass m', equal to $m/(1 + m/m_Z)$, m_Z being the mass of the nucleus, Bohr came up with a formula for the true hydrogen Rydberg: $R_H = (m_H'/m)R$. Theory required that the ratio R_{He}/R_H be 4.00163. Spectroscopists looked, and reported the ratio to be 4.0016. The impression made by this extraordinary confirmation—in which refinements required by the flawed mechanical theory were invoked to confirm the nonmechanical quantum postulate—may be gauged from Hevesy's descrip-

James Franck and Hans Marius Hansen (right) with Niels Bohr (left), in 1921. (AIP Niels Bohr Library, Margrethe Bohr Collection.)

tion (in a waywardly spelled letter to Bohr) of Einstein's reaction to the news that the Pickering series belongs to helium. "When he heard this, he was extremely astonished and told me: 'Than the frequency of the light does not depand at all on the frequency of the electron.... And this is an *enormous achiewement*. The theory of Bohr must be then wright."

Confirmations and extensions

The success with ionized helium capped Bohr's own initiatives. Further support of his views came in 1914, from three lines of inquiry taken up without reference to his theories or even to the general problem of atomic structure:

▶ One, begun as a study of the nature of x rays, continued as an exploration of characteristic x-ray spectra and ended in a search for new elements. The explorer Henry G. J. Moseley, whom Bohr had met at Manchester, discovered that the x-ray lines of highest frequency emitted by the metals he examined satisfied the equation $\nu = (3R/4)(Z-1)^2$, Z being the atomic number of the metal. The equation resembled Balmer's, and the unsuccessful theory that Moseley invented to derive it resembled Bohr's. The relations among them were made clear in 1915 by Walther Kossel, who interpreted x-ray emission as the transition of a vacancy in the electronic structure from the inner to the outer reaches of the atom.

▶ A second corroboration emerged from the experiments of James Franck and Gustav Hertz, who had started measuring what they thought were ionization potentials in gases before Bohr took up the study of atomic structure. Bohr was able to reinterpret the values they gave for "ionization potentials" as energies of the lowest *excited states* of the gas atoms; and he was able to extract, from their finding that an atom does not exchange energy with an electron whose energy is insufficient to "ionize" it, a demonstration of the existence of discrete electronic orbits or atomic stationary states.

▶ The third corroboration was squeezed from the discovery in 1913 by Johannes Stark that a strong electric field can split a spectral line into several lines. Because physicists at the time argued that on classical theory the effect ought not to have been detectable, Stark's results immediately challenged quantum theory, and several physicists showed that, with one or another adjustment of Bohr's quantum hypothesis, the observed splitting could be calculated.

In 1915 Arnold Sommerfeld began to rework Bohr's hodgepodge theory into a formal structure by imposing conditions on the electron orbits and by making the deduction of the energy levels of the atoms a straightforward algorithm. Bohr improved Sommerfeld's approach by bringing out connections between quantum formalism and the Hamilton–Jacobi formulation of classical mechanics. This effort, which occupied him from 1916 to 1919, sharpened the contradiction between the main elements in his theory, and, in a few cases, showed how to fashion or calculate quantum-theoretical quantities from a knowledge of "corresponding" classical concepts. Characteristically, as Bohr took the demands of classical mechanics more and more seriously to fix the fulcrum on which his correspondence principle would turn, he also restricted still further the reach of "ordinary concepts" (as he called the ideas of classical science) in atomic physics. Advance was possible there, Bohr wrote in the autumn of 1914, only by "departing from the usual considerations to an even greater extent than has [yet] been necessary." His chief guide and compass for this departure—for tracking down the true quantum theory that would replace his contradictory and makeshift one—were to be the usual considerations and ordinary concepts that no longer sufficed.

References

1. For a more detailed account of Bohr's early work, see J. L. Heilbron, T. S. Kuhn, Historical Studies in the Physical Sciences 1, 211 (1969). For a lively portrait of Bohr during the period covered in this article, see L. Rosenfeld, E. Rüdinger in *Niels Bohr: His Life and Work as Seen by His Friends and Colleagues*, S. Rozental, ed., North-Holland, Amsterdam (1968), p. 38.
2. For an overview of the early history of theories of atomic structure, 1900–1922, see J. L. Heilbron in *History of Twentieth-Century Physics*, C. Weiner, ed., Academic, New York (1977), p. 40.
3. The quotations by Bohr in this article are taken from his *Collected Works*, a multivolume series that began in 1972 and is continuing, L. Rosenfeld, gen. ed., vols. 1–4, E. Rüdinger, gen. ed., vol. 5, North-Holland, Amsterdam.
4. P. Langevin, M. de Broglie, eds., *La théorie du rayonnement et des quanta*, Gauthier-Villars, Paris (1912). □