100th Anniversary of Bohr's Model of the Atom**

*W. H. Eugen Schwarz**

atomic spectroscopy · Bohr, Niels · model of the atom ·
periodic system · quantum chemistry

*Dedicated to Professor W. Kutzelnigg on
the occasion of his 80th birthday*

One hundred years ago this autumn, the young 27-year-old Danish physicist Niels Bohr published his atomic models.[1] In 1911–1912 he had visited the centers of experimental and theoretical atomic physics: Cambridge (where Thomson, the Nobel Laureate of 1906, had discovered the electron in 1897) and Manchester (where Lord Rutherford, Chemistry Nobel Laureate of 1908 for studies in radioactivity, had discovered the atomic nucleus in 1911). The harvest of Bohr's postdoctoral stay comprised in particular three papers with the comprehensive title "On the Constitution of Atoms and Molecules" published in the *Philosophical Magazine* in the fall of 1913.[1a] The papers became famous as "Bohr's Trilogy". His "investigation of the structure of atoms" earned him the Nobel Prize in 1922 (Figure 1).[2]

We shall begin the present account by reviewing the atomistic concepts in chemistry and physics up to the beginning of the 20th century (Section 1), a time when many atomistic phenomena were known in detail but remained physically unexplainable. Some scientists had concluded that classical physics needed revision and hypothetical suggestions inconsistent with classical physics appeared. Against this background we shall then describe Bohr's fundamental steps and achievements during the period 1912–1913 as regards the physical structure and spectra of atoms, the periodic ordering of the elements, and chemical bonding (Section 2). Finally, we shall identify Bohr's lasting results for chemistry while also noting those conjectures that were short-lived (Section 3). In this context we shall highlight the importance of subsequent physical discoveries for chemistry, notably the electron spin, the Pauli exclusion principle, and the Heisenberg uncertainty principle. We shall conclude with some scientific and philosophical observations and also call attention to certain definitive and chemically relevant insights of Bohr that still have not yet found their way into many chemistry textbooks.

Figure 1. Niels Bohr in the year in which he received the Nobel Prize (1922).[2]

Recent short accounts of Bohr's atomic models are found in Refs. [3–5], a recommendable book in the present context is Ref. [6], the respective commented writings in "Niels Bohr Collected Works" are found in Refs. [7,8]. We will focus on Bohr's chemically relevant electronic theory, without nuclear chemistry.

1. Atomism in Chemistry and Physics before Bohr

From Antiquity to Maxwell's Electrodynamics. The concept that the world is made up of tiny indestructible and immutable particles which are subject to causal physical laws was proposed over 2500 years ago in ancient Greece.[9] In the first century BC, Titus Lucretius Carus in Rome explained many chemical and physicochemical phenomena with the atomistic model, of course in a simplistic and qualitative manner. For a long time this materialistic approach did not prevail over theological or teleological world views which embraced Aristoteles' continuum model, but it never completely died out during the Middle Ages.[10, 11]

The revival of "causal mechanical" atomism began in the Renaissance and continued to gain momentum. In 1611 the German astronomer Kepler explained the symmetry and structure of hexagonal snowflakes by the close-packing of

[*] Prof. Dr. W. H. E. Schwarz
Department of Chemistry, University of Siegen
57068 Siegen (Germany)
and
Tsinghua University Beijing
Beijing 100084 (China)
E-mail: schwarz@chemie.uni-siegen.de

hard, ball-like water particles. In 1646 the French physician Magnien deduced the first realistic value of molecular sizes from the diffusion of fragrances in the air. In 1661 the English polymath Robert Boyle advocated that physical elements should be deduced from experimental chemical analysis—a goal that was reached towards the end of the 18th century by a group of French chemists led by A. de Lavoisier. On this basis, the English scientist John Dalton introduced the concept of mechanical atomism into early 19th century chemistry which thereby became one of its fundamental concepts. Molecules are formed of unalterable nonpenetrating spherical atoms that stick together when bonded. The stoichiometric findings of chemical statics could then be explained quantitatively with the help of relative atomic weights and integer valence numbers.[9–12]

In the 18th century Daniel Bernoulli laid the basis for the kinetic theory of gases. This "kinetic" atomism was fully implemented by Clausius in the mid-19th century and shortly thereafter culminated in the statistical mechanics of indivisible particles put forth by Boltzmann, Maxwell, and Gibbs. Chemical reaction kinetics and reaction equilibria could be explained phenomenologically. Maxwell, also the father of electrodynamics, explicitly favored the concept of atoms as "immutable homogeneous hard vibrating bell-like elementary bodies", which can absorb and emit electromagnetic radiation.[11,13]

Speculations on Inter-Atomic Interactions. A further atomistic concept had been developed starting in the 18th century, namely a "dynamic" atomism of physical force centers. Isaac Newton and subsequently the Croatian polymath Ruđer Bošković assumed the atoms to be comparable to modulated gravitational (or electric) force centers. After Volta's invention of the electric battery in 1800 and the subsequent electrolysis of many compounds, Berzelius conjectured the heteropolar bonding of multipolar electric atoms. In 1844 Faraday, the father of electrochemistry, rejected the mechanical atomism in favor of the dynamic one. In his influential Faraday Lecture of 1881 in London, H. von Helmholtz discussed the problem of how long-range Coulomb interactions could give rise to short-range homopolar binding forces between atoms with an electrical structure.[11–14]

Common to all speculations during the century between Berzelius and Bohr was the notion that bonding is due to a *static* attraction between atoms, possibly derivable from some electromagnetic potential. Even when internal electric

W. H. Eugen Schwarz received a diploma in experimental physical chemistry from Hamburg University and a PhD in natural philosophy from Frankfurt University. From 1976 until 2002 he was a professor of theoretical chemistry at Siegen University. He worked on quantum chemical theory and applications (atomic core potentials, relativistic effects etc), on the elucidation of basic chemical concepts (bonding, periodic table), and on the history and philosophy of chemistry. As an emeritus professor he is still active at the Theoretical Chemistry Center of Tsinghua University Beijing.

motions in the atoms were considered for the exchange of radiation, they did not play a role in chemical bonding. This presumption survived in the atomic bonding models of Stark (Figure 2) and of Lewis and Kossel (Figures 3 and 5), and even in Slater's statement of 1933 that "the mechanism of this [homopolar] binding is one in which [electronic] charge concentrates between the nuclei and is attracted electrostatically by both nuclei, this attraction producing the binding".[15] The traditional view that valency has a purely electrostatic origin without contributions due to inner-atomic electronic kinematics has survived in many chemical textbooks and in Bader's theory of Atoms in Molecules (QTAIM).[16]
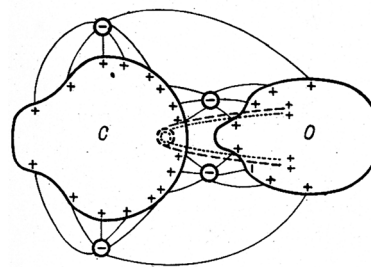

Figure 2. Stark's speculative model of electrostatic bonding in the CO molecule (1915).[17] Similarly complex models had been proposed repeatedly since Berzelius (1815).
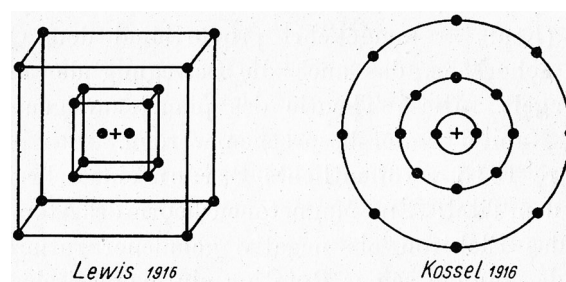

Figure 3. Cubic (left: Lewis)[18] and circular/spherical models (right: Kossel)[19] of the atomic shell structure (1916), accounting for the chemical and atom-spectroscopic observations that indicated stable shells containing two and eight electrons.

Speculations on the Intra-Atomic Structure. In fact, until 1890 nothing was known about atoms other than their gas/fluid/kinetic dimensions and masses, their chemical behavior (presumed to be related to electric properties but still irreducible to physics), and their UV/Vis spectra (of completely mysterious origin). In 1891 Stoney discussed the electron as a basic component of atoms and gave it this name.[20] A milestone toward the elucidation of the internal atomic structure was Thomson's discovery in 1897 of the electron as a very light particle.[21] Other physicists had also detected the electron but were dubious that such tiny particles could exist at all. In the same year the Dutch physicist Lorentz, using a model of oscillating electrons, explained the influence of a magnetic field on atomic spectral lines, which had been recently discovered by his former student Zeeman.[11–14]

In the first decade of the new century, Perrin in France, Nagaoka in Japan, and Lodge and Nicholson in England mentioned planetary atomic models. From the electrostatic point of view, a central positive point charge surrounded by negative electrons would collapse. Therefore Thomson suggested his "plum-pudding" model of the atom with "negatively electrified corpuscles enclosed in a sphere of uniform positive electrification".[21] From the electrodynamic point of view, moving electrons would radiate and lose energy. Therefore, various authors had concluded that stable atoms contain electrons at rest in symmetric arrangements consisting of concentric circles or spherical shells, each shell with a maximum occupation (Figures 3 and 4). Lewis speculated about the "cubic atom" and bond formation by completing shells of eight electrons by interatomic "electron sharing" (Figure 5).[18] Still today there are few chemistry textbooks (e.g. Ref. [53b,58]) that mention (dynamic) electron sharing as the physical origin of covalence.
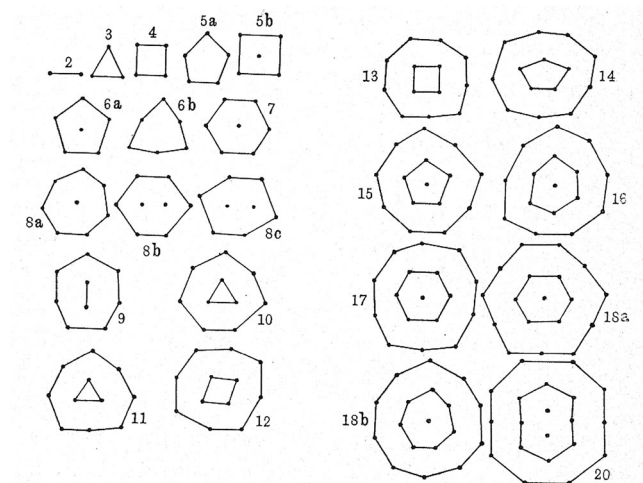

Figure 4. Classical electro- and magnetostatic models of atomic shell structure around 1900, for repulsive particles in a smoothly attracting field. Taken over by Thomson from A. J. Mayer's experimental model of floating magnets (1878).[21b]

Regarding the atomic weights, the English physician Prout had proposed around 1815: 1) that all atoms of an element are identical and 2) that they are formed by accretion of basic hydrogen atoms. But this second conjecture seemed to be disproven by Berzelius' accurate determinations of atomic weights around the same time. The consensus was then that the masses $m(Z)$ of all atoms of an element Z are equal but
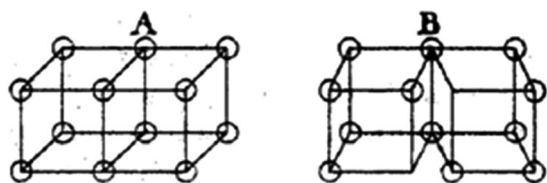

Figure 5. Lewis' model of double bond formation A←B,[18b] showing both the sharing and the resulting pairing of bonding electrons.

non-integer in terms of the unit $m(H)$. It was intriguing, however, that many masses were close to integer values. Crookes had surmised already in 1884 that individual atomic masses are integer but that "our atomic weights merely represent a mean value" of what was later called isotopes (a term introduced in 1913 by the chemist Soddy). In 1901 Lord Rayleigh estimated a chance of less than 1‰ for so many atomic weights having near-integer values, without any physical reason. The conjectures of Prout, Crookes, and Rayleigh were eventually confirmed in 1920 by Aston, who demonstrated the isotopy of many elements by means of the mass spectrograph.[10–14]

2. Bohr's Path to a New Atomic Model

When Atoms Were Incomprehensible. Niels Henrik David Bohr[23–26] was born in Copenhagen in the fall of 1885. His mother Ellen née Adler descended from a wealthy Jewish banking family; his father was a professor of physiology and, together with his two sons, an early promoter of soccer in Denmark. After finishing high school with very good exam grades, at least in the sciences, Niels Bohr enrolled at Copenhagen University taking courses in physics, mathematics, astronomy, chemistry, and philosophy. Despite his manual skills, the chemistry lab course proved not easy for him. Since his schooldays he was particularly interested in new physical discoveries such as X-rays (1895), radioactivity (1896), and the electron (1897). He did not finish his studies in the shortest time, but he finally completed his theoretical Master Thesis (1909) and Doctoral Dissertation (spring 1911) on the electron theory of metals, critically advancing ideas of Drude and Lorentz. He concluded: "It does not seem possible [… by the classical] electron theory to explain the magnetic properties". Wanting to learn more on recent developments of electron theory, he applied for a one-year postdoctoral scholarship from the Carlsberg Brewery Foundation. In the fall of 1911, he went to the Cavendish Laboratory at Cambridge directed by Thomson, the "father" of the electron. He attended lectures and lab courses, but scientific cooperation with Professor Thomson did not develop in the way that he had hoped.

By that time, the existence of atoms was generally accepted by physicists and chemists. Moreover, atoms were no longer thought of as indivisible: All atoms contained negatively charged, light electrons and a positive part of unknown mass. There was no evidence, though, on the number of positive and negative charge units in the atoms. The atoms could undergo radioactive changes emitting α-, β-, and γ-rays, and they could absorb and emit electromagnetic IR, Vis, UV, and X-radiation. Substances were known that were chemically identical but with different mass numbers. Various atomic models were discussed,[27,28] foremost Thomson's.[21,22] He first assumed the total mass of the atoms to stem from the electrons, which implied thousands of electrons per atom. Later it turned out that the number of electrons is of the order of the atomic mass number.[29] In his "plum-pudding" model Thomsen assumed that the electrons are immersed in a heavy positive background charge and

arranged them in stationary shells (Figure 4). In 1904, the Japanese physicist Nagaoka proposed the alternative "Saturnian" model of electronic rings around a very tiny nucleus.[30] Atomic shell models might have explained the periodicity of the elements, but the classical shell numbers of Thomson, Nagaoka, and others could not reproduce the chemical and the atom-spectroscopic proof.

Newton's classical mechanics and Maxwell's classical electrodynamics had been extremely successful in the continuous macroscopic regime. The conceptual inconsistencies between the two (e.g. unlimited versus limited velocities) had been resolved by Einstein in 1905, at the age of 26. In cases where microscopic discrete atomistic phenomena could not yet be explained, most physicists, in particular in the Commonwealth, were hesitant in accepting ad hoc hypotheses violating continuous classical physics.[23–27] However, in 1900–1901 Max Planck proposed discrete energy exchanges between quantized atoms and the electromagnetic field, thereby deriving the correct entropy of the observed "blackbody radiation".[31] In the "Annus Mirabilis" of 1905 Einstein also extended this idea by quantizing the electromagnetic field energy, as a "heuristic" guiding principle to explain the observations of the photoelectric effect.[32] And in 1910, Arthur Erich Haas[33] tried to explain why the size of all atoms is in the Å range, as first deduced by Loschmidt[34] in 1865 from the kinetic gas theory for the "molecules of air". Haas inferred that the size of the atom has a fundamental physical meaning. Only by combining Planck's constant h together with other known natural constants, was he able to obtain a length of the right order of magnitude. Initially, his dissertation was ridiculed, however.

Atomic Speculations and Facts. In the fall of 1911, Bohr happened to meet Professor Rutherford from Manchester, a center of research in radioactivity. Already in 1908 and 1909, Rutherford's senior co-worker Hans Geiger and undergraduate Ernest Marsden had measured a low but finite 0.01 % probability of backscattering of α-particles by thin Pt and Au foils.[35] Could that be explained by Thomson's atoms consisting of light electrons? In 1911 Rutherford gave a well-founded answer.[36] Supported by scattering calculations, he conjectured that atoms contain a heavy, positively charged "kernel" 10^5 times smaller than the whole atom. The physical community was not excited and Thomson even disbelieved it.

The first evidence on the atomic charge numbers appeared during the year 1911. Based on his analysis of Geiger–Marsden's data on α-scattering, Rutherford deduced nuclear charges Z of the order of approximately one-half of the atomic masses, $Z \approx A(Z)/2$.[36] From the analysis of X-ray scattering, the English physicist Barkla deduced total atomic electron numbers N of similar magnitudes.[29] The Dutch lawyer and hobby scientist van den Broek concluded in 1913 that the atomic number in the periodic system is equal to the nuclear charge and the number of atomic electrons.[37] The hydrogen atom probably had one electron in the field of a singly charged nucleus. All these conjectures were still under discussion, however.

In the spring of 1912, Bohr moved to Manchester where he worked again experimentally and theoretically.[1,6,7] He learned a lot about radioactivity from his friend, the Hungarian chemist von Hevesy, a postdoctoral associate in Rutherford's laboratory. It was known that α- and β-rays consist of particles with charges $+2$ and -1. Bohr believed in the "nuclear atom" and interpreted both rays as nuclear phenomena, while many colleagues related β-radiation to the electrons in the atom. In Bohr's eyes, only the electromagnetic spectra and chemistry were due to the atomic electrons. Bohr even anticipated the radioactive displacement laws, published a year later independently by the chemists Fajans and Soddy.

Classical Physics Corrected Empirically by Quantum Concepts. In the summer of 1912, Bohr integrated his knowledge of atoms and came up with an atomic model of a heavy core surrounded by orbiting electrons. He applied classical theories of mechanics and electrodynamics as far as consistent with the facts, and added ad hoc assumptions where needed to reproduce the observed atomic stability and the discrete radiative transitions. He sent seven handwritten pages to Rutherford (later called the "Rutherford Memorandum")[6,7,23,26] as an outline of his future manuscript "On the constitution of atoms and molekules".[1] He prepared to paint a great picture of the subatomic structure of all matter. But Rutherford was yet somewhat hesitant in accepting Bohr's bold visions, but supported the young scholar.

Electronic shell models like those in Figures 3 (right) and 4 were common at the time. In contrast to Thomson's model, electron rings attracted by a heavy central point charge are mechanically stable only in the presence of a kinetic rotational centrifugal force. For any stable system held together by Coulomb (as well as gravitational) forces, the virial theorem imposes a strict relation between the (negative) total energy E and its (positive) kinetic and (negative) potential contributions E_{kin} and E_{pot} [Eq. (1)].

$$E = E_{kin} + E_{pot}; \; E_{kin} = -E; \; E_{pot} = 2E. \qquad (1)$$

Two problems arise then, one mechanical, the other electromagnetic, which were "corrected" by Bohr.

First, the radius of the electron ring in the model atom depends on the speed of rotation, which is classically arbitrary, as for the planetary orbits. In order to obtain theoretically the *same* radius in the observed Å range for all atoms of a given element, an "appropriate" quantization is required. Motivated by the quanta hypothesis for electromagnetic radiation $E_{photon} = h\nu_{elmag}$, and the harmonic oscillator hypothesis $E = nh\nu_{osc}$, where $E_{kin} = \frac{1}{2}E$, Bohr at first considered the quantization of the atomic rotational kinetic energy as $E_{kin} = (n/2)h\nu_{orbit}$, ($n$ = "quantum" number 1, 2, 3, …; ν_{orbit} = orbiting frequency). But the equivalent quantization of angular momentum ℓ was more elegant and easier to generalize [Eq. (2)].

$$\ell = (n/2\pi) \cdot h = n \cdot \hbar \qquad (2)$$

The quantization rule had also been introduced in 1912 into a planetary atomic model by Nicholson,[38] however, within a complex scheme of unproductive hypotheses.[3,6,7,39]

Second, a rotating charge would emit radiation according to classical electrodynamics, and the orbiting electron would fall into the point nucleus within nanoseconds (Figure 6). The
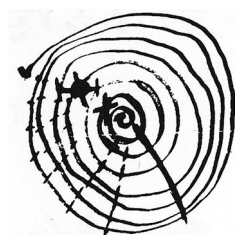

Figure 6. Bohr (Rutherford Memorandum 1912) on the instability of atoms in classical physics: an orbiting electron spirals into the nucleus.

nonclassical assumption of the quantization of angular momentum ensured the stability of the electron rings. In addition, Bohr posited that the atomic electrons would not emit electromagnetic radiation according to classical theory—neither continuous radiation upon continuous transition between the stationary orbits, nor discrete radiation with the rotational frequency of the initial or final orbits, nor radiation with deformative vibrations of the rings, a common assumption of the time. Instead, discrete nonclassical radiation should occur in accordance with the empirically derived Rydberg–Ritz combination principle (1888/1908) and the Planck–Einstein formulas (1901/1905) [Eq. (3)].

$$E_{\text{initial orbit}} - E_{\text{final orbit}} = E_{\text{rad}} = h\nu_{\text{rad}} \qquad (3)$$

Since his PhD dissertation of 1911, Bohr had been aware of the failures of classical theory in describing atoms and metals. Generally known were moreover Planck's nonclassical explanation of thermal radiation (1901), Einstein's nonclassical explanation of the photoelectric effect (1905), and Einstein's quantization of mechanical molecular vibrations (1907).[40] The latter explained the vanishing of the specific heat in solids at zero temperature. The Dutch physicist Peter Debye finally (1911) derived the accurate T^3 law from the quantum hypothesis. Rutherford was critical of Bohr's quantization assumptions; nonetheless he helped Bohr improve his extended manuscript.[1a] However, Thomson and other British atomic theoreticians reacted negatively.[6, 7]

Accurate Theory of the One-Electron Atom. In Part I of his trilogy[1a] Bohr discussed the H atom and its spectra, which were known with high precision. Bohr's model of one electron e^- orbiting around a heavy proton p^+ reproduced the spectral series reported by Balmer (a Swiss teacher, 1885) and Paschen (1908) and predicted the Lyman (already in the literature since 1906), Brackett (1922), and Pfund (1924) series. Bohr also explained why the Balmer series ended in laboratory experiments around quantum number $n = 12$. He noted that the atoms in the excited Rydberg states become too big (in the μm range) to remain unperturbed at the gas pressure of a few Torr used in the investigations. He furthermore recognized that the "hydrogen spectra" described by the American astronomer Pickering (1897) and the English physicist Fowler (1910) arose in fact from He$^+$. He explained with astonishing accuracy the small experimental deviation from the respective hydrogen lines,[1b] by a factor of $f_{\text{exp}} = 1.00040$, as being due to the ratios of the masses of the electron (m_e) and the hydrogen (M_H) and helium nuclei (M_{He}) [Eq. (4)].

$$f_{\text{theo}} = 1 + [m_e(M_{He} - M_H)/(M_{He} \cdot M_H)] = 1.00041 \qquad (4)$$

In addition, Bohr could derive the value of the spectroscopic Rydberg constant from the experimental values of e, m_e, h, c, and ε_0 at the level of experimental accuracy. The reactions from the physical community were diverse, from "pure nonsense" to "there may be a grain of truth in it" to "brilliant". The German physicist Sommerfeld was so impressed that he extended Bohr's model of circular orbits to elliptical orbits (Figure 7) corresponding to different angular momentum states in modern quantum theory. The relativistic extension even reproduced the spectroscopic fine structure.
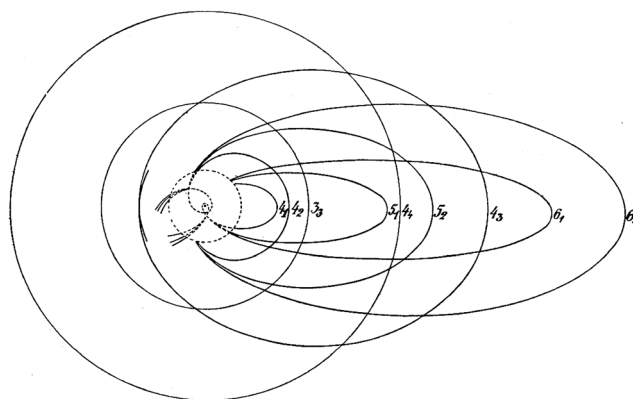

Figure 7. Sommerfeld's spectroscopic orbits of the potassium atom (4_1 to 6_2 corresponding, in modern nomenclature, to 4s to 6p), from Bohr's Nobel Lecture 1922.[41]

Successes and Failures for Many-Electron Atoms. In Part II of his trilogy,[1a] Bohr discussed atoms with several electrons. Since the Pauli exclusion principle (1925) was not yet known, no safe ground existed for deriving the maximum electronic occupations of the atomic orbits. Chemical evidence and atomic spectra were of some modest help. In modern notation, Bohr correctly assumed the configurations H 1s^1, He 1s^2, Li 1s^{2}2s^1, Be 1s^{2}2s^2, but then his speculations ran astray: B 1s^{2}2s^3, C 1s^{2}2s^4, N 1s^{4}2s^3, O 1s^{4}2s^{2}3s^2, F 1s^{4}2s^{4}3s^1, Ne 1s^{8}2s^2, etc. Bohr improved his suggestions over the years, but his electron configurations for the noble gas atoms proposed in 1921 (up to element Uuo = $_{118}$E) were still wrong (Figure 8).[42]

Remarkably,[42, 43] Bohr was also the first in 1922 to suggest a 5f-block of elements (see below Figure 12) as the homologue of the 4f-block of rare earth metals, a quarter century before Seaborg. Regarding the transition metals of the nth period, he stressed in 1923 that the orbits, now called $(n-1)$d shells, are more strongly bound than the most loosely bound electron in the outer valence ns shell of neutral atoms. From the atomic Vis, UV, and X-ray spectra, he derived the orbital energy levels of the neutral atoms and plotted them versus the nuclear charges Z (Figure 9). His deductions were more realistic than the descriptions in many current chemistry textbooks. Since he was not sure, for which Z values in the d- or f-blocks the $(n-1)$d or $(n-2)$f levels would fall below the ns levels, he dotted some of the curves in the respective Z ranges.

| Element | Atom-nummer | | | | | | | | | | | | | | | | | | | | | | | | |

Element	Atomnummer	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	6_4	6_5	6_6	7_1	7_2	7_3
		Anzahl der Elektronen in den n_k Bahnen																						
Helium	2	2																							
Neon	10	2	4	4																					
Argon	18	2	4	4	4	4	–																		
Krypton	36	2	4	4	6	6	6	4	4	–	–														
Xenon	54	2	4	4	6	6	6	6	6	6	–	4	4	–	–										
Niton	86	2	4	4	6	6	6	8	8	8	8	6	6	6	–	–	4	4	–	–	–	–			
?	118	2	4	4	6	6	6	8	8	8	8	8	8	8	8	–	6	6	6	–	–		4	4	–

Figure 8. Bohr's electron configurations (1921, still incorrect) for the rare gas elements up to "Niton" ($=$ radon) and E118.[42] n_k orbits correspond to $n_{\ell=k-1}$ orbitals (or to $n_{j=k-1/2}$ spinors), for example, 4_1, 4_2, 4_3, 4_4 to 4s, 4p, 4d, 4f.
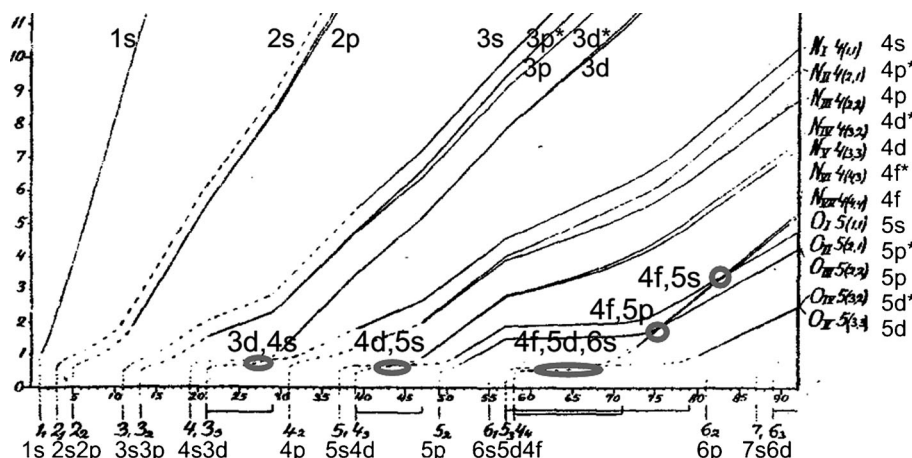

Figure 9. Plot of Bohr's atomic orbit energies ε (in terms of $\gamma = \sqrt{IE}$, $IE =$ orbit ionization energy in Rydberg $= 13.6$ eV; strongly bound orbits have high γ values) versus nuclear charge, $Z = 1$ through 92 (from 1923).[43] At the top and bottom and on the right of Bohr's diagram, we have added the modern orbital symbols 1s, 2s, 2p ... 4s, 4p*($=4p_{1/2}$), 4p ($= 2p_{3/2}$) etc. corresponding to Bohr's orbit symbols 1_1, 2_1, 2_2 ... N_I $4_{(1,1)}$, N_{II} $4_{(2,1)}$, N_{III} $4_{(2,2)}$ etc. We note Bohr's order of orbit energies when the orbits first become occupied, see the bottom line. For example, for the sixth row of the periodic table with $Z = 55, 56, 57, 58$ (Cs, Ba, La, Ce) he correctly gives 6s < 5d < 4f (while chemical textbooks traditionally give 6s < 4f < 5d). We also note the change of order of the valence orbit energies for the later lanthanoids and the 5d transition elements, where he correctly gives 4f < 5d < 6s (while chemical textbooks still teach 6s < 4f < 5d). Since Bohr was not sure of the exact Z value, where these crossings of the orbit energies occur, he dotted the beginnings of the orbit-energy curves. We have indicated the Z ranges, where the orbit(al) energy order changes, by bold ellipses or circles.

An approximate relation between the wavelengths λ_K of the characteristic X-radiation of the elements and their atomic weights A had already been found empirically, $1/\sqrt{\lambda_K} \sim A$. Several X-ray physicists had suggested "correcting" the chemical A values according to their observed wavelengths or absorbances. Concerning A for $_{27}$Co $= 58.9$, $_{28}$Ni $= 58.7$, and $_{29}$Cu $= 63.55$, the value for nickel should be increased by about $2\frac{1}{2}$ units and would then lie halfway between Co and Cu.[29] Bohr's identification of the characteristic K_α and K_β X-ray emissions as being caused by electronic 1s←2p,3p orbit jumps became a basic advance. Thereby the nuclear charges Z could be derived uniquely and accurately. In 1913–1914 the young English physicist Moseley[44] measured the characteristic X-ray lines of "all" elements (from Al to Au) in Rutherford's lab in Manchester (and later in Oxford) and, with the help of Bohr's atomic model, he established the nuclear charges [Figure 10 and Eq. (5)].

$$Z - \zeta = \text{const} \cdot \sqrt{\nu_{K\alpha}} \qquad (5)$$

ζ is a constant accounting for the nuclear screening by the other electrons. The chemical arrangement of Fe, Co, Ni, Cu in the periodic table could be verified by the physicists as following the Z and not the A values. Notably, the correct chemical positions of the lanthanoid elements could be deduced physically. Thus, the way was opened for a physical foundation of the periodic system of chemical elements.

Molecules Pose a Real Challenge. Part III of the trilogy[1a] was devoted to chemical bond formation. Bohr constructed bonds by "Lewis pairing" the atomic valence electrons on rings rotating in a quantized fashion around the interatomic axes. He had graphically displayed his ideas on the theory of chemical matter already in the "Rutherford Memorandum" of 1912 (Figure 11). As in the case of the hydrogen atom, Bohr devised a classical-mechanical model for the molecules and determined the ground state as a classical-mechanical force equilibrium (energy minimum) under the condition of the nonclassical ad hoc constraint of quantized angular momenta. Single bonds were represented by rotating electron pairs (Figure 11: the H–H bond in H_2 and the four C–H bonds in
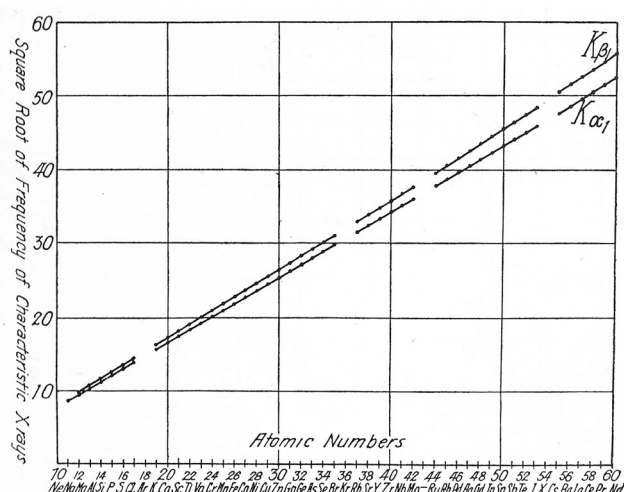
Figure 10. Moseley–Bohr's law (5) for nuclear charge Z and frequency of the K_α radiation, fixing the atomic numbers of the elements in the periodic system.[44]

Figure 12. Bohr's periodic table of 1922, for H up to Uuo, showing for the first time the seventh period including a 5f block.[42]

CH_4) and the double bond in O_2 by a rotating electron quartet (with six electrons in each O 1s inner core shell). The water molecule was assumed to be linear, H−O−H. Remarkably, Bohr had already a feeling for "structure resonance" in ozone: he represented O_3 (again linear) by two different models.

The H_2 molecule, only sketched in the "Rutherford Memorandum", was treated explicitly in the trilogy. Bohr obtained $R = 58$ pm for the bond length (correct value 74 pm) and $D = 2.7$ eV for the dissociation energy (correct value 4.75 eV, without zero-point correction). The HHe and He_2 molecules were correctly calculated as unstable, while the unstable H_3 molecule was predicted as stable and the stable
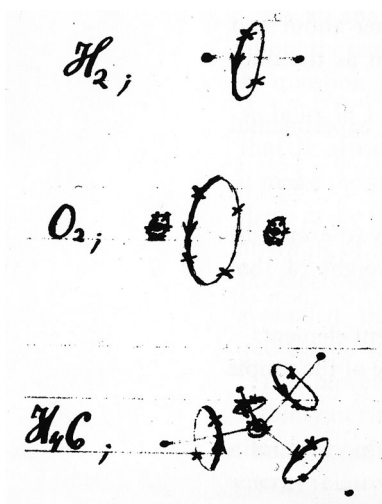

Figure 11. Bohr's models of H_2, O_2 and CH_4 molecules in the "Rutherford Memorandum" of 1912. He reproduced the chemical concepts of H−H and C−H single bonds and of O=O double bonds: Angular-correlated electron pairs rotate around the internuclear connection line, attracted by nuclei and atomic cores of H^+, $C(1s^2)^{4+}$ or $O(1s^6)^{2+}$. Angular momentum quantization was assumed as in the atoms.

H_3^+ molecule as unstable. Since the order of magnitude of the derived values was correct for H_2, there seemed to be a grain of truth in Bohr's concept of combining classical dynamics with the "arbitrary" constraint of angular momentum quantization. The quantitative accuracy in the smallest two-electron molecule was, however, not even remotely comparable to that in the one-electron atoms H and He^+. A few years later Pauli applied Sommerfeld's action-quantization to the one-electron molecule H_2^+, again assuming an angular momentum instead of a linear motion through the nuclei with $\ell_z = 0\hbar$ and predicted it metastable with a decomposition energy of $D = +6\frac{1}{2}$ eV at $R = 293$ pm (correct: $D = -2.8$ eV, $R = 106$ pm).[45] The Bohr and Sommerfeld models were not at all reliable for molecules.

The Periodic System of Elements.[6,8,42] In relating the chemical elements to the electron configurations, Bohr included more empirical facts and relations, in particular from chemistry. He replaced the classical-mechanical shell-filling by 2, 7, and 10 ± 2 electrons (see Figure 4) and his symmetry-driven choices (e.g. Figure 8) by the empirical octet rule, which originated in a suggestion from the German chemist Abegg in 1904.[46] Among the multitude of graphical representations of the periodic system in the literature, Bohr chose a "long table" design, in particular the one which exhibited the chemical differences and cross-relations between the s-, p-, d-, and f-block elements; he did not place the f elements in a footnote (Figure 12). This format had first been suggested by the English chemist Bayley in 1882 and by the Danish chemist Thomsen in 1895.[47] Remarkably correct, Bohr let the 4f elements begin with Ce, the first element indeed with 4f valence participation, and he first suggested a 5f block (though beginning only after the first trans-actinides). Extending his periodic table to element 118, Bohr discussed the possible structures and stabilities of then

unknown nuclei. Atoms of these elements have been synthesized in the past, with element 118 (called Eka-Radon or Ununoctium) being the heaviest so far.

3. Hindsights and Insights

The Old Quantum Concepts.[6,7] The foundations of classical physics were completed with Maxwell's electrodynamics and Boltzmann's statistical thermodynamics in the decades between 1860 and 1890. During this time, however, physical spectroscopy and chemical investigations began to produce a large body of data pertaining to atoms and molecules that challenged explanation by classical theory. Some leading scientists such as the Austrian physicist Mach, the Bohemian chemist Wald, the German chemists Ostwald and Kolbe, and the English chemist Brodie rejected physical atomism as being too speculative and anti-positivistic. Many leading physicists, notably in England, persisted in strictly applying classical physics in the microscopic regime.

The German-speaking physicists Planck, Einstein, and Haas realized that certain important microscopic phenomena could be rationalized by the introduction of "artificial" quantum concepts. Many scientists were unimpressed or even contemptuous of such ad hoc assumptions. Indeed, some speculations put forth at that time turned out to have little merit. In hindsight Bohr's reasoning differed from that of others in two respects. He perceived which basic physical concepts and logic were essential and should be maintained, and he embedded experimental quantum facts into the internally consistent classical continuum theory only where the latter proved to be inadequate or incorrect. While Bohr was a theoretical physicist by nature, he had experience in experimental techniques and was familiar with practical physics as well as chemistry. Several famous chemists such as Bjerrum, Brønsted, and von Hevesy were among his lifelong friends.

In the summer of 1912, during his stay with the creative Rutherford group, Bohr conceived the idea of quantizing both the stationary motion and the electromagnetic radiation of the electrons. From this basis, he set out to develop his ambitious program of explaining all atoms and molecules. He was aware that classical physics was insufficient and that he was searching without knowing the final answer. Several physicists were impressed by the accuracy of his theoretical results (derivation of the Rydberg constant, spectra of H and He$^+$) and by the relevance of his semiempirical deductions (orbit(al) energies in atoms, interpretation of the X-ray spectra of all elements, splitting of atomic lines by fields, etc.).

It may be noted that Bohr was lucky to benefit from some "error cancellation". Instead of quantizing the electronic motion in three-dimensional space (as Sommerfeld subsequently did, obtaining three quantum numbers: the principal, the angular momentum, and the directional ones), Bohr quantized only one dimension. He therefore missed some quantum kinetic zero-point energy, as became apparent much later on the background of Heisenberg's uncertainty relation. On the other hand, Bohr assumed the lowest angular momentum to be $1\hbar$ instead of $0\hbar$. These two "changes" cancel in the energy exactly in the case of H-like atoms, but not in general. Accordingly, Bohr's model did not work well for many-electron atoms and for molecules.

For most chemists, Bohr's derivations were too complicated, too unusual, or simply unacceptable. For instance, his hydrogen atom with a planar electron orbit did not fit well with Dalton's model of spherical atoms. Therefore, three-dimensional images of many-electron atoms were published, by Sommerfeld starting in 1918, by Bohr starting in 1921, and by colleagues subsequently.[39,49] Real models made of balls and wires were sketched and published.[5,6] Planetary models determined the iconography of the atoms for the general public. In particular, Bohr's model began to be mentioned in chemistry textbooks after he had received the Nobel Prize in 1922. By that time, however, the shortcomings of Bohr's approach were already apparent and the search for more radical modifications of classical physics was under way. Following the invention of wave mechanics, planetary models disappeared in the physics community. The chemistry community failed to absorb some of Bohr's chemically relevant qualitative insights.

The Periodic System.[8] During the decade after the trilogy, Bohr and his colleagues laid the foundation for a physical rationalization of basic chemical concepts, including the periodic system, by what may be viewed as an eclectically mixed theoretical–empirical approach. Bohr–Moseley's law yielded unique nuclear charges and element numbers for all elements. The update of Bohr's atomic model by Sommerfeld's three-dimensional action-quantization and the introduction of the spin and the exclusion principle by Pauli led to a well-grounded concept of atomic core and valence shells and to the correct filling numbers of 2, 8, 18, and 32 electrons for closed shells. Bohr and Pauli introduced the rules of the "Aufbau principle". The order and variation of the atomic orbit(al) level energies for the series of atoms were correctly derived from the empirical spectroscopic data (Figure 9).

Since the early 1920s, the orbit(al) energy order of the atomic inner shells was known:

$$1s \ll 2s < 2p \ll 3s < 3p < \mathbf{3d} \ll 4s < 4p < 4d < 4f \ll 5s \ldots \qquad (6)$$

In the valence shells the order is different, however.[50] The experimentally derived (and later theoretically verified) paradigm for all d- and p-block elements is, for the example of the 4th period:

$$\ldots 3p \ll \mathbf{3d} < 4s < 4p \ll \ldots \qquad (7)$$

The strong nuclear shielding by the core-shells of the first elements of a period results in a strong energetic destabilization of the valence d and f orbitals in the atoms of Groups 2 and 1. For Ca$^+$, as the paradigm of the alkaline earth metals of Group 2, Equation (8) holds.

$$\ldots 3p \ll 4s < \mathbf{3d} < 4p < 5s \qquad (8)$$

And for K, as the paradigm of the alkali metals of Group 1, Equation (9) holds.

$$\ldots 3p \ll 4s < 4p < 5s < \mathbf{3d} \qquad (9)$$

The spectra of the alkali metal atoms were the first after those of the hydrogen-like elements to be understood and assigned. The main drawback of Bohr's atomic model was that accurate values for the orbit(al) energies could not be obtained theoretically for any many-electron atom. His model worked only at the qualitative level; that is, it could be used to extract reliable orbit(al) energies from simply structured experimental atomic spectra.

Remarkably, the order (8) of the orbital energies of the alkaline earth metal atoms has since entered all chemistry textbooks as the standard valence orbital energy scheme for all other atoms, because it led to a simple (though incorrect) "physical deduction" of the structure of the periodic system. Since then, chemistry students have had to learn, in contradiction to the Aufbau principle, that in the nth period, transition metal compounds have an empty ns shell below the partially occupied $(n-1)$d valence shell, and that the valences of the main group atoms are due to the active shells ns below and np above the intermediate, filled $(n-1)$d^{10} core shell. Bohr had noticed early on the changes in the atomic level ordering along the series of elements. However, he was not yet sure in his Nobel lecture of 1922, for which groups of elements the reversal of the $(n-1)$d and ns valence levels would occur (see Figure 9). The valence electron spectra of the transition metal atoms were too complex to be analyzed by his model. This became possible only after the invention of wave mechanics starting in the late 1920s.

Chemical Bonding. Bohr's attempts to understand the bonding in molecules were less successful since the aspects that were missing in the "old quantum theory" are in fact essential for chemical binding. It is now known that there are three physical mechanisms that can lower the valence electron energy thereby creating bonds between atoms: 1) an increase in the effective nucleus–electron attraction in polar bonding, 2) an attenuation of the electron–electron repulsion in correlation and dispersion bonding, and 3) a damping of the electronic kinetic zero-point energy in homopolar bonding.[51] The third of these mechanisms is related to the uncertainty relation, which was formulated in 1927 by Heisenberg while working in Bohr's group, a mecca of theoretical physics of the time. In many-electron molecules, a correct energy assessment also requires taking into account Pauli's exclusion principle which was outlined in 1925. It was thus only in 1927, after the formulation of new wave mechanics, that the first sound quantitative determinations of covalent bonding became possible, namely for H_2 by Heitler and London in Germany and for H_2^+ by Burrau in Denmark. Physical understanding and well-founded explanations of bonding, however, were initiated only 35 years later when Ruedenberg[52] showed that a basic driving force is the attenuation of the quantum kinetic energy by "Lewis sharing" of electrons between atoms, an insight that was later greatly extended by Kutzelnigg[53] and others (see the collection of references in Ref. [52c]).

It therefore stands to reason that even the simplest chemical bond, that in the H_2 molecule, could not be treated with sufficient reliability by Bohr's quantum concepts. He derived the expression of the kinetic energy of his H_2 model (Figure 11 top) for minimum angular momenta of $\ell_z = 1\hbar$ for the two electrons in the orbit of radius r in the central plane: $E_{kin} = \hbar^2/m_e r^2$. Since this expression is the same as that for two separated H atoms, bonding is caused by an increase of the electron–nucleas attraction in Bohr's model—an explanation that was echoed twenty years later by Slater's conjecture mentioned above.[44] Although this simple classical electrostatic picture turned out to be flawed, it found its way into many chemistry textbooks and also into the Wikipedia: "The bond is caused by the electrostatic force of attraction between opposite charges"; in other words, electronic correlation and in particular kinetic energy effects are ignored.

An intriguing aspect of Bohr's models has more recently been uncovered by Herschbach,[45] who showed Bohr's expression for E_{kin} to be the high-dimensional limit of the wave-mechanical kinetic energy operator. His group determined reasonably accurate energy curves for many-electron molecules by a simple wave-mechanical first-order perturbation correction for the three-dimensional reality.

Science-Philosophical and -Historical Annotations. In the late 19th century, experimental atomic spectroscopy had reached a high level of reliability and accuracy, but most of the high-quality data simply gathered dust, since no theoretical framework existed for interpreting, assigning, organizing, or using them. The surprisingly accurate results of Bohr's model for the one-electron spectra of H and He$^+$ and the value of the Rydberg constant, and the various semiempirical deductions of effective one-electron energies instantly conveyed physical meaning to the large quantities of existing spectroscopic observations. It furthermore led to inferences that were fruitful in chemistry by establishing the reliable order of elements in the periodic system and by providing the first steps towards a physical explanation of the chemical periodicity. Bohr's work is an outstanding example of what determines the value of new theories, namely three points: the reproduction of existing experimental observations, the prediction of new facts, and the formulation of explanatory concepts that provide qualitative insights for both.

Every natural science is based on experimental facts, but the symbiosis with appropriate theoretical concepts is also necessary. If experimental scientists deliberate about the concepts and theory-based instruments they apply every day, they will realize that their business is not "purely empirical" science but heavily "theory-laden". One example are the so-called "experimental" molecular structures generated by the computers with software attached to the XRD and NMR instruments. On the other hand, representatives of "basic physical sciences" focus on structurally simple sectors of nature and then believe that more complex fields such as chemistry can be readily reduced to their science. Physicists such as Sommerfeld and Dirac thought that chemistry might become just a branch of applied theoretical physics.[60] In 1912, the young enthusiastic Bohr hoped to explain all atoms and molecules, despite his own experiences in chemistry and his close relations to experienced chemists.

Bohr's work is an outstanding example of the value of trying, in critical cases, "everything that goes" even if it goes against the grain of certain established, logically consistent

methods, in Bohr's case, however, under the strict constraints of the observed facts. The success of classical mechanics, electrodynamics, and thermodynamics had been so over-whelming that early in the 20th century many physicists strongly believed that the extrapolation of these macroscopi-cally successful theories into the microcosmos must also succeed without any modifications. The other extreme would have been a theory revolution[56] such as at the beginning of modern physics in the 17th century by Galilei and Newton or of modern chemistry at the end of the 18th century by Lavoisier. Bohr decided for an intermediate option and developed his theoretical-physical simulations of experimen-tal facts in a pragmatic and eclectic manner, as is usually more common among chemists. He was very successful, though only in a very limited range. Anyhow this success finally earned him acceptance in the physical community, which soon perceived that much more radical changes were required. After a dozen years, Bohr's model was washed away in physics by the scientific revolution of quantum mechanics, significantly supported in Bohr's famous discussion circle in Copenhagen.

Bohr's work had less impact in the chemical community than in physics. The success of the Bohr–Moseley law was readily accepted. His suggestion of a 5f-block of elements in the 7th row of the periodic table from element 87 through 118 was hardly considered until Seaborg's work in 1945.[59] A disappointing development was that Bohr's successful, basi-cally correct, description of the atomic orbit(al) level schemes was incorrectly taken over into chemistry. His molecular speculations, understandably, did not impress the chemists, but his predominantly classical model of covalent bonding did also not impede the development of a similar line of thinking in the chemical textbooks or in the QTAIM, which is now not easy for quantum theoreticians to correct (see the endeavors of Ruedenberg[51,52] and Kutzelnigg[53]). The phenomenon of "creating facts in a scientific thought collective" without a counterpart in reality was discussed by Ludwik Fleck already in the mid-1930s, in other contexts.[57]

Bohr's initiative towards a numerical theory and qualitative concepts for understanding the microworld behind the macroworld was mainly an enterprise of physically oriented scientists, although many scholars of different persuasions participated in the preparatory era. It was also a very international enterprise, even during the First World War, with contributions from English-empiristic and Germanic-theoretical circles as well as from many other European countries, Japan, and the USA. In physics, Bohr became the father figure of quantum theory. In chemistry, his insights are still being digested. His concepts of the atomic core and valence shells and element numbers were soon adopted. Bohr's and Sommerfeld's atomic orbit models are still useful in introductory courses, but have in recent decades been replaced increasingly by the wave-mechanical orbital cloud model.[3–8] However, even 90 years after Bohr's Nobel lecture, we are still waiting for many chemistry texts to teach the correct atomic orbital energy schemes [Figure 9 and Eqs. (6)–(9)], which can indeed be found in various quantum chemistry texts (see for example, Levine[58] and Kutzelnigg).[22,50]

[1] a) N. Bohr, *Philos. Mag. Ser. 6* **1913**, *26*, 1–25; N. Bohr, *Philos. Mag. Ser. 6* **1913**, *26*, 476–502; N. Bohr, *Philos. Mag. Ser. 6* **1913**, *26*, 857–875; b) N. Bohr, *Nature* **1913**, *92*, 231–232.
[2] The Nobel Prize in Physics **1922**, http://www.nobelprize.org/nobel_prizes/physics/laureates/1922/.
[3] H. Kragh, *Phys. Today* **2013**, *66*, 36–41.
[4] M. Eckert, *Phys. Unserer Zeit* **2013**, *44*, 168–173.
[5] a) A. Schirrmacher, *Phys. J.* **2013**, *12–7*, 43–47; b) A. Schirr-macher, *Kultur Technik* **2013**, *3*, 30–35; c) A. Schirrmacher in *Atombilder* (Eds.: C. Bigg, J. Hennig), Wallstein, Göttingen, **2009**, pp. 73–82.
[6] H. Kragh, *Niels Bohr and the Quantum Atom*, Oxford University Press, Oxford, **2012**.
[7] *Niels Bohr, Collected Works, Work on Atomic Physics, Vol. 2* (Ed.: U. Hoyer), North-Holland, Amsterdam, **1981**.
[8] Niels Bohr, *Collected Works, The Periodic System, Vol. 4* (Ed.: J. R. Nielsen), North-Holland, Amsterdam, **1977**.
[9] A. Stückelberger, *Antike Atomphysik*, Heimeran, München, **1979**.
[10] K. Ruedenberg, W. H. E. Schwarz, *Pioneers of Quantum Chemistry*, ACS Symp. Ser. 1122 (Eds.: E. T. Strom, A. K. Wilson), ACS, Washington, **2013**, pp. 1–45.
[11] B. Pabst, *Atomtheorien des Lateinischen Mittelalters*, Wissen-schaftliche Buchgesellschaft, Darmstadt, **1994**.
[12] A. J. Rocke, *Chemical Atomism in the Nineteenth Century*, Ohio State University, Columbus, **1984**.
[13] K. Simonyi, *Kulturgeschichte der Physik*, Urania, Leipzig, **1990**.
[14] *Atoms in Chemistry*, ACS Symp. Ser. 1044 (Ed.: C. J. Giunta), ACS, Washington, **2010**.
[15] J. C. Slater, *J. Chem. Phys.* **1933**, *1*, 687–691.
[16] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, University Press, Oxford, **1990**.
[17] J. Stark, *Die Elektrizität im chemischen Atom*, Hirzel, Leipzig, **1915**.
[18] a) G. N. Lewis, *J. Am. Chem. Soc.* **1916**, *38*, 762–785; b) G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, Chemical Catalog, New York, **1923**.
[19] W. Kossel, *Ann. Phys.* **1916**, *49*, 229–362.
[20] G. J. Stoney, *Proc. Br. Ass. Adv. Sci.* **1874**, *4*, 563; G. J. Stoney, *Sci. Trans. R. Dublin Soc.* **1891**, *4*, 563.
[21] a) J. J. Thomson, *Philos. Mag. Ser. 6* **1904**, *7*, 237–265; b) J. J. Thomson, *Elektrizität und Materie*, Vieweg, Braunschweig, **1904**.
[22] W. Kutzelnigg, *Einführung in die theoretische Chemie, Quanten-mechanische Grundlagen, Vol. 1*, Verlag Chemie, Weinheim, **1975**.
[23] a) *Niels Bohr, His Life and Work as Seen by His Friends and Colleagues* (Ed.: S. Rozental), North-Holland, Amsterdam, **1967**; b) R. Moore, *Niels Bohr: ein Mann und sein Werk verändern die Welt*, List, München, **1970**.
[24] a) U. Röseberg, *Niels Bohr, Leben und Werk eines Atom-physikers*, Akademie-Verlag, Berlin, **1985**; U. Röseberg, *Niels Bohr, Leben und Werk eines Atomphysikers, 3rd ed.*, Spektrum Akademischer Verlag, Heidelberg, **1992**; b) U. Röseberg in *Die großen Physiker* (Ed.: K. von Meÿenn), Beck, München, **1997**, pp. 276–284.
[25] A. Pais, *Niels Bohr's Times*, Clarendon, Oxford, **1991**; b) A. Pais, *Inward bound, Of Matter and Forces in the Physical World*, Clarendon, Oxford, **1986**.
[26] A. P. French, P. J. Kennedy, *Niels Bohr, A Centenary Volume*, Harvard University Press, Cambridge, **1985**.
[27] E. N. Andrade, *Proc. R. Soc. London Ser. A* **1958**, *244*, 437–455.
[28] C. Baily, *Eur. Phys. J. H* **2013**, *38*, 1–38.
[29] C. G. Barkla, C. A. Sadler, *Philos. Mag. Ser. 6* **1907**, *14*, 408–422.

[30] H. Nagaoka, *Nature* **1904**, *69*, 392–393; H. Nagaoka, *Philos. Mag. Ser. 6* **1904**, 7, 445–455.

[31] M. Planck, *Verh. Dtsch. Phys. Ges.* **1900**, *2*, 237; M. Planck, *Ann. Phys.* **1901**, *4*, 553–564.

[32] A. Einstein, *Ann. Phys.* **1905**, *17*, 132–184.

[33] a) A. E. Haas, *Sitzungsber. Kais. Akad. Wiss. Wien Math.-Naturwiss. Kl.* **1910**, *2a*, 119–144; b) A. Hermann, *Arthur Erich Haas, der erste Quantenansatz für das Atom*, Battenberg, Stuttgart, **1965**.

[34] J. Loschmidt, *Sitzungsber. Math.-Naturwiss. Kl. Kais. Akad. Wiss.* **1866**, *52II*, 395–413.

[35] H. Geiger, E. Marsden, *Philos. Mag. Ser. 6* **1913**, *25*, 604–623.

[36] E. Rutherford, *Philos. Mag. Ser. 6* **1911**, *21*, 669–688.

[37] A. van den Broek, *Phys. Z.* **1913**, *14*, 32–41.

[38] J. W. Nicholson, *Mon. Not. R. Astron. Soc.* **1912**, *72*, 729–739.

[39] H. Kragh, K. H. Nielsen, *Ann. Sci.* **2013**, *70*, 257–283.

[40] A. Einstein, *Ann. Phys.* **1907**, *22*, 180–190.

[41] N. Bohr, *Nature* **1923**, *112*, 29–44.

[42] a) N. Bohr, *Fys. Tidsskr.* **1921**, *19*, 153 (Danish); b) N. Bohr, *The Theory of Spectra and Atomic Constitution*, Cambridge University Press, Cambridge, **1922**.

[43] N. Bohr, D. Coster, *Z. Phys.* **1923**, *12*, 342–374.

[44] H. G. J. Moseley, *Philos. Mag. Ser. 6* **1913**, *26*, 1024–1034; H. G. J. Moseley, *Philos. Mag. Ser. 6* **1914**, *27*, 703–713.

[45] W. Pauli, *Ann. Phys.* **1922**, *68*, 177–240.

[46] R. Abegg, *Z. Anorg. Chem.* **1904**, *39*, 330–380.

[47] a) J. W. van Spronsen, *The Periodic System of Chemical Elements*, Elsevier, Amsterdam, **1969**; b) E. G. Mazurs, *Graphic Representations of the Periodic System during one Hundred Years*, University of Alabama Press, Tuscaloosa, **1974**.

[48] http://en.wikipedia.org/wiki/Ununoctium, August **2013**.

[49] a) H. Holst, H. A. Kramers, *Bohrs Atomteori Almenfatteligt Fremstillet*, Gyldental, Kjøbenhavn, **1922**; b) H. A. Kramers, H. Holst, *The Atom and the Bohr Theory of its Structure*, Gyldental, London, Knopf, New York, **1923**.

[50] a) S. G. Wang, W. H. E. Schwarz, *Angew. Chem.* **2009**, *121*, 3456–3467; *Angew. Chem. Int. Ed.* **2009**, *48*, 3404–3415; b) W. H. E. Schwarz, R. L. Rich, *J. Chem. Educ.* **2010**, *87*, 435–443.

[51] T. Bitter, K. Ruedenberg, W. H. E. Schwarz, *J. Comput. Chem.* **2007**, *28*, 411–422. T. Bitter, S. G. Wang, K. Ruedenberg, W. H. E. Schwarz, *Theor. Chem. Acc.* **2010**, *127*, 237–257.

[52] a) K. Ruedenberg, *Rev. Mod. Phys.* **1962**, *34*, 326–376; b) K. Ruedenberg, M. W. Schmidt, *J. Comput. Chem.* **2007**, *28*, 391–410; K. Ruedenberg, M. W. Schmidt, *J. Phys. Chem.* **2009**, *113*, 1954–1968; c) M. W. Schmidt, J. Ivanic, K. Ruedenberg, *The Nature of the Chemical Bond Revisited* (Eds.: G. Frenking, S. Shaik), Wiley-VCH, Weinheim, **2014**.

[53] a) W. Kutzelnigg, *Angew. Chem.* **1973**, *85*, 551–568; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 546–562; b) W. Kutzelnigg, *Die Chemische Bindung* (Vol. 2 of *Einführung in die theoretische Chemie*), VCH, Weinheim, **1978**; W. Kutzelnigg, *Die Chemische Bindung* (Vol. 2 of *Einführung in die theoretische Chemie*), VCH, Weinheim, **1993**; W. Kutzelnigg, *Die Chemische Bindung*, Vol. 2 of *Einführung in die theoretische Chemie*, VCH, Weinheim, **2002**; c) W. Kutzelnigg in *The Physical Origin of the Chemical Bond*, Vol. 2 (Eds.: Z. B. Maksic), Springer, Berlin, **1990**, p. 1.

[54] hhttp://en.wikipedia.org/wiki/Chemical_bonding, August **2013**.

[55] a) A. A. Svidzinsky, M. O. Scully, D. R. Herschbach, *Phys. Rev. Lett.* **2005**, *95*, 080401; b) A. Svidzinsky, S. Chin, G. Chen, M. Kim, D. Ma, R. Murawski, A. Sergeev, M. O. Scully, D. Herschbach, *Int. Rev. Phys. Chem.* **2008**, *27*, 665–723.

[56] T. S. Kuhn, *The Structure of Scientific Revolutions*, University Press, Chicago, **1962**.

[57] L. Fleck, *Entstehung und Entwicklung einer wissenschaftlichen Tatsache*, Schwabe, Basel, **1935**; L. Fleck, *The Genesis and Development of a Scientific Fact*, University of Chicago Press, Chicago, **1979**.

[58] I. N. Levine, *Quantum Chemistry*, various eds. **1970–2014**.

[59] G. T. Seaborg, *Chem. Eng. News* **1945**, *23*, 2190–2193; G. T. Seaborg, *Science* **1946**, *104*, 379–386.

[60] a) A. Sommerfeld, *Z. Angew. Chem.* **1928**, *41*, 1–6; b) P. A. M. Dirac, *Proc. R. Soc. London Ser. A* **1929**, *123*, 714–733.