9. Closing Remarks

MAPLE calculations are of direct practical interest for the comparison of commensurable structures.

An example is *Holmberg*'s discussion on the structure of ScOF[24], where X-ray and structure-chemical methods failed to distinguish between three alternatives. The MAPLE values calculated by us (cf. Table 10) show clearly that in agreement with *Holmberg*'s suggestion, only alternative I can be seriously considered[25]. Many other examples have similarly shown the value of MAPLE calculations for detailed structural discussions.

The discrepancy between the accuracy of modern X-ray structure determinations and the possibility of understanding and critically interpreting their results, even only semiquantitatively, is amazing, and never since the "golden twenties", with their exceptionally fruitful symbiosis of physics, chemistry, mineralogy, and crystallography has it been so striking as it is today. Solid state chemistry in the true sense begins only with crystal chemistry, and is in fact a lot more in the eyes of the experimental chemist. But even the value of the advance in structural chemistry as a first step of solid state chemistry is, however, doubtful so long as structural facts cannot be critically and quantitatively evaluated and checked for internal consistency or inconsistency. We are conscious of the limitations of the very one-sided structure-geometrical view taken here, but we nevertheless hope to stimulate further discussion.

[24] *B. Holmberg*, Acta chem. scand. *20*, 1082 (1966).

[25] Cf. also *W. Barker*, Acta crystallogr. *A 24*, 700 (1968). Our values differ from those of *Barker*'s values in that they show in detail the changes during the transition from one individual alternative to another.

Table 10. Crystal structure of ScOF [24]: MAPLE values in kcal/mole.

MAPLE	Alternative I	Alternative II	Alternative III (statistical distribution of O^{2-} and F^-)
Sc^{3+}	1122.0	1043.5	1083.3
O^{2-}	543.1	393.1	365.2
F^-	138.9	215.2	251.7
Σ	1804.0	1651.8	1700.2

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From Planck to Bohr

The First Fifteen Years in the Development of the Quantum Theory

By Armin Hermann[*]

The quantum theory, which is nowadays a fundamental basis of chemistry that is regarded as self-evident, initially presented immense difficulties to human thought. An insight into many particulars of its fascinating evolution is provided by the correspondence of those involved in the development of the theory between 1899 and 1913, which has now been thoroughly sifted for the first time by the author.

1. The Continuity Principle

The principle "*natura non facit saltus*", *i.e.* all natural processes take place continuously and not spasmodically, had played a very important part in the development of science during the 17th century. This is shown particularly clearly in the creation of differential and integral calculus, the spirit of which is also the spirit of physics. The entire philosophy of *Leibniz* in particular is permeated with the continuity principle in its widest sense.

Leibniz clearly stated "that the present always conceals the future in its bosom, and that any given state can only be explained naturally by the state immediately preceding it. Unless we accept this, there will be many things in the universe that defy the principle of sufficient reason and force us to marvel or to have recourse to chance for the explanation of the phenomena". The principle of the continuity of all natural processes was expressed by many scientists and philosophers in the 18th and 19th centuries, though it was not usually formulated as self-evident.

"An act of despair" was how *Max Planck* later described his theoretical proof of the law of black body radiation: "The entire affair can in short be described as an act of despair. I am peaceful by nature, and averse to hazardous adventures. However, ...a theoretical interpretation had to be... found at all costs... The two principal laws of heat seemed to me

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to be all that had to be retained in any circumstances. Apart from these, I was ready to make any sacrifice of my physical beliefs"[1].

2. The Birth of the Quantum Theory

December 14, 1900, the day on which *Planck* described the derivation of his radiation law to the Physical Society in Berlin, saw the birth of the quantum theory. As an unwilling revolutionary, *Planck* had smashed the principle of the continuity of natural processes by postulating discrete energy steps for the linear oscillator, expressed by the formula

$$\varepsilon = h\nu$$

Contrary to a widely held belief, however, *Planck* had no suspicion of this corollary at the turn of the century. If he had no impression in 1900 of having overthrown the continuity principle, what did he mean by "act of despair" and the "sacrifice of physical beliefs"?

The sacrifice that *Planck* had knowingly made was the surrender of the purely axiomatic thermodynamic view of the second law of heat and the acceptance of the atomistic-probabilistic interpretation, which he had until then vigorously rejected. Only a few years earlier, in 1896, he had carried on an argument on this topic in the Annalen der Physik, through his assistant *Ernst Zermelo*, with *Boltzmann*.

And *Planck* was now forced to adopt the detested "Boltzmann method" to derive the law of black body radiation! The need to divide the energy into discrete atomistic portions was then only a minor additional difficulty: "This was a purely formal assumption, and I did not really think too much about it, since my only concern was to obtain a positive result, whatever the cost."

Following *Planck*'s work, the theory of radiation was investigated in the first few years of the present century by *Rayleigh*, *Jeans*, and *Lorentz*. By various routes, but always adhering rigidly to the thought processes of classical physics, they all arrived at the Rayleigh-Jeans formula. It was felt that this had to be accepted; it had been shown that there is no true equilibrium of black body radiation, and the energy passes from the resonators into the radiation and to ever-decreasing wavelengths. This viewpoint was still defended by *Hendrik Antoon Lorentz* in April 1908 at the International Congress of Mathematicians in Rome.

Willy Wien commented on this in a letter to *Arnold Sommerfeld*: "I am very disappointed by the lecture given by *Lorentz* in Rome. I take a poor view of the fact that he merely presented the old Jeans theory without adding any new point of view ... In my opinion the theory is not worth considering, since observations show enormous deviations from the Jeans formula. It also seems rather odd to me to regard as the advantage of the Jeans theory the fact that the entire unlimited multiplicity of the electronic vibrations can be retained, despite its complete failure to represent the true facts. And the spectral lines? *Lorentz* has not shown himself to be a leader of science this time."

Lorentz's caution was in line with his personality, but it was undoubtedly also stamped with the prejudices of the turn of the century: Anyone who shook the foundations of science, whatever his motives, was suspected of being a revolutionary.

Rayleigh, *Jeans*, *Lorentz*, and *Planck* were all alike in this respect. In the early years the only difference between *Planck* and the others was that *Planck* had been familiar with the natural constant h at least since May 1899, and he knew that its value can be found very accurately from radiation measurements. In *Planck*'s eyes the constant h existed and had to be explained, however inconvenient this might often appear to be. As late as 1910 he addressed the following warning to the innovators, and above all to *Albert Einstein* and *Johannes Stark*: "In introducing the quantum of action h into the theory, one must proceed as conservatively as possible, *i.e.* changes in the existing theory should be restricted to those that have proved absolutely essential."

3. The Appearance of *Einstein*

In 1905 *Albert Einstein*, who was at that time 26 years of age and an "Expert, 3rd Class" at the Swiss Patent Office in Bern, published three papers of great importance in the celebrated Volume 17 of the Annalen der Physik: The Theory of Brownian Movement, The Special Theory of Relativity, and The Light Quantum Hypothesis.

With his later almost proverbial independence of thought and his intellectual lack of respect, unlike *Planck*, *Lorentz*, and *Rayleigh*, he did not look upon the electromagnetic theory of light and mechanics as venerable structures that had to be treated "as conservatively as possible". From the very beginning he considered the Maxwell equations to be valid only for average values in time and space. Thus matter could often be successfully dealt with on the basis of the continuum concept, as *e.g.* in the theory of elasticity, and it became necessary to consider the corpuscular structure only for finer effects.

According to *Einstein*, the same was true in electrodynamics. The Maxwell equations are valid for optical interferences, but the corpuscular structure of light must be taken into account for the "groups of phenomena concerned with the production and transformation of light". Also according to *Einstein* (in 1909), the electron is "an alien in electrodynamics", since it is still not understood how the finite electronic charge is stably concentrated in a small space despite the very large Coulomb repulsion forces between the various elements of charge.

Early in 1909, *Einstein* came to the conclusion that the two deficiencies of the Maxwell theory must be linked

[1] The sources of the quotations reproduced here are to be found in *A. Hermann*: Frühgeschichte der Quantentheorie (1899 to 1913). Physik-Verlag, Mosbach/Baden 1969. This book also includes a complete review of the published and unpublished literature.

with each other. He tried to explain both the quantum structure of radiation and the electron, *i.e.* he tried to derive a single theory embracing both the electron and the light quantum. Einstein believed in 1909 that the key to the solution of this problem was the fact that e^2/c and h have the same dimensions, those of an action. "It seems to me from the relation

$$h = e^2/c$$

that the same modification of the theory that contains the elementary quantum e as a consequence will also contain the quantum structure of radiation." It should be mentioned that *Max Planck* had put forward a similar (though more cautiously formulated) view in a letter to *Ehrenfest* as early as 1905. *Planck* thought it possible that from the elementary quantum of electricity, "there is a bridge to the existence of an elementary quantum of energy h".

The elementary quantum of electricity e and *Planck*'s quantum of action h are nowadays regarded as independent natural constants, and it is considered a prerequisite of any future theory of elementary particles that the value of the Sommerfeld fine structure constant

$$2\pi e^2/hc = 1/137$$

can be calculated from it.

Einstein's paper in the Physikalische Zeitschrift of March 1909 elicited a comment from *Willy Wien.* It was around that time that *Wien* was composing his article on radiation theory for the Mathematische Enzyklopädie, in which he wrote: "I cannot at present accept *Einstein*'s opinion ... that the magnitude of the element of energy is related to that of the elementary quantum of electricity... The element of energy, if indeed it has any physical significance, must derive from a universal property of the atom."

This was entirely different from *Planck*'s view. Faced with the need to find a derivation for the radiation law, *Planck* had overcome the positivistic objection of *Mach* and *Ostwald* to atomism, and even did atomism a considerable service by his interpretation of the Planck-Boltzmann constant k. However, *Planck*'s linear oscillator remained a physically anemic object; it did not occur to *Planck* at first to look for a way of bridging the gap between this and real atoms. *Planck* had always regarded the "search for the absolute as the highest aim of research", and the "absolute" was precisely what was independent of the special properties of matter.

Einstein and the majority of the German physicists and chemists had likewise scarcely thought about the question of the constitution of atoms. *Max Born* said about this: "Well, the atom was the central problem at that time, and the Germans didn't known it." It must however be added that the most important idea was the quantum concept, and the French and English didn't know that.

4. The First Model of the Atom Based on the Quantum Theory

Who then was the first to attempt a quantum-theoretical treatment of the atom? Well, it was not one of the leading physicists or chemists, but a historian of physics named *Arthur Erich Haas*: In 1909, *Haas* had submitted a paper on the history of physics as his thesis for habilitation at the University of Vienna. This paper was not appreciated by the physicists of the faculty, and they imposed upon *Haas* the additional condition that he prepare another purely physical paper. To satisfy this condition, *Haas* started to read the latest physical literature. This was firstly the book by *Joseph John Thomson* on "Electricity and Matter", which deals almost exclusively with the structure of atoms, and secondly the newly published Mathematische Ezyklopädie containing *Wien*'s article. *Haas* combined *Wien*'s suggestion of deriving the element of energy from a universal property of atoms with the Thomson model of the atom, and so produced an important forerunner of the Bohr theory of the atom.

In the Thomson model, which consisted of an extended positively charged atomic sphere with point electrons, *Haas* considered only the electron orbitals on the surface of the atomic sphere; his model is therefore mathematically equivalent to *Rutherford*'s. For the forces acting on the surface and in the external space of a spherically symmetrical charge distribution, one can think of the total charge as being united in the center.

To determine the two unknowns, *i.e.* the radius of the electron orbital and the frequency of revolution, *Haas* needed another equation as well as the classical expression that equates centrifugal force to the Coulomb attraction force. This second equation can be obtained only by a "quantum-theoretical" approach. *Haas* was very fortunate in that he equated potential energy to the Planck element of energy $h\nu$.

This agrees with the later Bohr condition for the ground state of the hydrogen atom, and *Haas* therefore correctly obtained the "Bohr" radius of the hydrogen atom, which we could thus historically call the "Haas" radius. It is significant, however, that he wrote

$$h = 2\pi e\sqrt{am}$$

and not the equation solved for a. *Haas*, like *Wien*, considered the property of the atom to be the fundamental quantity from which the quantum of action h was derived.

The Bohr radius a is not a measurable quantity, so that the Haas relation provides no basis for numerical calculations. Using a similar hypothesis, however, *Haas* also derived an expression for the Rydberg frequency, which was thus traced back, as it was later by *Bohr*, to the fundamental quantities of the electron theory and the quantum of action. *Haas*'s determination is wrong by a factor of only 8, which is due to the inaccuracy of the numerical values used for the elementary charge and the quantum of action.

The reaction to his ideas was described very vividly by *Haas* in his autobiography: "In Vienna I at first met only scorn, and even ridicule. When I lectured to the Wiener Physikalisch-Chemische Gesellschaft, *Lecher* thought he was being very funny when he called the whole thing a carnival joke ... *Hasenöhrl* explained that I could not be taken seriously, as I had naively mixed up two branches of science that could have absolutely nothing to do with each other, namely quantum theory (which was concerned with the theory of heat) and spectroscopy (which was optical)" [2].

Thus the attempt to produce a quantum theory of the atom had apparently come to nothing in February 1910. However, the ideas developed by *Haas* were soon re-examined and pursued further by *Schidlof*, by *Sommerfeld*, and by *Hasenöhrl*. At about the time of *Haas*'s "carnival joke", a decisive *volte-face* in favor of the quantum concept had occurred. Everyone that had supported a quantum theory had hitherto been treated as an outsider, whereas from 1910 onward the quantum concept became, so to speak, respectable. How did this change of opinion come about? To find the answer to this question, we must dig a little deeper.

5. *Einstein*'s Influence on *Stark*, *Sommerfeld*, and *Nernst*

Einstein's light quantum hypothesis was regarded by the experts as the most radical attempt to derive the law of black body radiation, and it was accordingly received with much skepticism. Using the corpuscular theory of light, *Einstein* was able to provide a simple model for the interaction of light with atoms, molecules, and solids. As is well known, the "Einstein equation" for the photoelectric effect, which was deduced in 1905, consists simply of the application of the energy theory. In this way *Einstein* was able to extend the range of validity of the quantum concept. This valuable extension remained only a theory at first, since the experimental verification of these effects dragged out over several years, *e.g.* up to 1915/16 in the case of the photoelectric effect.

In the search for new quantum phenomena, the first to follow *Einstein*, from about 1907 on, was *Johannes Stark*. He named a whole series of processes in which the quantum law should, in his opinion, be evident. In addition to many that were correct, such as the ultraviolet boundary of X-ray bremsstrahlung, these included many that were not.

Like *Einstein*, *Stark* thought nothing of opposing the prevailing opinion. Opposition to dogma seemed to him to be a necessity of life. When the many quantum approaches were united in the Bohr theory in 1913 (and this theory,more over, was confirmed by his own experiments), *Stark* suddenly turned against the quantum concept and continued to oppose it until his death. Up to 1913, however, he fought with the same vehemence in favor of the quantum idea, and for this reason *Stark*, who is still remembered as a conservative physicist of the older generation, had his merits at the time as an avantgardist.

In late 1909, *Johannes Stark* tried to wring an agreement with the quantum theory from *Sommerfeld*, virtually by brute force. However, *Sommerfeld* had no difficulty in demonstrating embarrassing physical errors to *Stark*. Thus *Sommerfeld* wrote: "Nothing could be further from my intention than to start a quarrel with you. This would be very unequal, since you are far above me in experimental ideas, and I above you in theoretical lucidity." *Sommerfeld* and *Stark* carried on a lively discussion of the quantum concept in X-ray bremsstrahlung in the Physikalische Zeitschrift and in their correspondence. They entered into an argument that was the start of a deadly enmity, which was to affect the subsequent lives of both men.

The outcome for *Sommerfeld*, *Planck*, and the experts was essentially a corroboration of the wave theory of light and of X-rays. *Sommerfeld* expressly demonstrated in 1910 that the quantum of action had nothing to do with X-ray bremsstrahlung.

In March 1910, however, *Arnold Sommerfeld* was subjected to pressure by his own assistant *Peter Debye*. The latter had developed what was perhaps the shortest and clearest derivation of the Planck radiation law. Like *Rayleigh* and *Jeans*, he considered the characteristic vibrations of the cavity, which, however, are now provided with the quantum-theoretical energy average. *Debye* told *Sommerfeld* that he had now reached a firm opinion in his considerations on radiation, and that he wished to publish his views. *Sommerfeld* felt responsible for all the work done by his co-workers. What should he do? It was recorded with surprise at *Sommerfeld*'s institute that he suddenly felt in need of a rest in the middle of the year and went off to spend a week in Switzerland. As his pupil *Paul S. Epstein* commented, *Sommerfeld*'s idea of recreation was to talk physics all day with *Einstein*.

Like the other experts, *Sommerfeld* had first met *Einstein* in 1909 at the Salzburg Naturforscherversammlung, where the two men had formed a friendship based on mutual respect. *Einstein* now wrote in a letter to *Johann Jacob Laub* that *Sommerfeld* had spent a whole week with him "to discuss the question of light and some matters concerning relativity. His presence was a real occasion to me. He has largely accepted my ideas ..."

For *Sommerfeld*, *Einstein*'s power of persuasion was based not only on the force of his personality but also on the proven success of the relativity theory. This had very rapidly gained acceptance among those that mattered up to about 1908. Though the two most important physical theories of the beginning of the 20th century, *i.e.* the quantum theory and the theory of relativity, have no direct logical connection, they are closely linked from a historical standpoint. The success of the theory of relativity now also accelerated the development of the quantum theory.

The quantum theory gained an important champion in the person of *Sommerfeld*. Unlike *Planck*, *Sommer-*

[2] *A. E. Haas*: Der erste Quantenansatz für das Atom (= Dokumente der Naturwissenschaft. Vol. 10). Battenberg, Stuttgart 1966, see p. 16.

feld had a large circle of pupils, with whom he was constantly exchanging ideas, and on whom he made a strong impression. Thus from about the beginning of 1911, enthusiastic efforts were being made even among the younger scientists to solve the quantum problem.

6. *Nernst* and the First Solvay Congress

Even before *Sommerfeld*, the quantum theory had won another important adherent, who also enjoyed absolute and authoritative rule over a large institute. This was *Walther Nernst*. *Nernst* was interested in thermodynamics. He had formulated the third law of thermodynamics in 1906, and had deduced from it that the specific heat of all substances must tend toward a constant limiting value as the temperature approaches absolute zero. *Nernst* had therefore already set out to measure specific heats at low temperatures over a wide front when the Einstein theory of specific heat came to his notice in late 1909 or early 1910.

When the term ended, in March 1910, *Nernst* hurried off to *Einstein* in Zürich with the results of his measurements. Both men were delighted. A letter written by *Einstein* reads: "There is no doubt in my mind about the correctness of the quantum theory. My predictions about specific heats appear to have been brilliantly confirmed."

In addition to thermal radiation, there was now a second field whose experimental results could be explained with the aid of the quantum concept, and only with its aid. The quantum concept now rested, in *Sommerfeld*'s words, on "two stout supporting pillars", and *Einstein* stated that *Nernst* had freed the problem from its "theoretical shadow existence" [3].

Nernst was filled with enthusiasm by this encounter with a problem of the utmost importance to the foundations of science, and he looked around for further work. He initiated moves to acquire *Albert Einstein* for the Preussische Akademie, and in June 1910 he began preparations for an international "Quantum Conference" to enable the leaders in the field to reconsider the foundations of their science. *Nernst* wanted this conference, like the Karlsruher Chemikertagung in 1860, to be a landmark, and this aim was achieved in full. The preparations for the congress, which attracted a great deal of attention, the Solvay Congress itself, which started on October 30, 1911, in Brussels, and the official and unofficial congress reports won over many who had previously been mere by-standers.

In this trail-blazing atmosphere, the Haas idea was also activated. *Sommerfeld* had adopted this idea, but in Brussels he switched to the opposite view, *i.e.* that "*h* is not explained by molecular dimensions; on the contrary, the existence of molecules may be regarded as a function and a consequence of the existence of an elementary quantum of action".

After the Solvay Congress, *Sommerfeld* expected *Einstein* to provide the fundamental clarification of the constitution of the atom with the aid of the quantum theory, as is shown by the correspondence that passed between *Einstein* and *Sommerfeld* [4]. On October 29, 1912, *Einstein* made the following reply to a question by *Sommerfeld*:

"Your letter perplexes me still further. I assure you, however, that I have nothing new of any interest to say about the quantum problem. I am in complete agreement with the Debye-Born view, and can find nothing in it to criticize. However, this achievement is of little help in the solution of the principal difficulties."

Sommerfeld subsequently wrote to *Hilbert*: "My writing to *Einstein* was in vain, as you can see from this. *Einstein* is evidently so steeped in gravitation that he is deaf to everything else."

7. The Bohr Model of the Atom

As everyone knows, it was *Bohr* that made the breakthrough in February and March 1913 with his quantum theory of the atom. This success was largely due to *Bohr*'s conviction that it was the quantum of action that was responsible for the stability of the planetary atom. This conviction was essentially the result of *Sommerfeld*'s lecture in Brussels.

The international congress in Brussels carried the quantum concept beyond the boundaries of the German-speaking world. It had a deep impression on the young *Léon Brillouin* and *Louis de Broglie* in France and on *William Nicholson* and *Niels Bohr* in England. The quantum concept found a fertile soil particularly in the traditions of English natural science. The positivistic objection to atomism had played no part in England, and unlike in Germany, the constitution of the atom had long been a center of interest here.

As a guest at *Rutherford's* Institute in Manchester, *Bohr* witnessed the new experiments on radioactivity and the scattering of α and β rays at the beginning of 1912, and like the rest of *Rutherford*'s coworkers he was convinced of the correctness of the planetary model of the atom. *Bohr* was interested by the questions that followed directly from the experiments, and he found the answer. In an interview of the Sources for History of Quantum Physics with *Georg von Hevesy* we find: "I asked *Rutherford*: ... 'Where do the beta particles come from?'. *Rutherford* answered: Ask *Bohr! Bohr* with no difficulty answered that electrons involved in radioactive transmutation process come from the nucleus, and all of the other electrons come from the exterior of the atom".

Bohr deduced information about many important properties of the atom on what was still, so to speak,

[3] Cf. *Einstein, Debye, Born, Kármán*: Die Quantentheorie der spezifischen Wärme (= Dokumente der Naturwissenschaft. Vol. 8). Battenberg, München 1967

[4] *A. Einstein, A. Sommerfeld*: Briefwechsel. Sechszig Briefe aus dem goldenen Zeitalter der modernen Physik. Schwabe Verlag, Basel/Stuttgart 1968, see p. 26.

a pre-quantum-theoretical basis. This was a frequently overlooked prerequisite for the successful treatment of the problem. Toward the end of 1912 *Bohr* was clear:

about the correctness of the planetary model of the atom,

about the concept of atomic number, *i.e.* about the assignment of the models with one, two *etc.* electrons to the actual atoms,

about the separation of the "nuclear" from the "atomic" phenomena,

about the possibility that one and the same atom can exist in various "states",

about the ability of the Planck quantum of action to ensure the stability of the atom,

and that no further "explanation" of such a quantum theory is necessary.

On *Rutherford*'s advice that he avoid unnecessary complications and calculations, *Bohr* concentrated on the simplest model, that of the hydrogen atom, with one electron. In a letter to *Rutherford*, *Bohr* wrote that he was considering only the ground state of the atom, the "natural permanent state", and had no intention of trying to apply his ideas to the line spectra. That was on January 31, 1913. On March 6, 1913, however, he submitted the finished article on the theory of the spectrum of hydrogen to *Rutherford* for publication in the Philosophical Magazine.

The decisive step must therefore have been made in February 1913. Who or what persuaded *Niels Bohr* to embark on a theory of spectral lines? And how did he achieve such speedy success?

On October 31, 1962 less than three weeks before his death, *Bohr* himself was asked about this by *Léon Rosenfeld* and *Thomas S. Kuhn* on behalf of the Sources for History of Quantum Physics [5]. The record reads: "*Rosenfeld*: 'How did you come to examine the spectra?' *Bohr*: 'The spectra was a very difficult problem... And I discovered it, you see . . . And I found the hydrogen spectrum. I was just reading the book of *Stark*, and at that moment I felt now we'll just see how the spectrum comes.' *Kuhn*: 'Was this at Manchester that you were reading *Stark?*' *Bohr*: 'No, no, that was later in Copenhagen . . . it was in January, I think of 1913."

The author must confess that he was quite bewildered by this information. Having been in possession of the major part of *Stark*'s scientific legacy for a number of years [6], he had repeatedly referred to the importance of *Stark*'s contribution to the development of the early quantum theory. He had never dared, however, to assume that it had had such a direct influence on the emergence of the Bohr theory. We know from *Rutherford*'s letter of January 31, 1913, that the date of this decisive stimulus was February 1913, and not January.

[5] The American-financed "Sources for History of Quantum Physics" has been recording the relevant source material for some years, and has also arranged interviews with the workers involved. The Director for Europe is Prof. *F. Hund* (Göttingen).

[6] *Stark*'s legacy is now in the possession of the Staatsbibliothek der Stiftung Preussischer Kulturbesitz in Berlin-Dahlem.

What, then, were the ideas of *Stark*'s that had such an unusual outcome? According to *Stark*, even a single electron can emit an entire spectrum of lines. The electron returns from the almost completely separated state to a very eccentric elliptic orbital near the center of the atom. The orbital is strongly curved at the perihelion, and the acceleration of the electron is accordingly high. At this point electromagnetic energy is emitted in the form of a light quantum.

Stark wrote: "The electron's residual kinetic energy carries it away from the center Z again; because of the loss of energy, however, it can no longer move away to its original distance, but curves back again at a shorter distance." According to *Stark*, this repeated return of the electron to the atom is accompanied by emission of a light quantum at the aphelion and at the perihelion of the movement.

Stark developed these ideas in 1908, and reproduced them in 1911 in his book "Prinzipien der Atomdynamik. II. Die elementare Strahlung" (Principles of Atomic Dynamics. II. Elementary Radiation). *Bohr* obtained this book in February 1913.

When one accepts, as *Bohr* did, the planetary model of the atom with Coulomb forces between the nucleus and the electron, the application of *Stark*'s ideas follows automatically:

The path of the electron is an ellipse before the emission of radiation.

The path is again an ellipse after the emission, but this ellipse is situated closer to the nucleus. The energy of the electron is now lower.

The question how the electron moves from one ellipse to another need not be answered immediately.

Application of *Stark*'s concept to the basis of the Rutherford model of the atom thus gives families of ellipses, which must be classified according to their electronic energy.

"As soon as I saw *Balmer*'s formula the whole thing was immediately clear to me", *Bohr* told *Rosenfeld* more than once. Compare this with *Bohr*'s other statement: "I was just reading the book of *Stark*, and at that moment I felt now we'll just see how the spectrum comes." Thus *Niels Bohr* must have read *Stark*'s book and seen the Balmer formula at roughly the same time, *i.e.* in February 1913.

Bohr's copy of *Stark*'s "Prinzipien der Atomdynamik II" was found among his books at the Niels Bohr Institute in Copenhagen. This book contained a scrap of paper on which *Bohr* had noted two references to articles published in 1912. It appears, therefore, that *Bohr* procured these articles in direct connection with the reading of *Stark*'s book. One of the two deals with the theory of spectral lines, and contains the formula

$$\nu = N\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

"As soon as I saw *Balmer*'s formula the whole thing was immediately clear to me": taken together with the idea of various elliptic orbitals, this formula gave the "transitions" between pairs of elliptic orbitals m and n. Since there was evidently no suggestion of classifying the elliptic orbitals on the basis of energy, *Bohr* could apparently write the following formula directly for the energy emitted in a spectral line:

$$h\nu = h \cdot \mathrm{N}\left(\frac{1}{\mathrm{n}^2} - \frac{1}{\mathrm{m}^2}\right)$$

All that remained now was to classify the various elliptic orbitals according to their energy; in other words, to complete the work, *Bohr* merely had to derive the formula

$$E_\mathrm{n} = h \cdot \mathrm{N} \cdot \frac{1}{\mathrm{n}^2}$$

Without knowing about *Haas*, *Bohr* had tried in the middle of 1912 to relate the kinetic energy to the frequency of revolution. In an unpublished manuscript by *Bohr* dated July 1912, which was edited by *Léon Rosenfeld* to celebrate the 50th anniversary of the Bohr model in 1963, we find the formula

$$E_\mathrm{kin} = K \cdot \nu$$

which at that time referred only to the ground state. The K in this formula should be closely related to the Planck constant.

It was now a simple matter for *Bohr* to find the correct expression by trial and error. Thus the "mechanism" of spectral lines, which had been sought since the discovery of spectral analysis by *Kirchhoff* and *Bunsen*, was found.

It is well known that the Bohr model of the hydrogen atom was then developed, by the addition of *Sommerfeld*'s quantum conditions, into a system of formulas that really deserved to be called a quantum theory. "Your spectral investigations", wrote *Einstein* to *Sommerfeld*, "are among my finest physical experiences. It is only through them that *Bohr*'s idea becomes totally convincing" [7].

Since the majority of physicists had accepted the quantum concept since 1912 and a corresponding theory had now been produced, developments entered a new phase. The early history of the quantum theory was closed.

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[7] Cf. Ref. [4], p. 41.

Polyurethane Ionomers, a New Class of Block Polymers

By D. Dieterich, W. Keberle, and H. Witt[*]

Dedicated to Professor K. Hansen on the occasion of his 60th birthday

Linear polyurethanes containing ionic centers at wide intervals are heteropolymers having a pronounced segment structure, i.e. ionomers. As a result of interactions between chains (Coulomb forces and hydrogen bonds), their properties are similar to those of crosslinked elastomers. They are strongly associated both in organic and in aqueous solutions. Polyurethane ionomers in polar organic solvents spontaneously form stable aqueous dispersions on addition of water, with the ionomer as the disperse phase. The particle size can be varied between 20 nm and 1 mm.

1. Polyelectrolytes by the Diisocyanate Polyaddition Process [1–3]

By reaction of diisocyanates *(1)* with diols containing tertiary amino groups *(2)*, *Schlack* obtained basic, linear polyurethanes, which dissolve in aqueous acids to form polyurethane polyammonium salts *(3)* [4].

Diisocyanates react with diaminobenzenesulfonates, or diaminobenzoates to form water-soluble polyurea polysulfonates or polycarboxylates *(4)* [5].

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[1] *O. Bayer*, *H. Rinke*, *W. Siefken*, *L. Orthner*, and *H. Schild*, DRP 728981 (Nov. 13, 1937), I.G. Farben: Chem. Zbl. *1940* II, 1796.

[2] *O. Bayer*, Angew. Chem. *60*, 257 (1948).

[3] *O. Bayer* and *E. Müller*, Angew. Chem. *72*, 934 (1960); *E. Müller*, Kautschuk u. Gummi, Kunststoffe *18*, 67 (1965); *H. Oertel*, Melliand Textilber. *46*, 51 (1965); *E. Windemuth*, Kunststoffe *57*, 337 (1967); *H. Rinke*, Chimia *22*, 164 (1968); other literature cited therein.

[4] *P. Schlack*, DDR-Pat. 5367 (April 25, 1942); 5379 (June 19, 1942); 5381 (June 24, 1942); all VEB Filmfabrik Agfa Wolfen; Chem. Zbl. *1956*, 10345, 10816, 11577.

[5] *W. Thoma*, *O. Bayer*, and *H. Rinke*, DAS 1067212 (Dec. 15, 1959); DAS 1042892 (April 6, 1957); both Farbenfabriken Bayer; Chem. Abstr. *55*, 10912f, 2184d (1961).