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## The Nobel Prize in Physics 1919

Johannes Stark

The Nobel Prize in Physics 1919

**Johannes Stark**


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 **Nobel Lecture**

## Nobel Lecture

Nobel Lecture, June 3, 1920

## Structural and Spectral Changes of Chemical Atoms

The question of the composition of perceptible objects is one which already occupied the mind of the ancient Greeks. They formed the concept, as a philosophical speculation, of the indivisible particle, the atom, as the smallest component of perceptible objects. However, they did not pass beyond this stage of the hypothesis; they did not bring it to productivity through experimental research.

It is otherwise with the mind of the Germanic peoples. They proceeded from the experience of their chemical dealings with matter, established the existence of a number of basic substances, or chemical elements, which could not be decomposed further, and proposed the hypothesis that a chemical element consists of homogeneous individuals, or atoms, which are responsible for the peculiar properties of the element, and which with the aid of chemical methods can neither be broken down further nor distinguished from one another.

Towards the end of the last century a certain torpidity fell upon this concept of the chemical atom. Its verification in thousands of chemical experiments led to the belief that the chemical atom not only could not be decomposed into further parts by familiar chemical methods, but that it was completely and absolutely indivisible. Moreover, the abundance of chemical compounds and their importance in daily life hindered the chemist from investigating the question, in what does the individuality of the atoms of different elements consist. In the last three decades the concept of the chemical atom has been set free from this torpidity by our experiences in physics. The discovery of various phenomena has led to a recognition of the fact that the chemical atom is an individual which again is itself made up of several units into a self-contained whole.

At the head of these new discoveries and insights comes the establishment of the facts that electricity is composed of discrete particles of equal size, or quanta, and that light is an electromagnetic wave motion. It followed necessarily from this that single separate electric quanta must be present in the composition of a chemical atom. For under certain conditions the chemical atoms emit light waves of a specific length or oscillation frequency - their familiar characteristic spectra - and these can come in the form of electromagnetic waves only from accelerated electric quanta.

Moreover, the discovery that the negative electron is a component of the chemical atom is of fundamental importance. In cathode rays the physicist became acquainted with free negative electric quanta capable of independent movement, the mass of which is smaller than a thousandth of the mass of the hydrogen atom. In the process of ionization he saw the liberation of such negative quanta or electrons from the chemical atoms. By exerting the influence of a

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magnetic field on the spectral lines of chemical elements, Zeeman and Lorentz even succeeded in detecting the negative electron in its place in, and as a component of, the atomic whole.

Furthermore, in these last three decades of great physical discoveries, as never before in history, Nature has drawn back the veil from a third undreamt-of secret before the eyes of the physicist. The discovery and investigation of radioactivity has made clear even for the most sceptical not only the separability of the parts of an atom, but also the chemical and physical individuality of a chemical atom - particularly of a parent atom, but equally of the atoms arising from its decay.

By recognizing that the chemical atom is composed of single separable electric quanta, humanity has taken a great step forward in the investigation of the natural world. However, this advance has faced us with a new, even greater problem - that of the structure of the atom. How many electric quanta are present in the atom of a chemical element? What are their fields of force? What are their mutual distances? What are their movements? What forces are roused on them if their state of equilibrium is disturbed by external interference?

We have been faced with these questions for a decade and a half. It is improbable that speculations will succeed in providing the answer to all these questions at one stroke, by one bold vision. It is more likely that more than a century will pass before we know the structure of the chemical atoms as thoroughly as we do our solar system. The path to this goal will lead, as it has so far, through the difficulties and surprises of experimental research. Many scientists will have to contribute to the solution of the great problem; they will have to follow up and measure all those phenomena in which the atomic structure is directly expressed.

With this in mind, for some twenty years I have set myself as my particular task the experimental investigation of the connexion between change in the structure and change in the spectra of chemical atoms. First of all, two questions may be posed in this connexion.

The first of them is tied up with the phenomenon of change in the structure of the surface of the atom. In order that we may have clearly set out before us every possibility in this respect, we shall proceed from the single atom, the parts of which are all arranged according to mutual equilibrium. We have learnt through experience that when an electrical ray strikes the surface of an atom, an electron, and in some circumstances a second and even a third electron, can be detached. In place of the structure of the neutral atom we are left with the structure of the corresponding monovalent, divalent, or trivalent atomic ion. We ask ourselves: what are the two spectra which belong to the two atomic structures - to neutral atoms and to positive atomic ions? And this question may be supplemented by the second question: is a specific spectrum emitted if the positive atomic ion is changed into a neutral atom?

To these questions I had given certain answers, at first in the form of working hypotheses, after a tentative examination of all previous observation known to me, in order to be able to think out a specific series of experiments to test the hypotheses.

The answer to the first of these questions was as follows: the spectral series of a chemical element are peculiar to the structure of the positive atomic ions, and are observed principally in arcs and sparks, and their lines, as Rydberg showed most successfully, can be grouped together, the lines of each group being a function of the integers.

The second hypothesis was as follows: during the attachment of negative electrons on the positive atomic ions of a chemical element its fine-structure band-spectra are emitted, as in numerous different orbits of attachment the potential energy is emitted in multiples of Planck's quantum constant.

These two working hypotheses have met with very different fates. Not long after its postulation I realized that the second of them was wrong, and neither bore it experimental fruit. However, what has been extraordinarily fruitful theoretically is the nucleus of it - that is, the assumption that energy is emitted in accordance with Planck's quantum law through an electron changing orbits about a positive charge. This assumption forms the startingpoint of Bohr's theory of the emission of serial lines. Although I myself once stood on the threshold of this theory, and although the final formulae give a series of frequency relationships in the spectral series which agree well with observed facts, I am nevertheless unable to believe it, because in its provisions it postulates suppositions which contradict, not only Maxwell's theory, but the very spirit of physics. This criticism is directed not at Planck's quantum of action, but at the hypotheses of Bohr which are bound up with it.

But let us return to the hypothesis that the positive atomic ions are responsible for the spectral series. Shortly after it was formed, I was able to make it bear experimental fruit through the following reflection.

By allowing the positive ions to pass through an electric field and thus giving them a certain velocity, it is possible to distinguish them from the neutral, stationary atoms. If it is possible to deduce their velocity from the spectral lines emitted by them, then this deduction implies the assignment of the displaced spectral lines to the moving atomic ions as emitters. The movement of the emitters of the spectral lines may be deduced on the basis of the Doppler principle.

We can in fact first place the beam of rays of moving positive atomic ions in a plane perpendicular to the axis in which we see the spectral lines emitted by them. These only appear

in the places in which they are normally situated in the spectrum when their emitters are stationary. Secondly we can allow the beam of positive atomic ions in our axis of vision to approach us, and then their spectral lines appear to us displaced from their normal place in the spectrum towards the shorter wavelengths, by an amount which is proportional to the velocity of the emitting system. And thirdly, if we make the atomic ions in our axis of vision travel away from us, then their spectral lines appear to us displaced from their normal position towards the opposite side.

In the year 1905 I set about proving experimentally the phenomenon just described. The state of research at that time meant that one had to regard as positive ions the canal rays, which approach the cathode of the glow current and emerge on the other side through perforations in it. I directed the axis of the collimator of my spectrograph first perpendicular to the axis of a beam of hydrogen canal rays, and on a second occasion I allowed the canal rays in the axis of the collimator to approach it. During the comparison of the two spectrograms so obtained, the anticipated Doppler effect in the serial lines of hydrogen appeared, and the same result was later obtained on the serial lines of numerous other chemical elements.

Thus at the beginning of 1906 it seemed to be established that the emitters of the spectral series of chemical elements are their positive atomic ions. This interpretation of my observations, it is true, was soon questioned. For, as particularly [W. Wien](#) and [J.J. Thomson](#) have shown, canal rays usually contain, beside the positive atomic-ion rays, also neutral rays, so that it was not possible to determine accurately whether the spectral lines showing a Doppler effect should be attributed to the former or the latter. However, cases came to light later in which canal rays containing only positive ions showed a Doppler effect in the spectral lines emitted by them. If even today I still regard the positive atomic ions of a chemical element as the emitters of their spectral series, nevertheless I do not take this concept now as restricted as I did when I only considered free positive atomic ions which owing to their positive total charge are accelerated by the electric field. Rather, in my present opinion, it is possible that the serial lines can in addition be emitted from a positive atomic ion which is not free, and to which a negative electron has already begun to attach itself; only the electron must not yet have come so close to the atomic ion that emission from the latter will already be sensitive to and disturbed by the electric field of the electron.

In this connexion the ultraviolet continuous spectrum of hydrogen may be mentioned. I expected that a continuous spectrum would be emitted when in the course of the attachment of the negative electron to the positive atomic hydrogen ion its encroachment has continued so far that the emission of the serial lines is noticeably disturbed. I therefore looked for - and found - a continuous spectrum in hydrogen canal rays.

Since the discovery of the Doppler effect in canal rays a great number of experiments on this phenomenon have taken place. The following results may, briefly, be deduced from them.

The emitters of the spectral series are without exception single atoms, not compounds of atoms. The spectra of atomic ions of higher valence are different from the spectra of atomic ions of the same element, but of lower valence.

The band-spectra - for example, those of hydrogen and nitrogen - do not as a rule show a canal-ray Doppler effect. Because I expected on the one hand that their emitters were positive molecular ions consisting of more than one atom, and because on the other hand positive molecular ions are also found as canal rays under low pressure, I was led to explain the absence of the Doppler effect in bands by the theory that when stimulation by collision takes place, so that light is emitted, the molecular ions of more than one atom are dissociated after a short period of existence. This concept also makes the canal-ray Doppler effect appear possible in bands, at a small velocity and low pressure. And in fact Mr. Rau of the Würzburg Institute of Physics has recently succeeded in proving this in the case of negative-nitrogen bands. All his observations, moreover, lead to the conclusion that the emitters of these bands are positive diatomic nitrogen molecular ions.

The announcement of this new step forward bids us recognize that research work on the canal-ray Doppler effect is by no means complete and the question of where the various spectra of chemical elements originate has not yet been conclusively answered.

If the experimental physicist has already done a great deal of work in this field, nevertheless the theoretical physicist has still hardly begun to evaluate the experimental material which may lead him to conclusions about the structure of the atom. It has, however, been established that the conversion of the structure of the neutral atom into the structure of the ion involves fundamental changes in the oscillation of the electric quanta which remain in the structure. What conclusions, however, may be drawn from this about the structure of the neutral atom and of the ion remains an unanswered question.

The removal of an electron from the surface of an atom - that is, the ionization of the atom - means a fundamental structural change in its surface layer. That this is accompanied by an equally fundamental change in the spectrum of the surface layer was to be expected from the very first. Matters are different in the case of the second sort of structural change which I made the subject of my experimental research.

We must always bear firmly in mind that the chemical atom is an individual, self-contained structure of positive and negative electric quanta. An external electric field, meeting it and

passing through it, affects the negative as much as the positive quanta of the atom, and pushes the former to one side, and the latter in the other direction. Certainly this displacement is soon stopped by the opposing forces which it awakens among the quanta, which are displaced relative to one another, but nevertheless the displacement does take place, and it means a deformation, an alteration of the atomic structure in comparison with its form before the influence of the external electric field. And the question arises whether this sort of alteration of the atomic structure, this deformation by an electric field, manifests itself in an alteration of the spectrum of the atom. In other words, the question of the effect of an electric field on spectral lines has thus arisen.

At the time when I became engaged on this question Voigt had already developed and worked out mathematically a theory of an electric analogue to the Zeeman effect. The result of this theory was not encouraging; because it implied that the alteration to the oscillation frequency, or wavelength, of spectral lines by an electric field would be so small that it would be immeasurable. And this result seemed to be confirmed by the complete absence of success in research to find this effect extending over a number of years.

However, I was unable to accept the presupposition of the theory - namely, the assumption that the emission of a spectral line on the part of an atom was the work of only one single independently moving electron in the atom. In my view the structure of the whole atom was that of an individual, with all its parts interconnected, and the emission of a spectral line appeared to me to be the result of the coherence and co-operation of several electric quanta. Therefore I expected that from the alteration of the atomic structure by an external electric field there would arise also an alteration of the spectrum of the atomic structure. And I tried to solve my problem by producing a strong electric field in a luminous gas. I achieved this by making canal rays, passing through perforations in the cathode, on the other side travel in a strong electric field between the cathode and a second supplementary electrode placed opposite it.

My very first spectrogram of canal rays in hydrogen and helium revealed the effect of the electric field on a number of spectral lines and gave some hint of the wealth of phenomena in the newly opened-up field. Moreover this discovery also showed again how much richer and more original are the works of Nature than the ideas of Man. In the event of the axis on which the observer views the luminous electric field being perpendicular to the axis of the field, the theory had postulated that every single spectral line would be splitted under the influence of the electric field into two components, both of which would appear, relative to the normal line, displaced towards the longer wavelengths, and of which one would vibrate parallel, the other perpendicular, to the field. How different the reality! For example, the red hydrogen line is splitted symmetrically to the normal line into nine components, of which the electric vibrations of six are parallel, and three perpendicular, to the field.

Since the discovery of the effect of an electrical field on spectral lines in the year 1913, already a great number of experiments on it have taken place. The most common and most important result of them is that the nature and size of the effect on corresponding series of different elements are largely an expression of the peculiarity of their atomic structure - or, at least, of the structure of the surface. Thus the effects on the hydrogen series, on the series of mono- and bivalent positive atomic helium ions, on the series of lithium, mercury, and aluminium, differ from one another in characteristic ways.

The following results may be of interest in detail.

Along a series of lines running from longer to shorter wavelengths the effect of the electric field becomes greater as the serial numbers increase - that is, as the wavelength decreases.

The proportion of the intensity of various series within a serial system is, in the case of several elements, dependent on the strength of the deforming electric field. Thus under its influence new series may become visible, which outside the electric field possess so little intensity that they are not observable.

The broadening and displacement of spectral lines which accompanies an increase in the pressure of the gas or in the density of ions, originates in the effect of the electric fields of single atoms on neighbouring light-emitting atoms. Connected with this is Haber's highly promising idea of tracing the heterogeneous catalysis in solid surfaces back to the deformation of the molecular structure by the molecular electric field. Perhaps it will be possible to spectro-analyse accurately such electric fields.

But let us leave these details and return to the problem of the structure of the atom. We must ask ourselves whether a conclusion about the structure of the atom, or at least about the process of the emission of serial lines, may be drawn from the effects of an electric field on serial lines. Now, Bohr and Epstein have developed a theory for the effect in question which gives the number and interval for the component lines in electric fields which agree surprisingly well with observed facts, at least in the case of the series of the monovalent atomic hydrogen ion and of the bivalent atomic helium ion-or, rather, in the case of the electron adhering to these ions. This agreement strongly supports Bohr's theory of the emission of spectral lines, and thus also his presupposition, originating from Rutherford, about the structure of the hydrogen and helium atoms.

In spite of my high estimation of this achievement by the theory, nevertheless I am unable to accept it as definitive; apart from the fact that I am unable to believe in some of its

presuppositions, it does not fully correspond to our experience. It cannot explain the following observation, which seems to me very important to research into the structure of the atom.

A beam of luminous hydrogen canal rays has, owing to its velocity, exactly the same direction as that of the electric field in which it may be made to move. If the axis of the beam is placed perpendicular to the axis of the field, the intensities of the components of every single line which is splitted are as symmetrical relative to the normal line as the intervals at which the components are situated to right and left of it. On the other hand, if the direction of the rays is the same as that of the field, then the intensity of those components which lie on the side towards the longer wavelengths increases. And if the canal rays are made to travel in the opposite direction to that of the field, then *vice versa*, the components towards the shorter wavelengths appear with greater intensity. It would therefore seem as if a hydrogen atom, or its ion, in an electric field possesses polarity along the axis of the field - that is, two sides may be distinguished in this axis.

This phenomenon is as remarkable as it is important. We may legitimately expect to be able to come, from its theoretical implications, to a conclusion about the structure of the hydrogen atom. It may well be successful, if we not only take into account, as has been the case up till now, the effect on a single electron at the surface of the atom, but take as the point of departure for our inferences from the observations the connexion between the parts of an atom which go to make up an individual structure.

Reference to this brings us back to the problem of the structure of the atom. We shall realize the immensity of this problem when we cast a glance behind us at the ground which has already been covered. Research into changes in the spectrum of chemical atoms as a result of changes in their structure has disclosed a whole series of new phenomena. The removal of an electron from the surface of an atom - or its reattachment - leads to fundamental changes in the spectrum of the atomic parts capable of oscillation; and the deformation of the atomic structure by an electric field is expressed by various forms of influence on the oscillation of those atomic parts. But even though these new phenomena have already so richly borne experimental fruit, even though the theories which are beginning to be built on them seem so promising, nevertheless they have hardly begun to clarify the great problem, have only shed light on a small part of the experimental work, and still less on the theoretical field. Research into these phenomena can do no more than contribute a little to the solution of the great problem of the structure of the atom. It will still need the work of many generations to reach that solution. Our advance from the speculative hypothesis of the atom formed by the Greek mind to the discovery of the electric nature of the structure of the atom through the Germanic research of the past century should be an encouragement and a lesson for the century to come.

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