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1954

[Link to publication](#)

Citation for published version (APA):

Bohr, N. (1954). Rydberg's discovery of the spectral laws. CWK Gleerup.

Total number of authors:

1

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Rydberg's discovery of the spectral laws

by

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It is a great pleasure to me to accept the invitation at this Rydberg Centennial Conference, where the present stand of our knowledge about spectroscopy will be reviewed by so many experts from different parts of the world, to remind about Rydberg's pioneering work in this field. Especially I shall stress the direct consequences of his great discoveries for the development of our ideas of atomic constitution and, in this connection, recall some personal remembrances.

As is well known, Rydberg's discovery of the spectral regularities was the outcome of his intense interest in the problem of the relationship between the chemical elements which, in the latter part of the former century, was brought into the foreground especially through the work of Mendelejew. The remarkable periodicity in the physical and chemical properties of the elements when arranged in order of increasing atomic weights took the fancy of the searching spirit of Rydberg who, with his disposition for numerical calculations, became especially interested in the optical spectra, where the great refinement of measurements permits the establishment of arithmetical relationships of high accuracy.

For Rydberg's great achievements in this respect, it was a happy intuition from the beginning to look for relations not between the directly measured wavelengths of the spectral lines, but between the reciprocal figures expressing the number of waves per unit length, now known as wave numbers. To this choice he was led through the constant differences between wave numbers occurring in so-called doublet and triplet lines. From Rydberg's side, the tracing of these equal spacings was an original discovery, but when his work was already far advanced, he became, as he modestly and honestly remarks, aware that the occurrence of such relations in complex lines had been pointed out by Hartley a few years before. Rydberg, however, went himself far deeper into the matter and extensively used wave number differences as a main tool for his disentangling of spectral regularities.

To this purpose, further directives were offered by the study of the so-called line series which, in the previous decade, were discovered in many spectra by Liveing and Dewar, and are characterized by similarity in appearance (sharp, diffuse, etc.) as well as by gradual harmonious decrease in intensity and separation. Rydberg now found that all the series in the spectra analyzed by him, when described by wave

numbers and suitably arranged by displacement of the wave number scale, showed such close relationship that he was led to represent the wave numbers for the lines in each series by the difference between a constant term and a term which, in a common manner, decreased when progressing through the series. This relation he expressed by the formula

$$\sigma = a - \varphi(n + a), \quad (1)$$

where n is an integer serving as ordinal index of the series lines, and φ a universal function, while a and a are constants specific for the individual series.

As a first attempt to determine this function φ , which obviously had to converge to zero for increasing n , Rydberg tried the expression

$$\varphi(n+a) = \frac{C}{n+a}, \quad (2)$$

but obtained neither a satisfactory agreement for any longer series nor the required constancy of C for all series. As a better choice, Rydberg next tried

$$\varphi(n+a) = \frac{R}{(n+a)^2}, \quad (3)$$

and he tells in his famous article in the Swedish Academy from 1889 that just when he was occupied by testing this formula he learned about Balmer's discovery of the simple law

$$\lambda = B \cdot \frac{n^2}{n^2 - 4} \quad (4)$$

which with such extraordinary accuracy represents the wavelengths of the well-known series of hydrogen lines. Substituting wavelength by the corresponding wave numbers, Rydberg wrote the Balmer formula in the form

$$\sigma = \frac{R}{2^2} - \frac{R}{n^2}, \quad (5)$$

representing a special case of his own formula. Guided in this way to an accurate fixation of the suspected universal constant R , now known as the Rydberg constant, he also soon found it possible not only to prove the far-reaching validity of formulae (1) and (3), but could with its help with considerable precision determine the constants a and a for any series.

This great advance made it possible for Rydberg to trace even more intimate connections between the different series composing the spectrum of an element. In fact, he found not only that certain series with different values of a exhibited the same value of a , but that quite generally the value of the constant term a in any series coincided with a member of the sequence of the variable terms in some other series of the element. In particular, Rydberg found that the difference between the limit for the principal series and the common limit for the diffuse and sharp series was just equal to the wave number of the first member of the principal series, a result

which, as is well known, was later independently obtained by Schuster. In his original paper, Rydberg thus proposed as a comprehensive formula for every spectral line of an element

$$\sigma = \frac{R}{(n_1 + \alpha_1)^2} - \frac{R}{(n_2 + \alpha_2)^2} \quad (6)$$

according to which each series corresponds to a constant value of n_1 and a sequence of values of n_2 . In this scheme, the characteristic complexity of many series lines is directly accounted for by a multiplicity of the α -values.

In arguing about the scope of his final formula, Rydberg expressed himself with remarkable caution and subtlety. On the one hand, he was quite aware that the special form of the two combining terms in formula (6) could not rigorously fit the observations. On the other hand, he stressed that his formula in essentials fulfilled the conditions of universality demanded of fundamental laws of nature. This attitude finds special expression in the discussion, in the last part of Rydberg's paper, of the type of series formulae just at that time used by Kayser and Runge to represent their extensive refined measurements of spectral lines. While fully appreciating the great accuracy of such formulae, he points out that it had not been his main intention to develop a proper interpolation formula for each individual series, but rather, by using the smallest number of specific constants in his computations, to trace universal relationships.

The search for a mechanism which might explain the spectral regularities, however, was at that time confronted with apparently insurmountable difficulties. Especially we may recall the pertinent remark of Rayleigh that any analysis of the normal modes of vibrations of a stable mechanical system leads to relations between the squares of the frequencies, and not between the frequencies themselves. It is true that Ritz, inspired by Lorentz' explanation of the Zeeman effect, attempted to account for the spectral laws by introducing the idea of atomic magnetic fields, whose effects on the electric constituents of the atom — in contrast to ordinary mechanical forces — depend intrinsically on the velocities. In spite of all ingenuity of these endeavours, it was not found possible, however, on such lines to arrive at an explanation of the spectral laws, consistent with the interpretation of other atomic properties.

Still, Ritz' penetrating inquiry into spectral problems, furthered especially by his close collaboration with Paschen, led him to various refinements of the numerical formulae for spectral series and to the prediction of new series which essentially completed the analysis of various line spectra. In connection with this work, in which Rydberg's discoveries and original conceptions proved of decisive importance, Ritz in 1908 enunciated a general law, now known as the Rydberg-Ritz combination principle, according to which the wave number of any line of a spectrum can be rigorously expressed as

$$\sigma = T_1 - T_2, \quad (7)$$

where T_1 and T_2 are two members of the set of terms characteristic of the element.

A new epoch in the development of our ideas of atomic structure was soon after

initiated by Rutherford's discovery, in 1911, of the atomic nucleus. This discovery led to a remarkably simple picture of the atom as a system of electrons moving round a central charge of minute extension, in which practically the whole mass of the atom is concentrated. Indeed, it became at once clear that all physical and chemical properties of an element, depending on the binding of the atomic electrons, were widely regulated by the total charge of the nucleus determining the number of electrons in the neutral atom. This so-called atomic number was obviously to be identified with the ordinal index of the element in the periodic table, which Rydberg had so clearly recognized as the principal factor governing the relationships between the properties of the elements. As is well known, this view found, a few years later, decisive confirmation by Moseley's fundamental researches on the characteristic X-ray spectra of the elements, and it is interesting to recall that his fixation of the atomic number of the whole sequence of chemical elements in several respects confirmed Rydberg's expectations of the lengths of the periods in Mendelejew's table.

An immediate consequence of Rutherford's discovery was, however, the stressing of the difficulties in accounting for the spectral regularities on the basis of classical physics. In fact, on the ideas of ordinary mechanics and electrodynamics, a system of point charges possesses no inherent stability which could account for the constancy of the specific properties of the elements so impressively revealed by their line spectra. In particular, the radiation from the motion of the electrons would give rise to a continuous dissipation of energy, accompanied by gradual alteration of frequencies of motion and shrinking of orbital dimensions until all electrons would be amalgamated with the nucleus within a minute neutral system.

A clue to the problem of atomic stability and to the origin of line spectra was, however, offered by the discovery of the universal quantum of action, to which Planck, in the first years of this century, was led by his ingenious analysis of the phenomena of thermal radiation. As is well known, Einstein a few years later pointed out not only that Planck's formula $E = nh\nu$ for the possible energy values of a harmonic oscillator of proper frequency ν permitted to explain observed anomalies of specific heats of various substances at low temperatures, but that also characteristic features of atomic photo effects demanded that exchange of the energy by radiation of frequency $\nu = c\lambda$ should take place in so-called light quanta or photons of energy $h\nu$. Notwithstanding the impossibility of a closer analysis of these phenomena on accustomed lines, conspicuous especially in the dilemma as regards the constitution of radiation implied in the concept of the photon, it was clear that we were here dealing with an essential feature of wholeness of atomic processes, quite foreign to the classical ideas of physics.

On this foundation, the idea suggested itself that, in any change of the energy of an atom, we have to do with a process consisting in a complete transition between two stationary quantum states, and that any radiation involved in such transition processes is exchanged in the form of a photon. In fact, this so-called quantum postulate offered an immediate interpretation of the combination principle by identifying the numerical value of each spectral term multiplied by hc with the energy of a possible

stationary state of the atom. Moreover, a solution was indicated of the puzzle of the apparently capricious occurrence of selective absorption of radiation by atoms. Under ordinary conditions, the atom will be in its normal state of lowest energy, corresponding to the largest spectral term, given by the limit of the principal series. We therefore understand that only this series appears in selective absorption and, in particular, that continuous absorption sets in at its limit, evidently corresponding to the removal of an electron from the atom. Soon after, these conclusions were also directly borne out by the famous experiments of Franck and Hertz on the excitation of spectral lines by impact of electrons. The experiments showed that any possible exchange of energy between electron and atom corresponds to a transition from the normal state of the atom to a higher stationary state, and that the minimum energy for producing ionization of the atom is just equal to hc times the wave number of the limit of the principal series.

Remembering the vivid discussions of those years, it may perhaps be of interest to recall a conversation between Einstein and Hevesy, to whom as a co-pupil of Rutherford I had early communicated the new views and prospects. When asked about his attitude to such ideas, Einstein answered that they were not completely foreign to his mind, but humorously added that he felt that, if they were to be taken seriously, it would mean the end of physics. Looking back, one will admit the pertinence of this utterance; surely, we have had to revise our ideas of what to understand by physical explanation. Meanwhile it proved possible step by step to make ever more extensive use of the spectral evidence to advance our knowledge of atomic constitution. The attainment of this goal should, as we know, demand the development of an appropriate mathematical formalism departing radically from that of classical physics. To begin with, however, one had to approach the problems in a tentative manner by more primitive methods. Guidance was mainly afforded by so-called correspondence considerations characterized by the endeavour to make use of ordinary physical concepts in all considerations not directly opposed to the quantum postulate.

The first step was the establishment of a relation

$$R = \frac{2\pi^2 e^4 m}{c h^3} \quad (8)$$

expressing Rydberg's constant in terms of the mass m and charge e of the electron, and the fundamental constants c and h . In fact, this relation could be shown to be a necessary condition for the asymptotic approach of the frequencies of the hydrogen spectrum and those of the motion of an electron in a Keplerian orbit around a heavy nucleus of unit charge. Such considerations also offered a simple explanation of the appearance of the Rydberg constant in the spectra of the other elements by assuming that the series in question originate from transition between stationary states in which one of the atomic electrons is bound more loosely to the nucleus than the others and that therefore the forces exerted on it by the residual ion, at any rate at large distances, closely resemble the forces to which the electron in the hydrogen atom is subjected.

A special problem arose, however, as regards the origin of the series of lines first observed in 1899 by Pickering in stellar spectra and expressed with great accuracy by the formula

$$\sigma = R \left(\frac{1}{2^2} - \frac{1}{(n+1/2)^2} \right). \quad (9)$$

Due to its close relation with the Balmer series, the Pickering series was attributed to hydrogen, and this assignment was apparently strongly supported by considerations of Rydberg who compared the relationship between the Balmer and the Pickering series with that of the diffuse and sharp series in other spectra, and in this connection predicted the existence of a further hydrogen series

$$\sigma = R \left(\frac{1}{(3/2)^2} - \frac{1}{n^2} \right), \quad (10)$$

corresponding to an ordinary principal series.

Just in 1912, not only the Pickering lines, but also a series of lines represented by (10) as well as a series of lines given by

$$\sigma = R \left(\frac{1}{(3/2)^2} - \frac{1}{(n+1/2)^2} \right) \quad (11)$$

were observed by Fowler in intense discharges through mixtures of hydrogen and helium gases. The assignment of all these lines to the hydrogen atom was, however, irreconcilable with correspondence considerations which, on the contrary, suggested that the Pickering series as well as the series (10) and (11) had to be attributed to the helium ion consisting of an electron bound to a nucleus of two unit charges. In fact, such a system would just be expected to give a spectrum of the same type as that of the hydrogen atom, but in which R was replaced by $4R$.

These ideas were to begin with contested by leading spectroscopists like Fowler and Runge. I especially recall the warning, given by the latter at a colloquium in Göttingen, against such apparently arbitrary use of spectral evidence by theoreticians who did not seem properly to appreciate the beauty and harmony of the general pattern of series spectra, revealed above all by the ingenuity of Rydberg. The dispute was, however, rapidly settled to the general satisfaction. Not only were the Pickering and Fowler lines soon after observed by Evans in highly purified helium, showing no trace of hydrogen lines, but it could even be shown that the slight deviations of the lines measured by Fowler from the formulae suggested by Rydberg corresponded exactly to a small correction in the Rydberg constant deduced from theoretical arguments when taking the actual masses of the atomic nuclei into account.

An important outcome of the whole discussion was the recognition that certain series of the magnesium spectrum observed by Fowler in intense spark discharges could be united into a simpler series scheme just by the replacement of the Rydberg constant by $4R$. Such series systems, to the discovery of which in many elements Fowler as well as Paschen contributed so largely in the following years, are now known

as spark spectra. In contrast to the ordinary arc spectra which originate from neutral atoms, these spectra are assigned to ions of unit charge, in which a loosely bound electron is exposed to conditions resembling those of the electron in the helium ion. The expectation that ions of still higher charge, Ne , would give rise to spectra of a generalized Rydberg scheme, in which the common constant is given by N^2R , has also been widely fulfilled. I hardly need to enlarge on this point in this beautiful institute directed by Edlén who, to the admiration of all physicists, has succeeded by such skill and perseverance through the years in producing and analyzing a multitude of spectra corresponding to a high degree of electron stripping of the atoms.

Within the compass of this short address, I have had to confine myself to Rydberg's pioneer work and to a few aspects of his discoveries which came to play such a decisive part in the initial stage of a development by which spectroscopic evidence gave us an ever deeper insight into the problem of atomic constitution, and in particular led to a classification of the states of electron binding in the shell structure of the atom, which in every detail accounts for the periodic relationships of the properties of the elements. A veritable culmination of the semi-empirical approach characteristic of this first tentative period was the enunciation by Pauli of the exclusion principle, which should subsequently find such an appropriate incorporation in the rational methods of quantum theory. These methods, though discarding accustomed pictorial representations, rival classical mechanics and electrodynamics in consistency and completeness, and provide the firm foundation for the exploitation of the inexhaustible wealth of spectroscopic evidence.

It has truly been a great adventure for our generation to witness this whole development which sometimes proceeded with almost tumultuous rapidity. Thus, I remember especially the successful conference in 1919 here in Lund, when a new stage was just being initiated by the work of Sommerfeld and his school, and the prospects were discussed with great enthusiasm and mutual benefit. We were assembled in the old Fysikum, where the rich traditions were happily upheld by Rydberg's young followers, among whom Siegbahn with such experimental mastery brilliantly pursued Moseley's work, and Heurlinger made so important contributions to the theoretical interpretation of band spectra. Although Rydberg himself by illness was prevented from attending the conference, we all felt most vividly his guiding spirit among us, just as we do today at this memorial meeting.