

# Walter Ritz as a theoretical physicist and his research on the theory of atomic spectra

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## Contents

1. General characteristics of Ritz's works	435
2. The state of theoretical spectroscopy at the beginning of the 20th century	438
3. Ritz's thesis on spectral series theory and his elastic atomic model	443
4. The magnetic atomic model and the combination principle	448
5. Conclusion	454
References	454

**Abstract.** An historical and methodological analysis is given of the scientific heritage of the remarkable Swiss theoretical physicist Walter Ritz (1878–1909) on the basis of a study of his complete works edited in 1911. The general characteristics of Ritz's works—including the papers on spectroscopy, the variational method and electrodynamics—are discussed, and his fundamental research in the theory of atomic spectra is considered in detail. The elastic and the magnetic atomic models, proposed by Ritz to explain the spectral laws and based on a classical approach, are discussed. It is shown that the generalised Balmer and Rydberg formulas and the combination principle, which later became a basis for the formulation of Bohr's frequency condition, were obtained by Ritz as a result of mathematical deductions from his models and were not of a semi-empirical character as is usually believed.

## 1. General characteristics of Ritz's works

The name of Walter Ritz, a Swiss scientist of the beginning of the 20th century, needs no special recommendations for physicists. In spectroscopy, the name of Ritz is connected primarily with the combination principle which played an important role in the construction by Niels Bohr in 1913 of the initial quantum theory of the atom and its spectrum.

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Ritz's variational method is well known to mathematicians and is successfully applied in theoretical physics; this method is widely presented not only in the corresponding monographs and textbooks, but also in encyclopaedic literature. In accounts of the history of appearance of relativistic concepts, a postulate contained in Ritz's works on the addition of the speed of light with that of its source (the so-called ballistic hypothesis) is given as a textbook example of the failure of any attempt to create an alternative to the special theory of relativity (STR).

At the same time, one may safely assert that the true nature of the scientific work by Ritz was that of a remarkable theoretical physicist, his actual role in the prehistory of theoretical spectroscopy was much more significant than is usually accepted, and the real scale and originality of his personality have not yet been given proper acknowledgement. Grounds for such a statement are given by an attentive study of the contents of Ritz's complete scientific works [1], which runs to more than 500 pages and was edited in 1911 in Paris by the publishers Gauthier–Villars on the initiative of the Swiss Physical Society with the active assistance of a group of scientists from Gottingen, the Institute of France (which unites five Academies, including the French Academy of 'Immortals' and Academy of Sciences) and the Federal Polytechnical School in Zurich (Switzerland). The book presents a posthumous edition of the works of the young scientist who died in 1909 at the age of 31 and actively worked in science only from 1902 to 1909 (which included a three-years' break because of illness). In a brief foreword to the readers (Avertissement) at the beginning of the book, its compilers wrote that the Swiss Physical Society 'not only intended, by making available scientific papers of a rare beauty, to draw once more the attention of physicists and mathematicians to work of a most refined mind (d'un esprit d'elite)'. It was 'convinced it was favouring the progress of Science by facilitating the dissemination of brave new ideas' (Ref. [1], p. V).

Included amongst Ritz's works [1] were 25 papers from 1902–1909 containing his research in three different topics in physics and mathematics.

The first of these topics, which was developed by Ritz during this period, was connected with spectroscopy and includes 13 papers, beginning with his thesis of 1902 'On the theory of spectral series' ([1], paper I, p. 1–77), in which for explanation of regularities in the atomic spectra he used the elastic atomic model based on classical concepts. The main part of the thesis, which represented extensive theoretical research, was published by Ritz as a large paper in 1903 [2]. A short version of the paper [3] and a small paper 'On the spectrum of potassium' [4] were published in the same year. Ritz subsequently rejected the elastic model and in 1907 he published two short papers 'On the origin of spectral series' [5, 6] in which the idea of the magnetic atomic model (also based on classical concepts) first appeared. Ritz implemented this idea in 1908 in a large paper entitled 'Atomic magnetic fields and spectral series' [7] devoted to the magnetic atomic model, and using this model, in the paper 'On the new law of spectral series (preliminary results)' [8], he formulated for the first time the combination principle for series of atomic spectra as a universal spectroscopic law. A shorter version of this important paper originally written in German was also published in 1908 in English [9]. A general paper in French by Ritz on 'Linear spectra and atomic structure' [10], as well as two short papers 'On several anomalous Zeeman effects in the spectrum of thorium' [11] and 'Series in the spectrum of barium' [12] were published by 1909. Ritz's papers on spectroscopy constitute about a third of his total work.

The second topic of Ritz's studies was generically connected with the mathematical methods applied by Ritz in his thesis for modelling atomic oscillation frequencies by oscillations of a two-dimensional square plate. He proposed a new method for solving problems in the calculus of variations and used it for a number of particular cases. In 1908 he published a long paper 'On the new method for solving some variational problems of mathematical physics' [14], and an extensive publication on an important application of the new method, 'Theory of the transverse oscillations of a square plate with free boundaries' [15], appeared in 1909. These three papers constitute about a quarter of Ritz's works.

Finally, the third topic of research was connected with an attempt by Ritz to reconstruct electrodynamics radically based on a field approach which was an alternative to the Maxwellian field-free approach, which went back to Gauss and Riemann. Nine papers by Ritz (more than a third of his total work) relate to this topic. From these 8 were published in 1908–1909 and included a very long paper on 'Critical studies on general electrodynamics' [16] and a shorter paper on the same subject, 'Critical studies of electrodynamic theories by J C Maxwell and H-A Lorentz' [17], the papers 'On the role of ether in physics' [18], 'Gravitation' and 'On the principles of electrodynamics and on black body radiation theory' [20]. This paper [20] was criticised by Einstein in 1909 in his well-known paper 'On the problem of radiation' [21], and Ritz's paper 'On the modern state of the theory of radiation (objections to the paper by A Einstein)' [22] and a short note under the same title written jointly with Einstein [23] were devoted to the discussion with Einstein. The introductory Göttingen talk 'The relativity principle in optics' remained in manuscript form and was published only in the collected works.

It should be emphasised that the clearly distinguished peak of Ritz's scientific activity falls in the last two years of

his life—during 1908–1909 he published 18 papers amounting in total to about 400 pages and devoted to all the three topics of his research.

Ritz's name acquired wide fame even during his lifetime, as is shown by the publication of the complete works of the scientist just after his death, and his works on the combination principle and the variational method were generally recognised by his contemporaries. Ritz was highly esteemed by the spectroscopists Kayser, Runge and Paschen, by the recognised masters of science such as the physicist Lorentz and mathematicians Gilbert and Poincaré; Einstein held respectful discussions with him [21, 23]; his untimely death was bitterly regretted by such scientists as Rayleigh [24], Sommerfeld (Ref. [25], p. 286) and Rozhdestvenskii (Ref. [26], p. 8). A detailed foreword to the works by Ritz was written by the specialist in magnetism Weiss (Ref. [1], p. VII–XXII) and contained, in particular, praise for Ritz's variational method from Poincaré. Acquaintance with Ritz's works was for Bohr one of the stimuli for formulating the second postulate of the initial quantum theory of atoms and spectra—the famous frequency condition. The quantum interpretation of the known spectroscopic corrections to spectral terms, studied by Ritz as early as 1902 in the framework of the pure classical approach (Rydberg corrections and corrections introduced by Ritz himself and bearing his name), was a subject of research by Sommerfeld, Bohr, Schrödinger and Born later on.

While describing the scientific work of Ritz, it should be stressed that the modern historiography devoted to him is extremely scanty. Better known (although it requires a more precise definition) is the history of Ritz's variational method: we note mathematical monographs by Mikhlin [27] and Gould [28], where interesting (however, somewhat fragmentary) background information is presented. Analysis of the elastic and magnetic atomic models proposed by Ritz to explain spectral regularities is completely absent; the discovery of the combination principle was not considered. It is usually accepted to have been empirically established by Ritz in 1908 (see, for example, the fundamental lectures on general physics by Sivukhin [29], p. 62, and also Ref. [30]). Practically no reference is made to Ritz's works in the account of the history of electrodynamics, although they, undoubtedly, are worthy of this. The only publication in the world which is specifically devoted to his scientific activity as a whole seems to be an article by the American science historian Forman published in volume 11 of the multivolume dictionary of scientific biography edited in 1976 (Ref. [31], p. 475). Regretfully, this excellently written and very informative essay is as little known to physicists as the complete works collection [1] itself. In our paper (see preprint [32]) we will make extensive use of the material from Forman's publication, especially the part that concerns Ritz's biography.

Walter Ritz was born in Sion (Switzerland) on February 22, 1878, to the family of the landscape painter Rafael Ritz. After having finished college in 1895, he attended a technical course in a lyceum and in 1897 he entered the federal polytechnic school in Zurich. Shortly afterwards he rejected his initial intention to become an engineer and moved to a mathematical division of the school (one of the students of which at that time was Albert Einstein). In the spring of 1901 Ritz moved to Göttingen. Here he studied at the university mainly with physicists Voigt and Riecke,

attended lectures by the mathematicians Gilbert and Klein, the physicist Abraham and other well-known scientists.

In 1902 Ritz carried out his already mentioned thesis study on the theory of spectra (Ref. [1], c. 1) and defended the thesis on December 19 of the same year with the highest acclamation 'summa cum laude' ('with the highest praise'); the choice of the thesis theme on the theory of spectra corresponded to the interests of professors Voigt and Riecke. After having defended the thesis, Ritz went to Leiden in Holland, meeting on the way (in Hannover) with Runge to discuss spectroscopic problems. In Leiden for six weeks Ritz attended lectures and seminars by Lorentz together with Ehrenfest, whom he met and became friends with in Gottingen (Ref. [33], p. 32) and whose intellectual development, as Klein stresses (Ref. [25], p. 165), he very strongly influenced. Ritz left Leiden, in Forman's words, 'little inclined (or not inclined at all) to Lorentz's view' (Ref. [31], p. 476).

In May and June 1903, Ritz worked at the Kayser Institute in Bonn, where the best conditions for spectroscopic studies in Germany in those years were created: he succeeded in detecting experimentally a missing line of the diffuse series of potassium [4], which he had predicted in his thesis. At the end of 1903, Ritz moved to Paris and, upon recommendation by Weiss, was taken on in Cotton's laboratory, where he was engaged in making photographic plates sensitive to the infrared region of the spectrum. The choice of this particular problem was connected with importance of studying this spectral band for different chemical elements.

In July 1904 Ritz had to return to Switzerland because of a sharp deterioration in his health, and during the subsequent three years he tried to recover it at diverse sanatoria. During this period he published nothing but a short paper on photography in the infrared spectral band [34]. From the beginning of 1907 Ritz renewed his intensive scientific activity despite bad health. From September 1907 he worked at Paschen in Tübingen, which was one of the centres for spectroscopic studies in Germany. In spring 1908 Ritz moved to Gottingen where he was cordially welcomed at the University and was given a lectureship, although he had no longer the strength to give lectures. An introductory lecture prepared by him (Antrittsrede zur Habilitation) was accepted with kindness by the judging committee of which Gilbert, Minkowski, Voigt and Runge (Ref. [1], p. XI) were the members, and was given on March 5, 1909 (Minkowski died shortly before this, on January 12, 1909).

Ritz passed away as a result of tuberculosis on July 7, 1909 †. His obsession with science is characterised by the words he said that day to a nurse who was taking care of him: 'Please, take good care of me, nurse, — it is vital that I live a few more years for the sake of science' (ibid.).

†Shortly prior to his death Ritz was visited by Ioffe, a close friend of Ehrenfest who worked in St Petersburg at that time. Ioffe wrote to Ehrenfest that he had talked with Ritz about many things, including the theory of quanta, and that Ritz was very grateful for kind regards from Ehrenfest ([35], p. 264). And in a short time Ehrenfest informed Ioffe that he had received news from Ritz's mother about his death: on July 7 'he peacefully passed away because of hemorrhage'. 'His death aroused in me above all such a feeling of how, in fact, everything is simple, how completely everything is determined', Ehrenfest wrote ([35], p. 45). In the foreword to the book [35] its compiler V Ya Frenkel' notes the friendship of Ehrenfest in Gottingen with 'the very talented student from Switzerland, Ritz'.

In all his scientific activity Ritz showed himself to be a deep theoretical physicist with a subtle understanding of the physical essence of the problems he studied and handled brilliantly using mathematical methods.

Below we will consider in detail the spectroscopic studies by Ritz and his closely connected attempts to construct atomic models, first elastic, and then magnetic. Such a choice is dictated by the large contribution by Ritz towards establishing the most important spectroscopic laws. An examination of this contribution is especially important because that aspect of Ritz's research, which turned out to be the most significant for modern physics development, has obtained quite insufficient interpretation in the literature both in physics and in scientific history. The lack of proper attention from physicists and historians of science to this line of Ritz's research is undoubtedly connected with the fact that his approach was fully classical, and the subsequent development of the quantum theory of atomic spectra, it would seem, should have rendered his theoretical arguments completely invalid. But nevertheless the astonishing, although now little known, fact remains that Ritz managed to construct mathematical models, from which one can logically derive, as natural consequences, analytical expressions for the spectral terms and their differences which not only excellently fitted the experiments, but were also confirmed later on by the quantum theory.

We will not consider in detail Ritz's studies on the variational method and electrodynamics. As for the variational method, it should be noted that this aspect of the widely known work by Ritz characterises him primarily as a mathematician and it is treated in scientific literature in some detail, in particular in monographs (see, e.g., the well-known book by Kantorovich and Krylov [36]). Here we will restrict ourselves to a short consideration of some questions concerning the history of the creation of this method, as well as the question of its originality. As is known, the basic idea of applying the variational method to solving the problem of integration with given initial and boundary conditions consists in its substitution by the problem of finding a function that provides an extremum to a certain integral. Dirichlet [37] was the progenitor of such an approach. However, general attention to the variational method was drawn after Ritz's classical papers had appeared in 1908 and 1909 [13–15], the history of which is quite interesting [31]. At the end of 1904 the Paris Academy of Sciences instituted a prize for the best study on the improvement in some important respect of the theory of analysis connected with the equilibrium of a plate in a hard frame, which was very close to the mathematical problems that Ritz had solved in his thesis. Ritz quickly carried out the study to obtain the announced prize, but the representative judges, including Poincaré, completely ignored his work. After the papers [13, 14] were published in 1908, Ritz's variational method induced such a rapid and positive resonance that in April 1909 Poincaré sought out Ritz in Gottingen to apologise to him on behalf of the Paris Academy for the admitted injustice and to inform him of the intention of the Academy to award him the prize that year. This prize was awarded to Ritz only after his death (Ref. [1], p. X; Ref. [31], p. 438).

Ritz proposed a general method applicable to a much wider field than the problem initially set. The efficiency of this method was convincingly demonstrated by Ritz for four particular examples. The first coincided with the

competitive theme announced by the Paris Academy; the others were: solution of the Dirichlet problem in its classical formulation (i.e. the search for a harmonic function with values specified at the boundary of a given region), application of the method to ordinary differential equations with variable coefficients, and finally the application of the method to oscillations of a string. Ritz's method was rapidly adopted and became an effective tool in different fields of mathematical and theoretical physics; it was widely used for calculating the physical characteristics of quantum mechanical systems (Refs [38, 39]). This method was the basis of the new approach to applied mathematics. We note the further evaluation given by Poincaré (see Ref. [1], p. XV, XVI), who stressed that 'this is the method of an engineer'. To conclude, we note that the question about the degree of originality of Ritz's approach itself is interesting in the purely historical aspect, as no single point of view about this exists in the literature. The prevailing standpoint is that according to which Ritz's individual authorship is unreservedly accepted. On the other hand, there are some sources where Rayleigh is also called the author of the approach (Rayleigh–Ritz method). Moreover, it is known that Rayleigh himself directly claimed priority in formulating the variational method, and in a paper in 1911 [24] he, while greatly praising the 'remarkable memoir by Ritz', also wondered that 'Ritz should consider his method as new' (Ref. [24], p. 226). Then Rayleigh makes reference to a number of his own papers (Refs [40–42]). A thorough analysis of all the papers cited by Rayleigh shows that the starting point of his approach is the same basic idea as was used by Ritz for reducing a variational problem to the more simple problem of a function extremum. However, Rayleigh limited himself to oscillation problems, whereas Ritz formulated the mathematical problem in a general form.

That Ritz came to the variational method formulation fully independently of Rayleigh is shown by the absence of references to Rayleigh's works in his papers. Taking into account Ritz's extreme punctiliousness in making references to literature sources and his respect for Rayleigh's scientific authority, one should conclude that Ritz was not acquainted with Rayleigh's method and came to the principal idea of the method quite independently of Rayleigh; this was made clear by Courant in his paper [43]. It seems that the most accurate estimate of the real relationship between Rayleigh's and Ritz's approaches is contained in Mikhlin's monographs. He wrote that 'in application to the problems of oscillations the method of Ritz is a far-reaching generalisation of the 'Rayleigh method'' (Ref. [27], p. 15).

The analysis of questions connected with Ritz's works on electrodynamics is important when characterising him as a theoretical physicist and requires a special and more detailed investigation. Such a study was undertaken by two of the authors (L M Tomil'chik and M A El'yashevich)†, and here it is necessary to emphasise that one cannot agree with the purely negative assessment of Ritz's studies on electrodynamics, which constitute a very significant part of his scientific heritage. Now one can say with confidence that such an assessment, which is widespread in the literature, is only partially correct. Usually attention is exclusively fixed on the point of Ritz's general concept which is connected with denying one of the basic postulates of special relativity

†The results of this study will be published in a separate paper.

theory, the principle of the independence of light speed from the source velocity. The ballistic hypothesis by Ritz indeed turned out to be incorrect and was refuted by direct experiment. A detailed analysis of the numerous important difficulties that arise in electrodynamics and optics if this hypothesis is accepted is contained in the classical monograph by Pauli on the theory of relativity [44]. Pauli's critical remarks relate to an 'emission' approach, and giving an account of Ritz's theoretical concept was not his intention. In fact, Ritz obtained his results by using a different method from that discussed by Pauli; most important is that the research program Ritz tried to carry out remained beyond the scope of that discussion. This program contained a number of significant aspects that were not logically connected to the ballistic hypothesis at all, and it had quite a rich historical tradition based on a field-free approach that was an alternative to the Maxwellian one and took retardation into account. This approach goes back to Gauss [45] and Riemann [46] and later on, in the middle of the 20th century, was used by Feynman, and proved itself quite viable in general (see 'Nobel Lecture' by Feynman [47] and in particular papers by Wheeler and Feynman [48, 49]). The field-free approach was developed further in subsequent years (see, for example, monograph [50]). In Ritz's studies on electrodynamics one can clearly distinguish the critical and constructive parts, each of which is worth further historical and methodological analysis. Such an analysis, however, is beyond the scope of the present review.

In what follows we will not concern ourselves with Ritz's studies on the variational method and electrodynamics but will focus on his spectroscopic investigations. To understand the role of these studies by Ritz, one needs to understand the state of theoretical spectroscopy at the beginning of his scientific career (1902); Section 2 is devoted to this, and is similar to the authors' paper on 'Rydberg and the development of atomic spectroscopy' [51]. The main sections are 3 and 4. Ritz's thesis on the theory of spectral series and the elastic atomic model developed by him are given, and Section 4 is devoted to his magnetic atomic model and the combination principle. Section 5 contains a short general conclusion.

## 2. The state of theoretical spectroscopy at the beginning of the 20th century

After the invention of spectral analysis in 1859 by Bunsen and Kirchhoff, extensive experimental data were sampled for the atomic spectra in which spectral series are observed—sequences of spectral lines converging towards certain limits (in the scale of wavelengths  $\lambda$  or wave numbers  $\nu = 1/\lambda$ )‡. As is known (see, for example, Ref. [52]), series structure was detected for hydrogen (Balmer series) and for alkaline, alkaline-earth and other elements (the characteristic principal, sharp and diffuse series). Towards 1902, the beginning of Ritz's scientific career, the data on atomic spectral series were put in systematic form by the Swedish scientist Rydberg, on the one hand, and by the German spectroscopists Kayser and

‡In what follows we denote by  $\nu$  (as is accepted in spectroscopy) both the wave number (usually expressed in  $\text{cm}^{-1}$ ) and the frequency  $\nu = c/\lambda$  (expressed in inverse seconds,  $\text{s}^{-1}$ ), where  $c$  is the speed of light.

Runge, on the other hand, on the basis of formulas found by them, which were of a sufficiently general character and correct to a high degree of accuracy (especially those by Kayser and Runge). The decisive role was played here by Rydberg's study (in the introduction we have already made reference to the authors' paper [51] where a detailed analysis of Rydberg's contribution to progress in atomic spectroscopy was given). In his fundamental work of 1890 [53], Rydberg represented for the first time the wave numbers of the spectral lines as the difference between two terms (two spectral terms, in the modern terminology). These terms have the form

$$T_m = \frac{N}{(m + \mu)^2}, \quad (1)$$

where  $m$  is a positive integer increasing from some small fixed value to  $\infty$ ,  $N$  is a universal constant (named after Rydberg and presently denoted by  $R$ ), and  $\mu$  (the Rydberg correction) is a constant peculiar to a certain spectral series (in particular, for main, sharp, or diffuse series) of the given element and equal to zero for hydrogen. The general formula proposed by Rydberg for the lines from spectral series can be written as [see Ref. [51], formula (13)]:

$$\nu = \frac{1}{\lambda} = T_{m_1} - T_{m_2} = \frac{N}{(m_1 + \mu_1)^2} - \frac{N}{(m_2 + \mu_2)^2}. \quad (2)$$

At constant  $m_1$  and variable  $m_2$  one gets a specific spectral series, lines of which converge towards some boundary as  $m_2 \rightarrow \infty$ . In case of hydrogen ( $\mu_1 = \mu_2 = 0$ ) at  $m_1 = 2$  and  $m_2 = 3, 4, 5, \dots$  one obtains a formula for the well-known Balmer series, and for arbitrary  $m_1$  and  $m_2$ —the so-called generalised Balmer formula:

$$\nu = N \left( \frac{1}{m_1^2} - \frac{1}{m_2^2} \right). \quad (3)$$

These were subsequently presented in this form by Ritz in his thesis (Ref. [1], p. 13) and other papers (with notations  $m_1 = n$  and  $m_2 = m$ ). Expression (2) should be considered as an initial formulation of the combination principle, which was given in a more general form by Ritz (see Section 4).

For the spectral series Kayser and Runge proposed an alternative formula of the form

$$\nu = \frac{1}{\lambda} = a + bm^{-2} + cm^{-4}, \quad (4)$$

containing three constants  $a$ ,  $b$ , and  $c$  peculiar to a certain series of the given element.

A very significant point is that Rydberg formulated the program for establishing a general relation between the spectral characteristics of matter and its internal structure and implemented it as a solution to the problem of putting the spectroscopic material into systematic order in the framework of some semi-empirical scheme, which bears, nevertheless, a quite simple and universal character (see Ref. [51], p. 149 for more detail). He discussed it with Kayser and Runge, who objected in principal to the desirability of a search for a universal function and proposed as a unique criterion of the correctness of the formula more precise reproduction of the experimental data. Rydberg proved to be right, and the deep physical meaning of his results became clear, as is known, much later, only in 1913, as a result of the development by Bohr of the quantum theory of the atom and its spectrum, when a

proportionality of the spectral terms to the atomic quantum state energies was established and the frequency condition was formulated based on relationship (2)†.

The studies by Rydberg were the accomplishment, at the end of the 19th century, of the first stage in establishing spectral regularities. It was characterised by the search for some sufficiently general dependences by means of ordering the experimental data on the grounds of empirical and semi-empirical schemes. As we will see below, the second period of establishing such regularities, which was connected with attempts to model them theoretically, was completed in the first decade of the 20th century by Ritz, who, unlike Rydberg with his semi-empirical approach, obtained his results using the particular theoretical models.

To understand Ritz's studies on theoretical spectroscopy, one needs to understand, as we already mentioned in the introduction, the state of the field of spectroscopy at the beginning of his career in 1902. At that time, the general situation in the theory of interaction of electromagnetic radiation with matter was characterised by the complete absence of any serious theoretical test, which would allow one to estimate correctly the regularities found in the atomic spectra and, in particular, to make a choice between Rydberg's formulas and those of Kayser and Runge.

Although an adequate physical explanation of the empirical regularities in the atomic spectra and their connection with the structure of matter became possible, as we well know, only on the basis of quantum ideas, the rich history of attempts to describe these phenomena classically is very instructive. The theoretical investigations of Ritz, who managed to come to a number of new and principally correct conclusions while remaining fully within classical physics, without any doubt, have a quite exceptional place.

The first attempts to explain the spectral regularities theoretically were undertaken as early as the end of the 1870s. They, however, were unsuccessful due to the absence at that time of adequate physical ideas about the nature of optical radiation and atomic structure. The recognition of Maxwell's electromagnetic theory by the scientific community at the end of the 19th century and the discovery of the electron, the appearance of the electronic theory of Lorentz and its impressive success in explaining the Zeeman effect provided quite new opportunities for theoretical explanation of the spectral regularities.

The laws of electricity and magnetism are known to be adequately expressed by Maxwellian electrodynamics [55, 56], the theory of which was completed at the beginning of the 1870s. The most important consequences of his theory were the establishment of the electromagnetic nature of light and the prediction of electromagnetic waves. However, for almost two decades the ideas and results of Maxwell did not attract the proper attention of scientists and only after the famous studies by Hertz at the end of the 1880s on the experimental discovery of electromagnetic waves [57] (see also Ref. [58], p. 203–231) was the significance of the

†Subsequently, in his unpublished autobiography, Kayser recollected with regret that he and Runge 'missed a real key to understanding the line series from the point of view of the atomic structure. This was achieved for the first time by Rydberg owing to a clever idea to represent the spectral line frequency as a difference between two terms' {Ref. [54], p. 138, Herzberg's obituary on Heinrich Kayser (1853–1940)}.

electromagnetic theory valued at its true worth. As was noted in 1931 by Bohr in his report 'Maxwell and modern theoretical physics' devoted to the centennial of the scientist, 'the theory of Maxwell was not only exceptionally fruitful in interpreting the phenomena, but also gave as much as can be given by any theory; namely, it selected certain assumptions and governed its development beyond the limits of its initial applicability'. Then Bohr stressed that using 'ideas by Maxwell in atomic theory... constitutes a whole chapter in physics' (Ref. [59], p. 72).

Having accepted the hypothesis of the existence of discrete electric charges in the structure of matter, Lorentz suggested extrapolating Maxwell's equations to the microscopic level, that is, using De Broglie's words, to consider the theory by Maxwell as 'applicable to describing atomic phenomena' (Ref. [60], p. 61). In 1892 in the fundamental paper 'The electromagnetic theory by Maxwell and its applications to moving bodies' (see Ref. [61], p. 164–343), Lorentz presented his basic physical assumptions as follows: 'It would be enough to admit..., that all heavy bodies contain many small particles which are charged positively or negatively, and that the electric phenomena are caused by the replacement of these particles. According to this point of view, the electric charge is produced by an excess of particles with charge of a definite sign' (Ref. [61], p. 228).

The first serious success of Lorentz's theory, which was named the electronic theory after the discovery of the electron (before this he had called it ionic), was the explanation of the dispersion laws interpreted at that time in terms of elasticity theory. For example, by developing Fresnel's idea of taking into account the influence of molecules of matter on the ether particles, Cauchy as early as in 1835 [62] proposed a variant of the formula that expressed the dependence of the refraction coefficient of matter  $n$  on the wavelength,  $n = A + B/\lambda_0^2 + C/\lambda_0^4 + \dots$ , where  $\lambda_0$  is the wavelength in vacuum,  $A$ ,  $B$ ,  $C$  are constants to be found experimentally for specific matter. This work is of definite interest as the historically first demonstration of the wave theory's ability to explain the dispersion of light. The discovery of the anomalous dispersion (F Le Roux, 1862, Ref. [63]), and the further investigation, using the crossed prisms method, of this phenomenon connected with light absorption (A Kundt, 1971, Ref. [64]) allowed Sellmeyer in 1872 [65] to give a complete theory based on the idea of interaction between the medium and ether molecules. A feature of Sellmeyer's theory was the assumption that the molecules had frequencies of oscillation characteristic to a given material, from which the refraction coefficient's dependence on frequency arose. On the basis of the electronic theory, Lorentz was able to determine the form of the dispersion curves by solving the quantum mechanical problem for the motion of a quasi-elastically coupled electric charge (taking account of decay) under a forcing action caused by the external electric field of a monochromatic wave of light, harmonically dependent on time (see his works, in particular the 1898 papers on 'Optical phenomena connected with the charge and mass of ions', I, II [66], p. 17–40).

A particularly significant result of Lorentz's studies was the development, on the basis of the electronic theory, of the classical theory of the splitting of atomic spectral lines in a magnetic field—the most important spectroscopic effect

discovered by the Dutch physicist Zeeman in 1896–1897 which immediately caused large interest and was named after him. An important stage in the development of theoretical spectroscopy was the explanation by Lorentz of the peculiarities in the Zeeman effect. This demonstrated the capabilities of the classical electronic theory, on the one hand, and its limitations, on the other hand. It is worth considering the history of the discovery and explanation of the Zeeman effect, which played a large role in the formation of quantum atomic theory and quantum mechanics.

As is known, the first experiment to show the connection between optical and electromagnetic phenomena was the discovery in 1845 of the rotation of the plane of light polarisation in optically inactive media under the action of a magnetic field—the magneto-optical Faraday effect [67]. This discovery stimulated further researches in the field of magneto-optics and electro-optics, one of the results of which was the discovery in 1877 of the magneto-optical effect of the rotation of the plane of light polarisation during reflection about the magnetic pole by Kerr [68] (before this, in 1875, Kerr discovered the well known electro-optical effect of birefringence in an electric field [69], which was also named after him). As early as in 1862, Faraday studied the effect of a magnetic field on the spectral lines of alkaline metals in a flame (those were his very last experiments), but discovered no effect [70], owing to the insufficient resolution of his spectral apparatus for the magnetic fields he used in his experiments. Maxwell wrote about these experiments in 1878 in his article about Faraday for *Encyclopaedia Britannica* [71]: '...we will mention that in 1862 he chose the question of the connection between magnetism and light as the subject of his very last work. He tried, unsuccessfully, to discover changes in the spectral lines of a flame under the influence of a strong magnet' (Ref. [71], p. 216).

Zeeman, who worked at Kamerling-Onnes's laboratory in Leiden, in the 1890s studied in detail the magneto-optical effect of Kerr and tried also to verify whether a magnetic field influenced the spectrum of a flame, but with a negative result [72]. However, then he became acquainted with the paper by Maxwell [71] about Faraday and resumed the experiments. At the very beginning of his first paper in English (March 1897) about the new phenomenon he had discovered, 'On the effect of magnetism on the nature of light emitted by matter' [73]†, Zeeman wrote: 'If Faraday considered the above relationship possible, then it may worth repeating the experiment with the excellent experimental equipment of modern spectroscopy'. Zeeman's experiment was successful—he discovered a noticeable broadening of the sodium D line in a flame placed between magnetic poles. It is this result that was reported to the Amsterdam Academy of Sciences by Kamerling-Onnes on October 31, 1896, and Lorentz, who was present at this session, in a few days was able not only to give an explanation for the new effect, but also to predict a number of important characteristics, including the polarisation of the broadened line wings. The essence of this explanation was formulated by Lorentz himself (at the beginning of the paper 'The magnetic field effect on the

†Before this, on October 31 and November 28, 1896, Zeeman published two communications in Dutch, which were presented to the Amsterdam Academy of Science [74].

emission of light' [75]) as follows: 'If one spectral line only is considered, it is sufficient to assume that each luminous molecule (or atom) contains only one mobile ion, which is subjected, once it leaves its equilibrium state, to the action of a force tending to return it back to the initial state; this force is proportional to the displacement but is independent of its direction. All motions of such an ion can be decomposed into linear oscillations directed along the field lines, and rotational oscillations in planes perpendicular to these lines. The magnetic field does not change the period of the first of these oscillations, but, in contrast, increases the period of the second ones or decreases it depending on the direction of the rotation.' It follows from this that by making longitudinal observations (along the field) one should detect a doublet with two shifted components circularly polarised in opposite directions, and by transverse observing (perpendicular to the field)—a triplet with the central unshifted component linearly polarised parallel to the field, and two shifted extreme components linearly polarised perpendicular to the field. For a partial splitting the wings of the spectral lines broadened by the field should be polarised appropriately. In Ref. [73] Zeeman, having presented his first results on the spectral line broadening of sodium in a magnetic field, wrote 'Professor Lorentz... has immediately informed me kindly about the way in which, according to his theory, the motion of an ion in a magnetic field should be calculated, and pointed out to me that, if the explanation that follows from his theory is correct, the line wings in the spectrum must be polarised. The value of the broadening can then be used for the determination of the charge to mass ratio, which in his theory should be ascribed to the particle exciting the oscillation of light. The above mentioned remarkable conclusion by Professor Lorentz about the polarisation of magnetically broadened lines I found to be fully confirmed by the experiment...'. Zeeman describes this experiment, and before this he presents for the first time the Lorentzian classical theory of motion of a quasi-elastically coupled charged particle in a magnetic field, leading to *normal splitting*—a distance (in the frequency scale) between the shifted and undisplaced components, —equal to

$$\nu_0 = \frac{eH}{4\pi m_0 c}, \quad (5)$$

where  $H$  is the magnetic field,  $e$  and  $m_0$  are the charge and mass of the oscillating particle, and  $c$  is the speed of light. At the end of paper [73] Zeeman gives a correct estimate of the quantity  $e/m_0$ . The paper is dated 1897†.

In subsequent studies Zeeman managed to discover the spectral line splitting, doublets and triplets, and to measure its value for a number of atoms [76]. The  $e/m$  ratio turned out to be approximately coincident with the same ratio for the electron, which was discovered in 1897, and the direction of circular polarisation of the shifted doublet components was evidence for the negative sign of the charged particle‡. Based on the results of Zeeman and

† In the appendix to Ref. [73] of February 1897, Zeeman makes reference to an earlier book [70] unknown to him about Faraday's life and his studies in 1862, as well as to works of other scientists who tried to discover the effect of the magnetic field on spectral lines.

‡ In Ref. [73] (in the note on page 58) Zeeman firstly determined this sign incorrectly as positive, however by the first of the studies [76] he had corrected his mistake.

other scientists who studied the effect experimentally, the most important conclusion was that the oscillating particles in atoms were electrons and, thus, that electrons were a constituent of atoms. It was at that time Lorentz's theory was renamed 'electronic' instead of 'ionic'.

We stress that after Zeeman's discovery dozens of papers were published devoted to experimental and theoretical studies of the new effect. Among the experimental studies we note the paper by Michelson [77], who obtained the full splitting of the sodium lines for the first time using an interferometer for comparatively weak fields. Among the theoretical papers, we note an important paper by Larmor 'On the theory of magnetic influence on spectra and on the emission of moving ions' [78]. The paper showed that the magnetic field effect for a charged particle moving in an atom on a closed orbit is reduced to the previous motion of the particle relative to a coordinate frame that rotates with a constant angular velocity around the field direction (Larmor precession).

As a result of numerous experimental studies of the Zeeman effect, it was clear already by 1902 that only certain spectral lines produced triplets with the splitting value (5)—this case, which is consistent with Lorentz's theory for oscillations of a separate, elastically connected electron, was named the *normal Zeeman effect*. For some lines, triplet splitting is observed (the ordinary Zeeman effect, according to modern terminology), with a splitting value different from (5), in particular, twice as high in certain cases. However, splitting into more than three components is observed most frequently (the complex Zeeman effect, in modern terminology), with a symmetric splitting pattern and conserved polarisation properties, as a rule, and the triplet components are split, in turn, by separate equally spaced components. The Zeeman effect which is not the *normal* one is called the *anomalous* one; Lorentz and other theoreticians tried to explain it (a major part of the paper by Lorentz [75] was devoted to this). However, the correct explanation of the anomalous Zeeman effect was possible only on the basis of quantum theory. Bohr with his atomic theory succeeded in interpreting this effect as a result of quantum transitions between combined energy levels which split differently in a magnetic field, but only after the spin of electron had been discovered in 1924 did that explanation obtain a solid base.

Preston [79] and other scientists established an important connection between the Zeeman effect and series regularities. It proved to be the case that all spectral lines from the same series of a given element and from the analogous series of other elements were characterised by the same picture of Zeeman splitting: the same number of components and spacing between them (in the frequency scale; the so-called Preston's rule). In his Nobel prize lecture in December 1902 [80]§, Lorentz spoke about the failure of

§Lorentz together with Zeeman were awarded the Nobel prize in physics 'for discovering the influence of magnetism on radiation processes' (this was the second Nobel prize in physics; the first one was awarded to Röntgen 'for discovering the rays named after him' in 1901). We note that according to the initial 'Application rules' for the prize, it can be awarded only for experimental research, so the corresponding item in the 'Rules' was urgently changed by the Swedish Academy of Sciences, and since then the prizes have been awarded for theoretical studies as well. See, for example, Ref. [72], p. 48.



the attempts to explain the anomalous Zeeman effect and about the prospects for theoretical spectroscopy: 'I am sure that the theory will achieve significant success only when it applies not only to a separate spectral line, but to the whole sample of lines for a chemical element. The different forms of the Zeeman effect will be fruitfully studied only when at last we are in a position to justify theoretically the spectral structure, only then and not earlier. I say moreover: in the future, studies of regularities in spectra and of the Zeeman effect must be carried out together. Thus they will lead to the theory of light propagation, which is one of the most noble purposes to be achieved by modern physics'. The prediction by Lorentz was fully justified, and Ritz, in trying to solve theoretical spectroscopy problems on the basis of classical ideas (which failed), turned his attention to the anomalous Zeeman effect theory, as well as attempts to explain the spectral regularities (see Section 4).

Precisely at the beginning of the 20th century favourable conditions arose for attempts to explain the spectral regularities. Kayser's review of 1902, which is contained in the second volume of his multivolume work on spectroscopy [81], provides a sufficiently full representation of the theoretical approaches to spectroscopy to justify such an explanation. In Chapter 8 on 'Regularities in spectra' (Ref. [81], p. 467–609), a special section on 'Theoretical studies' is devoted to the attempts to explain the spectral regularities (Ref. [81], p. 596–609)†.

Kayser subdivided all the known theoretical studies on atomic spectra into two large groups: the first of them contained attempts to describe quantitatively the observed regularities in the real spectra; the second one included the studies aimed at explaining the most general qualitative similarities—such as dependences like  $1/n^2$  and the presence of the series limits—using elastic analogies.

Kayser related the works by Larmor, Hershel, Jeans and Sutherland to the first group. Their sources go back to Stoney's paper 'On the reason for discontinuous spectra of gases' [82]. It should be said that the approaches used by these authors strongly differ from each other.

For example, Larmor [78], by analogy with the Zeeman effect, tried to connect the presence of spectral doublets with a mutual influence of positive and negative charges in the atom.

Herschel [83], using the acoustic analogy of a model of a sound resonator, showed that one can obtain an expression apparently similar to the formula for the Balmer series by a particular choice of the parameters of the model. However, the attempts to use that analogy for spectral series complicated the model to such an extent that it was impossible to interpret.

Starting with the electronic theory, Jeans [84] modelled the atom as a series of concentric layers, of alternating sign. Each layer consisted of particles of the same charge. He showed that in each of such layers two types of oscillations emerged, giving rise to series with an infinite number of lines converging at a particular point in the spectrum. The number of such series formed is equal to twice the number of envelopes. Although such a representation allowed him to reproduce individual spectral features qualitatively, a shortcoming of the model which could not be overcome was

the complete indeterminacy in choosing the number of layers, and the number, sizes and mutual positions of separate particles inside each layer. It is not surprising that comparison of the theoretical conclusions with individual spectra was not made.

The model of Sutherland [85] was a peculiar hybrid of elastic and electromagnetic ideas. According to Sutherland, there was a heavy elastic mass in the atomic centre, in which standing oscillations were excited. Positive and negative charges, rotating around the mass, gained energy by encountering nodes of these oscillations, which resulted in light radiation. This model, as far as one can judge from Kayser's assessment (Ref. [81], p. 603), was not taken seriously by his contemporaries, but it is interesting because it demonstrates very clearly the degree of artificiality of the assumptions used in attempts to explain the spectra in the framework of classical physics.

The second group of theoretical approaches to the description of spectral regularities took the form of searching for bodies or systems of bodies whose oscillations would reproduce the observed spectral structure. The early attempts of such a kind were connected with names of Cornu [86] and Loschmidt [87]. Cornu considered a cylinder with a diameter commensurate with its length as the source of the oscillations; Loschmidt—a hollow sphere. In both cases the desired result was not achieved. Subsequent development of this approach occurred in the 1890s. The works by Fitzgerald [88], Schuster [89] and Rayleigh [90, 91] are characterised by the common idea that in order to reproduce the spectral boundary, the rate of propagation in the model bodies and systems should depend on the length. However, the result was reached here at the expense of introducing a number of special assumptions, and in particular, by the introduction of a particular system of bodies for each spectral line. Another principal defect of that approach, which was noted for the first time by Rayleigh, was that the classical dynamics of oscillations led of necessity to relations that were quadratic and not linear in frequency. As became clear later, this was a general problem and was the principal restriction on the possibilities of using arbitrary mechanical models to explain the optical spectra.

Kolacek [92] considered electromagnetic oscillations in a conducting polarising sphere embedded in a dielectric ether. He discovered that these oscillations produced double line series with constant or diminishing differences, which turned out to be comparable with the spectral series of the alkaline metals.

In 1890, a paper by Riecke [93] appeared in which he noted that in order to reproduce an unlimited number of oscillations, one could use a model which was continuous at least in one dimension. Riecke suggested the idea of standing oscillations in a circular ring. Below we will return to this idea, since it served as one of the starting points of the initial theoretical constructions by Ritz.

In total, the numerous attempts to explain the empirical spectral laws using the theory of elasticity and classical electrodynamics did not lead to significant success. Poincaré, in his report of 1904 on 'The current state and future prospects of mathematical physics' (reprinted in Ref. [94]), pointed directly to the principal character of the difficulties arising. During his discussion of the approaches to the theory of the dynamics of electrons in the section on 'Electrons and spectra', he wrote that 'among the ways

†We note that the concluding Chapter IX 'Oscillations of light in the magnetic field' was devoted to the Zeeman effect (Ref. [81], p. 613–672).



leading to a theory, there is one, which was somewhat neglected, although it belongs to those which promise the most unexpected things'. And further: 'The point is that the spectral emission lines are generated by the motion of electrons, as is proved by the Zeeman effect: this is what is oscillating in a glowing body, undergoes magnetic effects, and is thus electrified. This is a very important starting point, but no-one has gone further yet. Why are the spectral lines distributed according to a precise rule? The experimenters have studied these rules in the smallest details, and they are very precise and comparatively simple. The first studies of these distributions included an idea about the harmonic relationships encountered in the acoustics; however, the difference proved to be significant; not only are the frequencies not sequential multiples of the same number, but here we find nothing corresponding to those transcendental equations to which many problems of mathematical physics lead, such as, for example, the problem of oscillations of an elastic body of arbitrary form and Fourier's problem of solid body cooling. The spectral line rules are more simple, but their nature is quite different; I will restrict myself to only one example of such a difference: for high order harmonics, the number of oscillations leads to a finite limit instead of increasing infinitely. These phenomena have not been explained yet, and I believe that here we deal with one of the most important mysteries of nature.' (Ref. [94], p. 249).

At the beginning of the 20th century, there was first of all no clarity in understanding the radiation mechanism. In trying to draw the researchers' attention to that problem, Kayser wrote in his report 'Development of modern spectroscopy' [95]: 'The ubiquitous light ether is sprinkled with molecules and atoms. Subjected to some motions, they induce waves in the light ether, which spread out in all directions and are interpreted by us as rays independently of whether the molecules themselves or their constituent parts, or electric charges, so-called electrons, which are on these molecules or inside them, are oscillating. The wavelength of the rays ... directly depends on the motions of the oscillating corpuscles, the centres of radiation...' (Ref. [95], p. 4). A unique relationship between the frequency of radiation and the oscillation frequency for the emitters, whose existence followed from the Maxwell equations, required there to be a correspondence between the number of emission centres and the number of lines in the spectra. Meanwhile, the observed abundance of those lines unavoidably led to unjustified complications in interpretations of the structure of the atom considered as the emitter. 'It is impossible to accept that there should be so many different particles in one atom, each of them emitting one line; we must suppose that each emission centre undergoes a complex motion, which, when dispersed by a prism or a grating, yields a whole sample of spectral lines', Kayser writes further (Ref. [95], p. 5).

In fact, by the beginning of the 20th century, two reasons were already known in mathematical physics which made the problem of adequate theoretical description of the observed spectral regularities principally unsolvable in the framework of classical ideas.

Firstly, one of the main difficulties, which we have already mentioned above and to which Rayleigh [90] had turned his attention, was that any model of an elastically or quasi-elastically bound electron, unavoidably led, in solving the mechanical equations, to expressions containing the

square of the frequency, whereas the simple rules for the atomic spectra are linear with respect to frequency.

Secondly, as was stressed by Poincaré as early as in 1894 [96], in solving the well-known differential equation  $\Delta u + k^2 u = 0$ , which is the basis for oscillation problems in the theory of elasticity and in electrodynamics, there are no boundary conditions which can make the eigenvalue series reach a limit at a final value, which is in contradiction with experimental data (see the extract from a later paper by Poincaré [94] cited above).

Such was the state of the theoretical basis of atomic spectroscopy at the beginning of the 20th century, about which Bohr gave a resume (in the report of 1954 on 'Discovery of spectral laws by Rydberg'): '... searches for a mechanism that could explain the spectral regularities, ... have run across difficulties which seemed insurmountable. Here, it is especially relevant to keep in mind Rayleigh's remark that any analysis of normal types of oscillations of a stable mechanical system leads to relationships between squares of frequencies and not between the frequencies themselves' (Ref. [59], p. 473).

It was in this situation that Ritz undertook the most thorough-going and far-reaching attempts to describe theoretically the spectral regularities in the framework of classical ideas. As we have already emphasised, this important part of his research activity was, in fact, not referred to in the historical scientific literature. We will consider the pertinent studies by Ritz starting with his thesis of 1902.

### 3. Ritz's thesis on spectral series theory and his elastic atomic model

The thesis by Ritz (Ref. [1], p. 1–77) deserves a thorough analysis; its main part was published in *Annalen der Physik* [2].

It can be seen from the introduction that Ritz definitely understood the principal character of the difficulties described above, which were encountered while trying to explain the observed atomic spectral features. Under the conditions where the basic mechanics and electrodynamics equations could not successfully be used to calculate the spectrum, and 'from the oscillation frequencies of a completely unknown system one cannot conclude anything definite about its law of its motion as yet...'. Ritz formulated the problem as follows: 'While relying upon mechanics and electrodynamics as much as possible, it is necessary to point out physically meaningful mathematical operations, the interpretation of which as oscillations of an appropriate 'model' should lead to the spectral series laws; it should allow one to improve the empirical formulas, to put them in a unique order and to discover new rules' (Ref. [1], p. 3).

It is important to emphasise that it is obvious from his setting of the problem that Ritz was trying not so much to explain the spectral regularities as to provide a unified theoretical description. Such a setting of the problem turned out to be quite justified, since all the subsequent successes of Ritz's approach proved to be connected with the use of purely mathematical properties of his model. The attempts to obtain a physical interpretation of the corresponding mathematical structures, naturally, did not lead, and as we know now, cannot lead to a positive result.

The informative part of Ritz's thesis starts with a thorough analysis of the contemporary state of spectroscopy, its empirical laws and attempts to model them theoretically. Here he demonstrates an exclusively profound and multilateral acquaintance with the problem. In particular, he knew all Rydberg's publications very well beginning with the seminal paper of 1890 [53], papers of 1896 and 1897 [97, 98] and the concluding review of 1900 [99], a series of articles 'On the spectra of elements' 1889–1892 by Kayser and Runge [100], and a fundamental treatise by Kayser on spectroscopy, which constitutes the second volume of *Handbuch der Spektroskopie* [81].

As a result of thorough consideration of the question of using Rydberg's formulas, on the one hand, and Kayser and Runge's ones, on the other hand, Ritz gave a well-defined preference, as a unique basis for the description of linear spectra, to Rydberg's results, which were based on representation of the wave numbers using equation (2) which has a clearly expressed 'differential' structure.

Ritz especially stresses the correctness of a statement contained in the works of the Swedish scientist about the coincidence between boundaries for the sharp (second auxiliary) and the diffuse (first auxiliary) series, and the conclusion made by Rydberg about the numerical coincidence of wave numbers for the first lines of the main and the sharp series (see Ref. [51], p. 152).

Ritz pays special attention to the question of the universality of the spectral constant deduced by Rydberg. As Ritz points out†, Rydberg compares the formula for spectral series written in the form

$$\frac{1}{\lambda} = A + \frac{B}{(n + \mu)^2}, \quad (6)$$

where  $A$ ,  $B$ ,  $\mu$  are constants,  $\lambda$  is the wavelength and  $n$  is an integer number, with Balmer's formula for the hydrogen spectral series, and draws a conclusion about the universal character of the constant  $B$ . As a result, a two-parametric expression with the constants  $A$  and  $\mu$  arises, which describes the spectral series.

Meanwhile, the experimental data of that time did not show any evidence at all in favour of the universality of the constant  $B$ . For small  $n$ , small deviations from Rydberg's formula were observed, and a three-parametric formula proposed by Kayser and Runge and written by Ritz as

$$\frac{1}{\lambda} = a' + b'n^{-2} + c'n^{-4}, \quad (7)$$

where  $a'$ ,  $b'$ ,  $c'$  are independent empirical constants, gave a much better correspondence with experiment.

However, Ritz draws attention to the fact that in the region of applicability of Rydberg's formula, the second parameter in the Kayser–Runge expression (i.e.  $b'$ ) remains almost constant, whereas the values of  $a'$  and  $c'$  strongly vary from series to series. He concludes that it is necessary to maintain the general structure of Rydberg's formula (6) with the universal constant  $B$ , which he subsequently denotes as  $N$ ; to achieve an agreement with experiment for small  $n$ , Ritz suggests improving this formula by introducing a dependence of the parameter  $\mu$  on the integer number  $n$ . He finds a particular shape of that dependence, as well as a justification of the universality of

the Rydberg constant  $N$ , in the framework of his theoretical model. He writes about his improved formula: 'As I anticipated, I note that for the small ordinal numbers, the much more accurate formulas I derived on theoretical grounds give a much better agreement of Rydberg's rules with experiment: *for all elements for which both series are known, the extrapolated main line of the second auxiliary series proves to be in the immediate proximity of the main line of the principal series...*' (Ref. [1], p.12) (italics by Ritz).

By analysing the regularities found by Rydberg, Ritz derives a generalised Balmer formula for all series of the hydrogen atom, which can be written in the form‡

$$\nu = \frac{1}{\lambda} = N \frac{m^2 - n^2}{n^2 m^2} = N \left( \frac{1}{n^2} - \frac{1}{m^2} \right), \quad (8)$$

and he refers to the fact that Balmer considered his formula as a partial case of the expression  $1/\lambda = N(m^2 - n^2)/m^2 n^2$ . Using expression (8) and taking into account the characteristic structure (2) of the series formulas, Ritz came to a general conclusion that, according to Rydberg, '*... series formulas, properly speaking, should be written with two arbitrary integer numbers*' (Ref. [1], p. 13) (italics by Ritz). Additionally, based on formula (8), Ritz managed to predict for hydrogen, apart from the already known Balmer series ( $n = 2$ ), the existence of other series lying in the ultraviolet and infrared spectral bands. Subsequently, the series with  $n = 1$  were discovered by Lyman [101] in the far ultraviolet region (which is referred to by Ritz in Ref. [7]; see Ref. [1], p. 105), and the series with  $n = 3$  was discovered by Paschen [102] in the far infrared band in accordance with Ritz's prediction (see Ref. [1], p. 581). For alkaline metals, too, Ritz predicted the existence of spectral lines which were experimentally discovered later; one of them was found by Ritz himself in the spectrum of potassium in 1903 [4], as was mentioned earlier.

The idea that series formulas should be written with two arbitrary integer numbers was very important for Ritz, as it decisively influenced the choice of mathematical model used. Here, one should note the undoubted influence on Ritz of the works by Professor Riecke [93], Ritz's teacher. The point is not only that in a short review of the known theoretical attempts the results of Riecke are clearly distinguished by Ritz. More important is that Ritz used some significant features of Riecke's approach in his finished plan.

Riecke noted that if in the problem of natural oscillations of an elastic ring one requires that for partial solutions of the form

$$\begin{aligned} f_1(\varphi, t) &= \sin 2\pi\nu t \sin m\varphi, \\ f_2(\varphi, t) &= \cos 2\pi\nu t \sin m\varphi, \end{aligned} \quad (9)$$

(where  $f_1$  and  $f_2$  are small reciprocally perpendicular elastic shifts and  $m$  is the number of node points on the ring), a dependence of the frequency on the integer number  $m$

‡ He also gives a formula with half-integer numbers

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

for series of the ionised helium atom, which were attributed to the hydrogen atom at that time (see Ref. [51], p. 153).

† Here and below we mainly use the notation used in the original papers by Ritz.

arises, which corresponds to Kayser and Runge's formula (4), then the functions  $f_1$  and  $f_2$  will satisfy the following systems of two 5th order equations:

$$\begin{aligned} \frac{\partial^5 f_1}{\partial t \partial \varphi^4} - a \frac{\partial^4 f_2}{\partial \varphi^4} + b \frac{\partial^2 f_2}{\partial \varphi^2} - c f_2 &= 0, \\ \frac{\partial^5 f_2}{\partial t \partial \varphi^4} + a \frac{\partial^4 f_1}{\partial \varphi^4} - b \frac{\partial^2 f_1}{\partial \varphi^2} + c f_1 &= 0. \end{aligned} \quad (10)$$

The inversion of system (10) into an identity by substituting expressions (9) under condition (4) is straightforwardly verified. We note that  $f_1$  and  $f_2$  separately satisfy a 10th order differential equation.

Obviously, in the framework of such an approach the use of the Rydberg formula (and not of Kayser and Runge's one) naturally led Ritz to the assumption that '*the linear spectra are due to the natural oscillations of two-dimensional structures*' (Ref. [1], p. 18) (italics by Ritz). The idea thus arose of using an analogue model of an elastic membrane which is characterised by having a two-fold infinite number of node points.

We stress that Ritz was the first researcher to draw attention to the fact that the determination of spectral line frequencies as functions of independent integer numbers should be used in the process of choosing a model for the emitter. In his thesis he calls this feature the 'two-fold infinite number of lines' (Ref. [1], p. 17).

It is interesting to note that after the Bohr's theory the presentation of an analogous starting idea (the double enumeration of each frequency in the spectrum) served for Heisenberg as a starting point for the matrix formulation of quantum mechanics.

The partial solutions of the form (9) in the case of oscillations of a square membrane of side  $2a$  fixed at its perimeter, which satisfy the necessary boundary conditions, for small shifts of the membrane's points perpendicular to its plane  $xy$ , are written by Ritz as follows:

$$f(x, y, t) = A \sin(2\pi\nu t + c) \sin m \frac{\pi x}{a} \sin n \frac{\pi y}{a}. \quad (11)$$

In the ordinary case when the potential energy of the membrane is proportional to its area, the equation for oscillations has a standard form

$$\frac{1}{b} \frac{\partial^2 f}{\partial t^2} - \Delta f = 0, \quad (12)$$

where  $\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2$  is a two-dimensional Laplacian and  $b$  is the square of the expansion velocity for surface elastic waves. By substituting expression (11) into this equation the following dependence for  $\nu$  arises:

$$(2\pi\nu)^2 = b \left(\frac{\pi}{a}\right)^2 (m^2 + n^2). \quad (13)$$

This dependence, however, is completely different from the empirical spectral rule (8). A significant difference between formulas (8) and (13), which both depend on two integer numbers  $m$  and  $n$ †, is that (Ref. [1], p. 13):

1. With infinitely increasing  $m$  and  $n$  the frequency  $\nu$  in (13) tends to infinity, whereas it tends to a finite limit in (8).

†Such a dependence, as Ritz stresses, is connected with the partial solutions (11) common for both the cases (13) and (8) containing only sines and cosines while the roots of more complex transcendental functions are absent (Ref. [1], p. 13).

2. Formula (13) contains squares of the frequency  $\nu$ , whereas formula (8) only contains its first power.

3. Formula (13) is symmetric with respect to  $m$  and  $n$ , whereas formula (8) is not.

Later on, Ritz uses the fact that solution (11) satisfies the following 10th order equation (Ref. [1], p. 29):

$$\rho \frac{\partial^{10} f(x, y, t)}{\partial t^2 \partial x^4 \partial y^4} + 32\tau^2 \Delta' \Delta' f(x, y, t) = 0 \quad (14)$$

provided that condition (8) is fulfilled. In Eqn (14)  $\rho$  is the membrane's surface mass density and  $\tau$  is a constant entering the potential energy of the membrane. Ritz reaches this equation as a result of a difficult calculation of the system's choice of potential energy, making use of the variational principle (see below, the end of Section 3). Here, an important step to obtain the required dependence (8) for  $\nu$  is a substitution of the two-dimensional Laplacian  $\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2$  symmetric relative to  $x$  and  $y$ , which enters Eqn (12) and acts on function  $f(x, y, t)$ , by a nonsymmetric operator (with respect to  $x$  and  $y$ )  $\Delta' = \partial^2/\partial x^2 - \partial^2/\partial y^2$ . That substitution leads to non-symmetry of formula (8) relative to  $m$  and  $n$ , which is fundamental to the whole of Ritz's approach‡. With such a modified mathematical model, the Rydberg constant from Eqn (8) is expressed in terms of the model parameters  $-\rho$ ,  $\tau$  and the length  $a$  (which is a half of the membrane's side length) according to the formula

$$N = \frac{1}{2\pi c} \left(\frac{32}{\rho}\right)^{1/2} \tau \frac{a^2}{\pi^2}, \quad (16)$$

which guarantees the universal nature of this constant. The spectra of different elements are produced by varying the boundary conditions. For example, the requirement that the boundary is rigidly fixed (i.e.  $f(\pm a, y, t) = f(x, \pm a, t) = 0$ ) leads exactly to the generalised Balmer formula (8). The rejection of this condition while preserving the periodicity requirement of the solution yields the Rydberg formula (2). It was the analysis of nonzero boundary conditions that led Ritz to a significant improvement of Rydberg's formula by establishing a clear dependence of corrections  $\mu$  on integer number.

It is very instructive to follow Ritz's study to this point, which is the most important from the point of view of the significance of the final result. Ritz uses here the classical results of Poincare [103] on the theory of asymptotic representations of periodical solutions to linear differential equations. Firstly, he notes that the basic equation has such solutions, for which the frequencies are determined by the formula  $\nu \sim (1/k^2 - 1/l^2)$  in the case of noninteger  $ok$  and  $l$ . Secondly, he shows that there are such solutions for which the following expressions hold (Ref. [1], p. 50):

$$\begin{aligned} \alpha(k) \sin ka + \beta(k) \cos ka &= 0 \quad (\text{for all } y), \\ \alpha'(l) \sin la + \beta'(l) \cos la &= 0 \quad (\text{for all } x), \end{aligned} \quad (17)$$

‡Before this substitution, Ritz reached the equation (Ref. [1], p. 22)

$$\rho \frac{\partial^{10} f(x, y, t)}{\partial t^2 \partial x^4 \partial y^4} + 32\tau^2 \Delta \Delta f(x, y, t) = 0, \quad (15)$$

which satisfies the condition for the frequency  $\nu$  to tend to its finite limit with infinitely increasing  $m$  and  $n$ , and contains its first power. However, this condition is symmetric with respect to  $m$  and  $n$ , i.e. only two significant features of the regularity (8) considered above are fulfilled. The third one arises only by substituting  $\Delta$  by  $\Delta'$ .

where  $\alpha(k)$ ,  $\alpha'(l)$ ,  $\beta(k)$ ,  $\beta'(l)$  are some functions of  $k$  and  $l$ . From here originate the relationships that hold at the boundary of the square for  $x$  and  $y$ , respectively:

$$\begin{aligned}\tan ka &= -\frac{\beta(k)}{\alpha(k)} = \gamma(k), \\ \tan la &= -\frac{\beta'(l)}{\alpha'(l)} = \gamma'(l).\end{aligned}\quad (18)$$

Ritz distinguishes a particular class of boundary conditions, for which

$$\lim_{k \rightarrow \infty} \gamma(k) = \text{const} \neq 0. \quad (19)$$

Then it is easy to show that the following boundary condition must be approximately valid for large  $k$

$$\sin(ka - C_0) = 0 \quad (\text{const} = \tan C_0), \quad (20)$$

from which we get

$$ka - C_0 = m\pi, \quad (21)$$

or

$$k = \frac{m\pi}{a} + \frac{C_0}{a}, \quad (22)$$

which obviously lead to a term of Rydberg's type

$$\frac{1}{k^2} \sim \frac{1}{(m + \mu)^2}, \quad \mu = \frac{C_0}{\pi}. \quad (23)$$

If one takes account of the next terms in the series expansion of the function  $\gamma(k)$ , a relationship arises

$$ka = m\pi + C_0 + \frac{C_1}{k} + \frac{C_2}{k^2} + \dots, \quad (24)$$

or approximately

$$ka = m\pi + C_0 + \frac{C_1 a}{m\pi + C_0} + \frac{C_2 a^2}{(m\pi + C_0)^2} + \dots \quad (25)$$

A special choice of boundary condition enables one to obtain a function  $\gamma(k)$  whose expansion will contain only even negative powers of  $k$ . Ritz analyses exactly such a case as an illustration, using the simpler example of an analogous one-dimensional problem, in which the order of the equation used is not 10, as in the main problem, but only 6.

On the basis of such analysis, Ritz comes to the conclusion that Rydberg's formula (2), where  $N$  is a universal constant and  $\mu_1$  and  $\mu_2$  are numerical parameters, is reproduced in the framework of his theoretical approach only for large  $m$  and  $n$ . The parameters  $\mu_1$  and  $\mu_2$  are essentially identified with the first constant terms in the asymptotic expansions of the functions  $\gamma(k)$ ,  $\gamma'(l)$ . An inherent possibility of generalisation of Rydberg's formulas to the case of small  $m$  and  $n$  involves taking into account the subsequent terms of the expansion.

Ritz especially stressed that *'The Rydberg formula for small  $m$  and  $n$  needs to be corrected, not by changing the coefficient  $N$ , as has been done until now, but by substituting for  $\mu_1$  and  $\mu_2$  by expansions in series'* (Ref. [1], p. 51) (italics by Ritz).

From the formal point of view, improvement of the Rydberg formula (2) was obtained by substituting for the parameters  $\mu_1$  and  $\mu_2$  expressions like

$$\mu + \frac{b}{m + \mu} + \frac{c}{(m + \mu)^2} \quad \text{or} \quad \mu + \frac{b'}{(m + \mu)^2} + \frac{c'}{(m + \mu)^4}. \quad (26)$$

By comparing the results with experiment, Ritz selected the form

$$\nu = N \left[ \frac{1}{(m + \mu + b/m^2)^2} - \frac{1}{(n + \mu' + b'/n^2)^2} \right]. \quad (27)$$

The characteristic correction for series is not now a constant, as in Rydberg's work, but has become a function of an integer. Note that a dependence for series corrections on an integer number precisely of that kind was justified by the quantum theory later on.

Ritz writes series formulas for individual series when  $m$  is fixed and  $n$  is arbitrary in the form

$$\nu = A - \frac{N}{(n + \mu + b/n^2)^2}. \quad (28)$$

He also widely uses an alternative form

$$\nu = A - \frac{N}{[n + \alpha + \beta(A - \nu)]^2}, \quad (29)$$

where  $\alpha$ ,  $\beta$ ,  $A$  are constants. Both formulas are equivalent to an accuracy of the third order in  $n$ .

The form (29) is interesting because it is this form that was reproduced later by Bohr–Sommerfeld's quantum theory.

It is known that the explanation of the mechanism of line formation in the hydrogen spectrum given in 1913 was naturally carried over to other atoms as well by considering movement of an 'optical electron' in a central force field, which can be considered Coulomb at a sufficiently great distance from the atomic shell. In that case the dependence of the stationary state energy on the integer number  $n$  is conserved:

$$E_n = -\frac{Rch}{n^2}, \quad (30)$$

where  $n = 1, 2, 3, \dots$ ,  $R$  is the Rydberg constant (in the modern notation),  $c$  is the speed of light and  $h$  is the Planck constant. The existence of numerous series in hydrogen-like spectra, each of which is more or less similar to the corresponding hydrogen series, was explained only in 1915 when Sommerfeld introduced the azimuthal quantum number  $k$  determining the angular momentum quantisation (and connected with the orbital quantum number  $l$  by the relationship  $k = l + 1$ ), after which a comparison was made between the values  $k = 1, 2$  and  $3$  for the sharp, main and diffuse series and  $s, p$  and  $d$  terms, respectively. In the course of his attempt to estimate the term values for hydrogen-like spectra, Sommerfeld [104] obtained the formula (where  $Z$  is the atomic number)

$$E(n, k) = -\frac{RhcZ^2}{[n + a(k) + b(k)E]^2}, \quad (31)$$

which, as is easy to see, corresponds to expression (29) found by Ritz†. Here, together with the dependence on the principal quantum number  $n$ , there was a dependence on  $k$ , which was explained later on the basis of the idea of motion of an ‘optical electron’ in a field with a strong influence on the shell of the atom. The field potential can be represented by the series

$$U(r) = -\frac{e^2 Z}{r} \left[ 1 + C_1 \frac{a}{r} + C_2 \left( \frac{a}{r} \right)^2 + C_3 \left( \frac{a}{r} \right)^3 + \dots \right], \quad (32)$$

where  $r$  is the distance from the electron to the nucleus.

The selection rule for  $k$  (i.e.  $\Delta k = \pm 1$ ), established by Bohr in 1918, was very important, as it justified the simple explanation of spectral series.

In 1921, attempts were made firstly by Schrodinger [106] and then by Bohr [107] to interpret Rydberg’s correction as a difference  $n - n^*$  by comparing Sommerfeld’s theoretical formula written in the form

$$E = -\frac{R hc Z^2}{n^{*2}}, \quad (33)$$

(where  $n^*$  is an ‘effective quantum number’ differing from an integer by some constant), with an expression of the form

$$E = -\frac{R hc Z^2}{(n + \mu)^2}, \quad (34)$$

where  $\mu$  is a constant Rydberg’s series correction. The results were confirmed by the computations contained in lectures on atomic mechanics given by Born in Gottingen in 1923–1924 [28].

Born represents  $n^*$  in the form  $n^* = n + \delta_1 + \delta_2/n^2 + \dots$  where  $\delta_1 = \mu$  is Rydberg’s correction and  $\delta_2/n^2 = b/n^2$  [see (28)] are Ritz’s corrections. He shows that if one takes into account the influence of the first additional term in the expansion of the potential energy

$$-\frac{e^2 Z C_1}{r} \frac{a}{r}$$

on the term value, then Rydberg’s correction is  $\delta_1 = -Z C_1/k$ ; taking account of the second additional term

$$-\frac{e^2 Z C_1}{r} \left( \frac{a}{r} \right)^2$$

yields  $\delta_1 = -Z^2 C_2/k^3$ , respectively. It is essential that the deviation from the integer number  $n$  by an amount  $\delta$  depends on  $k$  and the greater  $k$  is, the smaller its value. In fact, this is connected with the influence of the atomic shell electrons on the ‘optical electron’, which leads to some divergence of the field from the Coulomb value.

If one takes into account the third term in the expansion,

$$-\frac{e^2 Z C_3}{r} \left( \frac{a}{r} \right)^3,$$

then by solving the problem of the motion of an electron in that central field we get  $n^*$  in the form  $n^* = n + \delta_1 + \delta_2/n^2$ , where  $\delta_1 = -3Z^3 C_3/k^5$  is Rydberg’s correction which was

discussed above;  $\delta_2/n^2 = Z^3 C_3/2k^3 n^2$  is Ritz’s correction which was introduced for the first time, as we have seen, in his thesis long before it obtained the correct theoretical justification.

As a result of comparison with experiment, it turned out that the most significant additional term in the expansion of the potential energy (32) is the quantity  $(-e^2 Z C_3/r)(a/r)^3$ , which has an obvious physical interpretation. For example, if one assumes the shell is not absolutely rigid but undergoes a deformation in the field of the ‘optical electron’, this term is modelled by an induced electric dipole producing a potential  $-\alpha e^2/2r^4$ , where  $\alpha$  is the frame polarisability of the shell (see Ref. [108], p. 169).

An adequate theoretical treatment of the dependence of the series corrections on the integer number  $n$  given by Sommerfeld [104], Schrodinger [106], Bohr [107] and Born [108] is known to be possible only on the basis of quantum theory. Nevertheless, it is important to note that a rule of such form was used by Ritz in his approach as a theoretically justified statement, as it arose as a result of solving some oscillation problem. An external justification for the correctness of the result obtained was that the apparent improvement to the Rydberg formula was experimentally verified with a high degree of accuracy. Ritz’s priority in these questions was well known to Sommerfeld and to Bohr, who make reference to him directly in their works.

At the same time, the contemporary physical and historical scientific literature [109, 110] somewhat underestimates the contribution by Ritz towards the establishment of that rule. For example, while Born in his ‘Lectures on atomic mechanics’ widely uses such terms as ‘Rydberg–Ritz’s formula’ and ‘Ritz’s correction’ when describing spectra, the corresponding sections of Frish’s fundamental monograph *Optical Atomic Spectra* contain only references to Rydberg even in those cases when the modifications of his formulas made specifically by Ritz are discussed (Ref. [109], p. 12).

It seems that on the basis of such ‘discrimination’ rests a general tendency, characteristic of contemporary physical thought as a whole, to underestimate the theoretical status of the principal spectroscopic laws that have quantum nature but were initially established prior to the formulation of modern quantum atomic theory.

As we have already noted in Ref. [51], the formulas suggested by Rydberg should not be treated as purely empirical. This applies to Ritz in even greater degree. It is not possible to ignore the fact that his approach contained the original and to a significant degree the theoretical ground for both the Rydberg formulas and also their modification, which was suggested by Ritz himself. It is due to this fact that the model by Ritz, despite its physical inconsistency, which was cleared up afterwards, succeeded in playing an important heuristic role in establishing spectral laws and in further systematisation of empirical data.

It should be noted that two lines are presented in Ritz’s thesis which are extremely interesting in a mathematical sense, but far from the equivalent from the point of view of their application to the real problem of describing the observed spectral regularities.

The first of them, which contains the analysis of the boundary conditions, turned out to be very productive, because it led to an improvement of Rydberg’s formula.

†This circumstance was clearly noted by Sommerfeld [104] (see also Ref. [105], p. 80).

The second line of Ritz's investigations is connected with the search for an appropriate physical interpretation for the mathematical model he constructed. The use of the variational principle underlies this part of Ritz's work. Here, the main problem is in choosing a proper expression for the system's potential energy. The part of the Lagrange function corresponding to the kinetic energy is given and is determined by the relation

$$E_{\text{kin}} = \frac{\rho}{2} \left( \frac{\partial f}{\partial t} \right)^2,$$

where  $\rho$  is the membrane's surface mass density,  $f(x, y, t)$  is the amplitude of displacement of its points.

It is known that the ordinary equations for elastic oscillations of a membrane can be obtained using the variational principle under the assumption that the potential energy density is directly proportional to the membrane's surface. The approach used by Ritz to determine the form of the action functional for the variational problem he set seemed to be very unusual. First of all, in order to describe the surface forces Ritz was forced to fit quite complex and not obvious analytical structures with nothing in common with the usual expression for elastic forces. Such a procedure in itself required extraordinary mathematical intuition.

The second interesting feature of Ritz's approach is that by choosing the Lagrangian form, he started from an analogy with Maxwellian electrodynamics, in which Lagrange's function of density of the electromagnetic field has the form  $\mathcal{L} = (\mathbf{H}^2 - \mathbf{E}^2)/8\pi$ , which, in turn, leads to a known expression for the familiar energy density of the field  $\mathcal{E} = (\mathbf{H}^2 + \mathbf{E}^2)/8\pi$ .

As a result, Ritz writes down the initial functional as follows:

$$A = \int_{t_0}^{t_1} dt \int ds \left[ \frac{\rho}{2} \left( \frac{\partial f}{\partial t} \right)^2 - \Phi^2 \right]. \quad (35)$$

Here  $ds$  is an element of the area of the membrane and the quantity  $\Phi$  is defined by the relation

$$\begin{aligned} \Phi(x, y, t) = \tau \iint ds & \left[ (x - x') - \frac{(x - x')^2}{2a} \right] \\ & \times \left[ (y - y') - \frac{(y - y')^2}{2a} \right] \Delta' f, \end{aligned} \quad (36)$$

where  $\tau$  is a constant,  $\Delta' = \partial^2/\partial x^2 - \partial^2/\partial y^2$ . An external analogy between expression (35) and the Maxwellian case is obvious, and Ritz further stresses this once more after computing the expression for the energy of the considered system, which naturally has the form

$$\mathcal{E} = \iint ds \left[ \frac{\rho}{2} \left( \frac{\partial f}{\partial t} \right)^2 + \Phi^2 \right]. \quad (37)$$

At this point in his thesis Ritz writes: 'If one introduces the quantities  $A = (\rho/2)^{1/2} (\partial f/\partial t)$ ,  $\Phi = B$  to describe a state, then *the analogy between the expression obtained here for the energy  $\iint (A^2 + B^2) ds$  and the expression valid for the electromagnetic energy of the ether, becomes striking*' (Ref. [1], p. 32) (italics by Ritz).

Although this analogy turned out to be purely formal and led to no informative results later on, nevertheless the use of it by Ritz is notable enough, since, on the one hand, it

characterises the peculiarities of his scientific thinking style, and on the other hand, proves his thorough acquaintance with the basis of Maxwell's electrodynamic theory at that time (1902).

Returning to consideration of the constructive part of this section of Ritz's thesis, we note that the required 10th order equation (14) cannot be obtained from the functional (35) in the form of a Euler-Lagrange equation. However, by means of a sophisticated analysis of the problem taking account of the boundary conditions Ritz shows that definition (36) gives rise to the equation

$$\frac{\partial^4 \Phi}{\partial x^2 \partial y^2} = 4\tau \Delta' f. \quad (38)$$

For the desired function  $f$  and an auxiliary quantity  $\Psi$  defined by the relation

$$\frac{\partial^4 \Psi}{\partial x^2 \partial y^2} = 4\Phi, \quad (39)$$

using the conventional variational procedure, one obtains the following 2nd order equation

$$\rho \frac{\partial^2 f}{\partial t^2} + 2\tau \Delta' \Psi = 0. \quad (40)$$

It is easy to verify that this equation, making use of Eqns (38) and (39) is fully equivalent to the fundamental 10th order equation (14) used by Ritz for obtaining spectral formulas of the Balmer type. By requiring the solution at the membrane's boundary to vanish, one obtains expression (16) for the Rydberg constant. As was already stressed, the value of  $N$  is determined only by the model parameters  $(\rho, \tau, a)$ , which is proof of its universality in the framework of the approach used. It is easy to see, however, that the whole procedure, irreproachable in mathematical rigour, has not led, and as we know today, could not lead to the correct physical result. Indeed, it can be seen from equation (40) that a quantity

$$F = -2\tau \Delta' \Psi \quad (41)$$

plays the role of the force density at the point  $(x, y)$  of the membrane. Quite obviously, such a 'force' determined by the use of expressions (36) and (38) does not permit a reasonable physical interpretation.

It is beyond doubt, however, that this part of the thesis was important in the development of Ritz's research which culminated in the derivation of a widely known variational method called after him (see Section 1).

#### 4. The magnetic atomic model and the combination principle

The next important stage in Ritz's scientific career in the field of spectroscopy is connected with his attempts to construct a magnetic atomic model. Undoubtedly, the idea of using magnetic forces to explain the linear spectral structure arose as a result of a thorough analysis by Ritz of the unsuccessful attempts to use elastic models for this purpose.

For equations of mathematical physics the traditional presence of the second derivative with respect to time automatically yielded relations containing the square of the frequency. A procedure for obtaining the required dependences in the framework of the elastic model by means of taking the root necessarily led to the introduction

of higher derivatives with respect to the coordinates and a change in the type of equation (from two-dimensional Laplacian  $\Delta$  to the hyperbolic operator  $\Delta'$ ). Naturally, such exotic structures did not have a reasonable physical interpretation. The results of his attempts in this area were summarised by Ritz himself in the paper of 1908 on ‘Magnetic atomic field and spectral series’ [7] as follows: ‘The author studied some of the cases corresponding to series laws (Ref. [1], paper I, p. 1; *Ann. Phys.* **12** (1903); extract from his PhD thesis). It is likely that the complexity of the assumptions required, for which it is impossible to find a satisfactory physical interpretation, makes it necessary to reject the theory given there ...’ (the note at the beginning of Ref. [7]).

Furthermore, Ritz emphasises that the differential equations of the 1st order with respect to time (which lead to relations for the frequency  $\nu$  and not for its square  $\nu^2$ ) can be derived if one assumes that ‘the acting forces depend not on the position of the parts of the system but on the velocities’ (Ref. [1], p. 99). Ritz points out that this is the case for magnetic forces and that ‘the assumption of intense magnetic fields ... can hardly be avoided’ (ibid.)†. ‘... It is possible that *oscillations in the spectral series are produced by purely magnetic forces*, and it should be shown later on that this assumption leads in a simple way to understanding the spectral series laws and anomalous Zeeman effects’, he writes (ibid., italics by Ritz).

It should be noted that Ritz did not immediately have the idea of treating spectral lines arising as a result of Zeeman splitting of a special sort. For example, his thesis mentions (Ref. [1], p. 15) the paper by Larmor [78] where the similarity of natural spectral doublets and triplets with those of the Zeeman effect is noted. However, judging by critical commentary by Ritz at this point, he did not take this idea seriously at that time. Perhaps, such a position was also caused by some prejudice Ritz had at that time, according to Forman’s evidence (Ref. [31], p. 476), about Lorentz’s electronic theory. At the same time, as follows from the appendix to the thesis devoted to the problem under study as a whole (Ref. [1], p. 75–77), Ritz hoped that this problem would be solved by combining elastic models with electrodynamic ones (for example, considering oscillating continuum structures with a continuum charge distribution).

It is interesting to follow the thinking that led Ritz to the magnetic atomic model. During the five year period that came after his thesis, up to the paper of 1908 [7] which contained the first detailed attempt to apply this model, Ritz published five small papers. Two of them [3, 4] published in 1903 are a natural continuation of his thesis and contain no new ideas. The third one [34] is devoted to a particular question of the manufacture of photoplates sensitive in the infrared band. In contrast, in two short communications of 1907 [5, 6] following immediately one after another (and presented to the Paris Academy of Sciences in March and July, respectively), a quite new point appears in his research program. Here, for the first time, a new physical mechanism for linear spectra was put forward based on the identification of each spectral frequency with one of Larmor’s, produced by a field of

appropriate configuration. However, Ritz initially implements this idea in the spirit of the synthesis of elastic and electromagnetic concepts outlined in his thesis. In the first of the publications [5] he uses the model of an elastically distorted electrically charged filament fixed at the endpoints and in the middle and rotating with a constant angular velocity  $\omega$  around the axis connecting its stable points (Fig. 1).

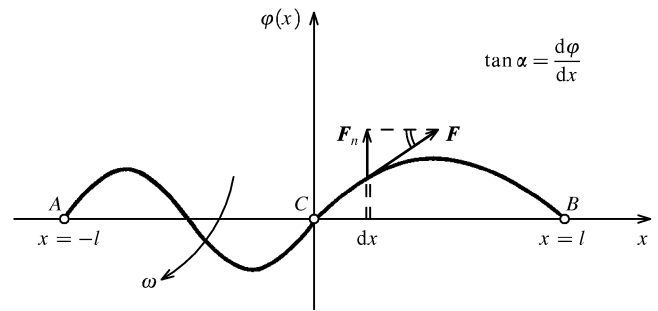


Figure 1.

Let  $T$  be the tension coefficient equal to the modulus of the force acting tangentially per unit length at each point of the filament, then  $|\mathbf{F}| = T$ . It is seen from Fig. 1 that the normal component of the tension force acting on an element  $dx$  is determined by the expression

$$dF_n = d(F \sin \alpha) \approx T d(\tan \alpha) = T d\left(\frac{d\phi}{dx}\right) = T \frac{d^2\phi}{dx^2} dx \quad (42)$$

for small angles  $\alpha$ . It is easy to see that the centripetal force acting on this element perpendicular to the axis  $x$  is  $dF_{c.p.} = -\rho\omega^2\phi dx$ , where  $\rho$  is the linear mass density of the filament. The condition  $dF_n = dF_{c.p.}$  yields a differential equation

$$\frac{d^2\phi}{dx^2} + k^2\phi = 0, \quad (43)$$

where  $k^2 = \rho\omega^2/T$ . The solution to this equation is well known to have the form

$$\phi(x) = A \sin kx + B \cos kx, \quad (44)$$

and by using the natural boundary conditions  $\phi(0) = 0$  at the point  $C$  and  $\phi(l) = \phi(-l) = 0$  at the points  $A$  and  $B$ , respectively, the relations typical for such problems are obtained:

$$\begin{aligned} kl &= m\pi & \text{for the point } B, \\ -kl &= n\pi & \text{for the point } A. \end{aligned} \quad (45)$$

(The situation shown in Fig. 1 corresponds to the case  $m = 1, n = 2$ ). From this, for the tension on the sides of the points  $A$  and  $B$  one gets, respectively ‡

‡It is interesting that from a formal mathematical point of view this result originates in the same way as the energy quantisation in an infinitely deep one-dimensional potential well obtained using the corresponding Schrodinger equation. In both cases, a one-dimensional problem of standing oscillations with identical boundary conditions is considered. The difference in the physical nature of the oscillating processes is evident from the fact that the parameter of the problem, which is energy for the quantum mechanical case, is the inverse tension coefficient for Ritz’s case.

†We note that the magnetic Lorentz force was the only nondissipative force known in physics at that time; it causes, in particular, the Zeeman effect.



$$T_A = \frac{\mu\omega^2}{k^2} = \frac{\mu\omega^2 l^2}{\pi^2} \frac{1}{n^2},$$

$$T_B = \frac{\mu\omega^2}{k^2} = \frac{\mu\omega^2 l^2}{\pi^2} \frac{1}{m^2}. \tag{46}$$

Now, if one imagines that the point *C* to which the tension forces are applied from the sides of points *A* and *B* is able to move along *x*, this displacement will be due to the action of a force proportional to the difference  $T = T_A - T_B$  and, hence, to the quantity  $(1/n^2 - 1/m^2)$ . Furthermore, Ritz gives qualitative arguments in favour of the idea that both the electric polarisation of the system and the magnetic field along the axis will be proportional to this quantity, which naturally leads to a Balmer-type formula. One may suppose that Ritz was immediately struck by the artificial character of such a mechanism of formation for a magnetic field of the required configuration. In any case, already in the subsequent short communication presented to the Paris Academy of Sciences four months later [6], the elastic filament is completely absent, and the magnetic field source is taken as a specially chosen linear chain of magnetic dipoles composed of elementary magnetic charges. Ritz develops precisely this idea in detail in Ref. [7].

The following considerations form the basis of Ritz's magnetic atomic model. If two magnetic poles are positioned as shown in Fig. 2, the magnetic field **H** at point *P* is

$$\mathbf{H} = \mu \left[ \frac{1}{r_1^2} - \frac{1}{(l+r_1)^2} \right] = \mu \left( \frac{1}{r_1^2} - \frac{1}{r_2^2} \right). \tag{47}$$

Obviously, exactly the same field will be created by a chain of magnets arranged as shown in Fig. 3. If the number of elementary magnets is  $n - 2$ , the length of each of them is *a*, the distance to the point *P* is  $r_1 = 2a$ ; then for the field **H** we have

$$\mathbf{H} = \frac{\mu}{a^2} \left( \frac{1}{2^2} - \frac{1}{n^2} \right). \tag{48}$$

In the general case when the number of elementary magnets is  $n - m$ ,  $r_1 = ma$ ,  $r_2 = (n - m)a$ , one obtains

$$\mathbf{H} = \frac{\mu}{a^2} \left( \frac{1}{m^2} - \frac{1}{n^2} \right). \tag{49}$$

Now, if one puts at point *P* a charge undergoing periodic small amplitude motions in the plane perpendicular to the dipole axis, it will be embedded into an almost homogeneous field determined by formula (49), and taking into account the relation between the field and frequency (5)  $\nu = e\mathbf{H}/(4\pi m_0 c)$  (as for the Zeeman effect), for the frequency spectrum we find an expression

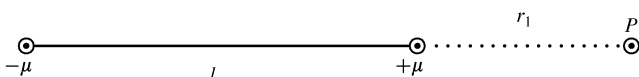


Figure 2.

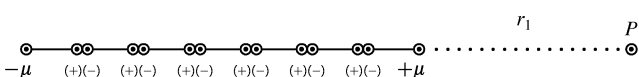


Figure 3.

$$\nu = \frac{\mu e}{4\pi m_0 c a^2} \left( \frac{1}{m^2} - \frac{1}{n^2} \right), \tag{50}$$

which reproduces the generalised Balmer formula (8).

Obviously, under such an approach the length and number of the elementary magnets are variable parameters of the model. In particular, in order to obtain Rydberg's correction in this framework, it is sufficient to change the length of one of the extreme elements of the chain.

Thus, if the first elementary magnet has a length distinct from *a* and equal to  $(1 + \alpha)a = a/2$ , keeping the distance  $r_1$  the same, we obtain a new series having a common boundary with the previous one, whose frequencies are determined by the expression ( $\alpha = -1/2$ )

$$\nu = \frac{\mu e}{4\pi m_0 c a^2} \left[ \frac{1}{2^2} - \frac{1}{(n - 1/2)^2} \right]. \tag{51}$$

This formula corresponds to the Pickering series, which, as is known, had been erroneously ascribed to hydrogen until 1913 (see Ref. [51], p. 153, for more detail).

In the general case, parameter  $\alpha$  is arbitrary, i.e.  $r_1 = ma$  and  $r_2 = (n + \alpha)a$ . Then we come to an expression corresponding to the general Rydberg formula

$$\nu = N \left[ \frac{1}{m^2} - \frac{1}{(n + \alpha)^2} \right], \tag{52}$$

where *N* is the Rydberg constant expressed in terms of the model parameters as follows:

$$N = \frac{\mu e}{4\pi m_0 c a^2}. \tag{53}$$

To obtain the next corrections, it is sufficient to assume that the length of the second (the third etc.) magnet differs from that of the subsequent ones, which are equal to each other. For example, to interpret Ritz's correction in the framework of this model, the assumption was made that the length of the second magnet differs from *a* (and from  $(1 + \alpha)a$ ).

Thus, the magnetic model not only reproduced the shape of the known spectral formulas, including (28) and (29), but also confirmed the presence of series having certain limits, and, in Ritz's opinion, taking account of the formulas which 'corresponded very precisely to experiment', contained proof of the universal character of the Rydberg constant (Ref. [1], p. 101).

It is also important to note that in the magnetic model Ritz, undoubtedly, saw the basis for a theoretical explanation of the combination principle. Indeed, in the framework of that model, each of the two terms in the expression which determines the spectral line frequency represents the contribution of one of the poles. Therefore, the different combinations of spectral terms are a simple consequence of the possible variations of the radiation locations of the poles inside the atom. Ritz stressed this point in Ref. [8] (see below).

The attempt by Ritz to use the magnetic atomic model to explain the anomalous Zeeman effect, which more than half of his paper of January 1908 is devoted to, is also of significant interest. At that time, extensive experimental data were stored on Zeeman splitting, and along with the confirmation of Preston's rule (on the identical splitting for all members of one spectral series and analogous series of different elements; see above) the important Runge's rule was established [111]. According to this rule, for complex splitting, the spacings  $\nu'$  (in the frequency scale) between the

components (relating them to the same magnetic field value) are rational fractions of the normal splitting  $\nu_0$  determined by formula (5), and the denominators of these fractions are small integer numbers. For example, the sodium  $D_2$  line is split into six equally spaced components with a distance between them of  $(2/3)\nu_0$ .

Ritz's approach to the anomalous Zeeman effect is based on the following considerations. Because according to the magnetic model each spectral line in the absence of the magnetic field  $\mathbf{H}$  is itself a result of Zeeman splitting owing to the action of the inner magnetic field  $\mathbf{H}_0$ , the general picture of the effect represents a result of superposition of the these two fields. Here Ritz takes into account that the intrinsic magnetic field  $\mathbf{H}_0$  is higher (by the order of  $10^4$ ) than the external field  $\mathbf{H}$  used for Zeeman effect studies, which is tens of thousands of Gauss.

If the fields  $\mathbf{H}_0$  and  $\mathbf{H}$  are parallel or antiparallel to each other, ultimately, according to Ritz, two frequencies  $\nu = e(\mathbf{H}_0 \pm \mathbf{H})/(4\pi m_0 c)$  naturally appear, which correspond to two circularly polarised components observed along the field direction with a split twice as high as the normal one.

In order to describe the phenomenon as a whole, Ritz supposes that in the general case the sources of the internal atomic field can undergo rotational motions that result in precession of the field  $\mathbf{H}_0$  around the external magnetic field direction.

The next assumption by Ritz is the periodicity condition for this motion, which is expressed by the fact that the sines and cosines of Euler's angles connecting the two coordinate frames are directed along  $\mathbf{H}_0$  and  $\mathbf{H}$ , respectively, and become periodic functions of time which can be represented by Fourier series.

In the general case, such splitting should lead to an unlimited number of components, which, of course, does not correspond to observations. Agreement between theory and experiment on this point has been achieved by taking account of the strong dependence of the intensity on the number of harmonics. For example, according to Ritz's estimate, only those lines that have a certain minimum intensity can be observed to split.

On the grounds of the assumptions made, Ritz was able to explain Runge's rule as a result of the frequencies of two rotational periodic motions being in rational proportion. He considered a number of specific cases of a complex picture of Zeeman splitting, in particular, the spectral lines of neon and mercury.

Ritz was certain that his scheme for the explanation of the anomalous Zeeman effect had an advantage over Lorentz's approach. Lorentz tried, beginning with Ref. [75], to explain this effect by internal atomic interactions. Like other theoreticians, however, he did not consider the series structure of spectra. Ritz especially emphasised the point that his model of the molecular field  $\mathbf{H}_0$  was not only suitable 'for a much larger range than Lorentz's hypothesis, ... for representation of the Zeeman effect phenomena in their great diversity and with their characteristic features, ... but is also able to explain the series laws—the problem which Lorentz completely ignored' (Ref. [1], p. 132).

Now we know that the explanation of the series structure is connected not with magnetic, but electrostatic interactions within an atom, but Ritz's idea of considering the precession of magnetic momenta turned out to be

correct with regard to the spin and orbital magnetic momenta of electrons. It should be specially noted that here once again appeared the characteristic of the whole of Ritz's scientific career: the ability to anticipate correct physical results on the basis of theoretical methods inadequate to the problem.

In the case under consideration, despite the physical inconsistency of Ritz's theoretical approach to the anomalous Zeeman effect, his scheme of explanation contained an important constructive element—the idea that the precession of the internal atomic magnetic momenta around the external magnetic field direction underlies the phenomenon. In our opinion, this fact is interesting despite the obvious point that the internal atomic magnetic moment in Ritz's magnetic atomic model has nothing in common with the actual magnetic momenta of real atoms and their structural constituents (nuclei and electrons).

It seems certain that Ritz himself understood the artificial character of the magnetic model and the necessity of bringing together additional physical arguments and specific ideas about atomic structure. In particular, he wrote: '... from the point of view of electronic theory, one cannot essentially object to the assumptions made, at least in principle. Of course, the required distribution of electricity is not a simple one. However, we do not completely know a priori whether the simple laws of molecular interactions relate to the electronic density or to the forces acting... And since the full theory of linear atomic spectra seems to be impossible to obtain without special assumptions about atomic structure, from the gnoseological point of view it is an advantage rather than a shortcoming of this hypothesis that it does not require an assumption about the form of the electrons the atom appears to be constructed from, and operates only with intervals or distances which are thought to be rigid. However, in questions of such a kind, where it is hardly possible to make any conclusion about the reason for the action and, on the one hand, the observed facts differ from all known phenomena and are very complicated, and on the other hand, there is such great uncertainty in the assumptions, one can hardly expect that an inclusion [of these facts] into our conventional range of perceptions that is satisfactory in all respects is possible; moreover, it will be difficult to unify opinion about what to consider as a 'satisfactory explanation' in that case' (Ref. [1], p. 110).

In trying to find a physical motivation for the magnetic model, Ritz made use of the familiar ideas on equivalency of looped currents and permanent magnets, and proved the corresponding theorems using mathematical methods of potential theory. He also understood that in order to provide stability to such structures, forces that are non-electric in origin are required.

It seems certain that Ritz's magnetic model was inspired by the general increase in interest in the problem of magnetism which was characteristic of the physics of the beginning of the 20th century.

If one studies the extensive physical literature of that time, both technical and popular, concerning the problem of atomic structure (see, for example, Refs [112, 113]), an interesting feature becomes apparent. Practically every such publication contains references to the experiments performed by Mayer as early as 1897 [114]. The essence of these very simple but now completely forgotten experiments is the following.

Mayer used a system of floats each of which was a cork circle pierced in the middle by a long thin magnetised needle. The floats were placed on the water surface in such a way that the poles of all the needle-like magnets were oriented in the same direction. Naturally, in the absence of any external magnetic field the floats tended to withdraw from each other as far as possible. However, under the influence of a magnetic field created by suspending the pole of a large magnet above the floats, of opposite sign to the poles of the magnetised needles that are above the water surface, the floats come closer by forming some stable configuration of a regular form. For example, three floats take up positions in the corners of an equilateral triangle, four—in the corners of a square; with an increasing number of floats the picture becomes more complicated but keeps the same structure (see Ref. [114]). These quite effective results did not attract attention until Thomson's atomic model [115] was developed shortly after the discovery of the electron, advancing the fundamental problem of equilibrium electronic configurations inside the atom. Then, interest in the results of Mayer's experiments, which were used as an extremely visual physical analogy, illustrating the possibility of the formation and the specific forms of such configurations, increased dramatically.

Important steps that led to the understanding of the nature of magnetic phenomena took place at that time. In 1895 Pierre Curie published the results of his famous experimental study [116] of the dependence of diamagnetic, paramagnetic and ferromagnetic properties of matter on temperature. Then in 1905 the classical work by Langevin [117] appeared, in which he attempted to explain the magnetic properties of diamagnetic and paramagnetic materials on the basis of the electronic theory. Studies by Weiss [118] reported in 1907 allowed the description of some features of ferromagnetic behaviour using the idea of an internal magnetic field ('Weiss's field'). We note that Weiss assumed the existence of an elementary magnetic charge or magneton, similar in concept to the elementary electric charge, the electron.

Thus, the idea of the possibility of using elementary magnets as constituents of atomic structure may have appeared quite natural to the 'scientific community' of the beginning of the 20th century.

Of course, the atomic magnetic model itself seems today nothing but a historical curiosity. But one should bear in mind that it played an important role in the general context of Ritz's research as a kind of theoretical basis for justification of the combination principle. It is known that in the history of physics Ritz's name is associated primarily with that spectroscopic law. For the spectral series, this principle, in fact, was contained, although in partial form, in Rydberg's fundamental work of 1890 [53] [see Eqn (2)]. As has already been mentioned, Ritz must have been well acquainted with this work, since in his thesis as well as in subsequent papers he repeatedly cites Rydberg. The paper by Ritz 'On the new law for spectral lines' [8], where the combination principle was presented as a spectroscopic law, begins with an analysis of the differential structure of spectral formulas and contains a reference to Rydberg's paper [99]. Therefore, one should consider that the statement, widely spread in the literature of scientific history and even in the literature of physics, that Ritz came to the combination principle independently

of Rydberg, does not correspond to the reality. Nevertheless, the significance of Ritz's contribution to this problem is beyond doubt.

The generic connection between Rydberg's and Ritz's results relating to spectral systematisation was directly noted by Bohr in 1913 in the first part of his trilogy on the structure of atoms and molecules (Ref. [119], p. 84) and in a more developed form in his paper 'On the spectrum of hydrogen' (Ref. [119], p. 152). However, Bohr stresses here the principal difference in the theoretical status of the combination principle which results from Rydberg's approach, on the one hand, and Ritz's, on the other. For example, Bohr writes 'Rydberg had proved already in his first paper that simple relations exist between the constants of different spectral series. These rules were generalised by Ritz into the so-called combination principle' (Ref. [119], p. 153). In other words, the generalising character of Ritz's formulation seems to be obvious to Bohr.

The text of the paper by Ritz 'On the new law for spectral series' [8] (dated June 1908) demonstrates exactly what Bohr means by the generalisation of Rydberg's approach. As the basis of consideration, Ritz uses the series formula (29) obtained in his thesis, introducing the following designation for a term:

$$(m, \alpha, \beta) = \frac{N}{(m + \alpha + (\beta N/m^2) - (2\alpha\beta N/m^3) + \dots)^2}. \quad (54)$$

Ritz began by showing that this formula can describe all the relations between different spectral series of a chemical element proposed by Rydberg, by making the corresponding identification of the parameters  $\alpha$ ,  $\beta$  with empirical constants. For example,  $\alpha = p$ ,  $\beta = \pi$  for the principal series;  $\alpha = s$ ,  $\beta = \sigma$  for the second auxiliary (sharp) series;  $\alpha = d$ ,  $\beta = \delta$  for the first auxiliary (diffuse) series. All the frequencies for these series are described, according to Ritz, by the following formulas:

$$\begin{aligned} \nu &= (1, 5, s, \sigma) - (m, p, \pi) \quad (\text{principal series}), \\ \nu &= (2, p, \pi) - (m, d, \delta) \quad (\text{diffuse series}), \\ \nu &= (2, p, \pi) - (m, s, \sigma) \quad (\text{sharp series}). \end{aligned} \quad (55)$$

The major part of Ref. [8] is devoted to a demonstration that using formulas of this kind one can describe practically all the series of alkaline and alkaline-earth elements known at that time without involving any new constants†.

Ritz confirms the possibility of representing wave numbers as a difference of two terms using much more extensive experimental data than Rydberg.

Of special importance is that he clearly treats such a representation as some universal spectroscopic law. This is shown, in particular, by the introduction of the term 'combination principle'. It is without doubt that the magnetic atomic model played here an important heuristic role here.

†Note that in the paper 'On the spectra of alkaline metals' of March 1908 Ritz, relying upon the series formulas of Rydberg, gave an interpretation of the K, Rb and Cs spectra discovered shortly before by Bergman in the red and infrared spectral bands, and showed the erroneous approach of Runge, Ref. [121], who proposed another interpretation. In paper [8] Ritz gives a reference to his paper [120]. Now we know this series corresponds to  $d-f$  type transitions.

Thus, in the concluding part of the introductory section to his article, Ritz writes: ‘In the paper [7] which recently appeared I showed that one can indicate the simplest systems whose energy is purely electromagnetic and which yield the Balmer formula, the series laws, anomalous Zeeman effects etc.’ (Ref. [1], p. 147). And further: ‘For all spectra the atomic magnetic field can be considered as being induced by two poles of opposite signs; each of the two terms in  $(m, \alpha, \beta) - (n, \alpha', \beta')$  represents the influence of one pole; for example, in the case of hydrogen they are equidistantly located on a straight line. The interchange of these positions corresponds to the combination principle. In a more general form one can apparently suppose that the *simple laws are connected with the location of these poles inside the atom*’ (Ref. [1], p. 147–148; italics by Ritz).

In analysing Ritz’s works on the combination principle, it is essential to consider the question of the formulation of this principle in Ritz’s papers themselves. The usual reference is to his article of 1908 [8], or more precisely, to the author’s summary attached. In our opinion, however, there are more than sufficient grounds to doubt the correctness of that reference. The point is that the article itself has the subtitle ‘Preliminary communication’, from which it follows that Ritz definitely counted on publishing some more general material on this subject. It is difficult to judge how legitimate is the treatment of that assertion contained in the author’s summary attached to the article, and usually it is cited (moreover, in a somewhat abbreviated form) in literature as a general formulation of the combination principle.

It should be taken into account that the paper was published in *Physikalische Zeitschrift* without this text. The author’s summary itself was found among Ritz’s papers after his death and was placed as an appendix to the corresponding paper in the posthumous edition [1] of his works in 1911 (see the compilers’ note on p. 162).

Although the purpose of that extract was unclear, its general sense had something in common with the article by Ritz so that unification of the texts in the complete works seems quite appropriate. However, the citation of Ritz’s paper of 1908 as a reference where the formulation of the combination principle is given cannot be justified. It is interesting to compare the complete text of the corresponding statement from the author’s summary with the citation given by Jemmer [110].

In the original, the phrase reads as follows: ‘By combining, by means of adding or subtracting, either the series formulas themselves or constants entering into them, one can construct new formulas which allow one to compute new lines of the alkaline metals discovered by Lenard and others during recent years and which also make possible far-reaching applications to other elements, in particular He’ (Ref. [1], p. 162).

Jemmer writes: ‘By combining (adding or subtracting) either the formulas for series themselves or constants entering into them, one can construct the formulas that allow one to express fully some newly discovered lines through the known earlier ones’ (Ref. [110], the note on p. 77 with reference to Refs [8] and [9]).

It is clear that Ritz writes about an unconditional application of the combination procedure to alkaline metal lines and the possibility of its use for the spectra of other elements. In the quotation given by Jemmer, this reference to specific spectra, as well as the possibility of further

generalisation of the approach, are completely omitted, which results in the statement acquiring a status of universality absent in the original.

In fact, the most extended and comprehensive formulation of the combination principle is given by Ritz in his general review of 1909 on ‘Linear spectra and the structure of atoms’ (Ref. [10], paper XI in [1]). It is difficult to judge to what extent this review can be considered as a completion of that ‘preliminary communication’ [8], which was published by Ritz in 1908. Perhaps, the initial plans were significantly altered by that tragic ‘Zeitnot’ which accompanied the scientist in the last year of his life. In any case, the two publications on that subject are chronologically immediately next to each other. One cannot agree with Forman in assessing this review as a ‘semi-popular article’ (Ref. [31], p. 479) and simultaneously should note that Forman does not cite Ritz’s original formulations fully nor in the context of the review itself.

The general review by Ritz [8] contains a quite rigorous, although mostly qualitative presentation of the problem outlined by the title ‘on the basis of the magnetic model’. The review comprises five small sections.

1. Generalisations. New empirical laws. 2. Hypothesis of atomic fields. 3. Hydrogen spectra. Series. 4. Anomalous Zeeman effects. 5. Other methods of explanation. Conclusions.

The first section is of special interest. Ritz performs a short analysis of spectral regularities on the basis of Balmer’s, Rydberg’s and his own formulas. The section is ended by the following general conclusion: ‘... it is seen that:

1. Simple rules always depend on  $1/2$ , i.e. the frequency;
2. On infinitely increasing one or another of the integers, the frequencies obtained tend to a limit;
3. Each of the two terms of the formula is independent to a certain extent, and the spectral lines are obtained by combining such terms’ (Ref. [1], p. 173).

One can partially agree with Forman in that the combination principle ‘was not formulated too precisely’ (Ref. [31], p. 479). However, as it seems to us, the formulation given in the appendix to the review cited above may lay claim to the status of authorship both owing to its generality and because it belongs fully to Ritz and was published by him.

Thus, the confirmation of the combination principle as a general spectroscopic law seems quite natural in Ritz’s approach if one takes into account that, by relying upon the magnetic atomic model, Ritz considered the formulas he used not as empirically established, as in Rydberg’s case, but as theoretically justified relationships. The works by Rydberg, as we mentioned in Section 2, completed, at the end of the 19th century, the first stage in establishing spectral regularities on the basis of empirical and semi-empirical schemes. The works by Ritz should be considered as a completion, in the first decade of the 20th century, of attempts to provide theoretical justification for such regularities on the basis of classical ideas. The approach by Ritz is that of a typical theoretical physicist.

Unfortunately, this important part of Ritz’s career is very poorly described by the historical scientific literature. The paper by Forman [31] makes up that deficiency to a certain but quite insufficient extent. It should be stressed that Bohr was undoubtedly well acquainted with Ritz’s studies, and in particular, with the intimate connection

between the magnetic atomic model and the justification of the combination principle. It is no mere chance that in his report of 1954 on 'The discovery of the spectral laws by Rydberg' dedicated to Rydberg's centennial [122], Bohr gave an extensive appraisal of this direction of Ritz's investigations (see the authors' paper [51], p. 155†), during which Bohr stresses the ingenuity of Ritz's attempts to explain the spectral rules on the basis of the idea of atomic magnetic fields, and the failure of these attempts. Bohr specially notes the establishment by Ritz in 1908 of 'a general law, known now as Rydberg-Ritz's combination principle, according to which the wave number for any spectral line can be represented in the form  $\nu = T_1 - T_2$ , where  $T_1$  and  $T_2$  are two terms from a sample of terms characteristic for the given atom' (Ref. [59], p. 473). It is quite clear that Bohr's appraisal did not have a retrospective character, but reflected his reaction to Ritz's works at the time he was developing the quantum theory of atomic spectra. As is well known, in an interview Bohr gave to Rosenfeld and Kun shortly before his death (see Ref. [123], p. 172), he said that at the beginning of 1913 '... I found the hydrogen spectrum. I had just been reading Stark's book and at that moment I felt that now we see just how the spectrum arises'. The story goes that Bohr found out about Balmer's formula for the first time and read a book by Stark 'Principles of Atomic Dynamics', part II, 'Elementary Processes of Radiation' [124]. In Stark's book 'Structural Characteristics of Optical Frequencies', the section 'Spectral series', chapter II, considered in detail the Balmer series and spectral line series according to Rydberg and Ritz, whose papers are properly referenced. In particular, Stark writes about the spectral formulas of Rydberg such as  $\nu = \nu(n, \mu) - \nu(m, \kappa)$  depending on two variable integers  $n$  and  $m$  and cites the paper by Ritz 'On the new law for spectral series', noting that 'this is a contribution by Ritz [8] towards understanding the actual meaning of Rydberg's ideas' (Ref. [124], p. 51).

The important role Ritz's works on the combination principle played when Bohr formulated his famous frequency condition in the first part of his 'trilogy' (Ref. [119], p. 90–91; see also Bohr's paper 'On the spectrum of hydrogen', [119], p.160), is not in doubt. At the same time, it is natural to assume that Bohr's knowledge of Ritz's attempts to model the spectral laws theoretically on the basis of classical ideas strengthened Bohr's conviction of the inapplicability of this method for describing atomic structure and its interaction with radiation.

## 5. Conclusion

The range and standard of Ritz's scientific research, as well as his substantial contribution to the development of physics and mathematics, all provide grounds to speak of him as one of the outstanding representatives of the generation of theoretical physicists which included Einstein, Bohr and Ehrenfest. Ritz's studies in atomic spectroscopy completed the pre-quantum development period of one of the most important topics in physics at the beginning of the 20th century.

In the field of atomic spectroscopy, Ritz's first contribution was in obtaining the correct series formulas,

including the corrections, and in establishing their universal applicability in all the range of the optical spectrum available at that time. The second very important result was the formulation of the combination principle as a general spectroscopic law. The spectroscopic works by Ritz, especially his thesis, include all necessary criteria of a developed theoretical study: clear statement of the problem, resonance choice of the initial model, logical use of the mathematical methods which were developed. Therefore the fact that the well-known Balmer's and Rydberg's series formulas, as well as a generalisation of the latter found by Ritz himself, appeared as a purely mathematical consequence of the model in use, gave them definite theoretical status. It was after Ritz's studies that the use of formulas with a fixed differential structure and a characteristic dependence of each of the two terms on the square of an integer became the conventional means for describing the observed spectral regularities, which, in turn, stimulated the appearance of Bohr's initial quantum theory with its frequency condition.

Ritz did not use quantum ideas at all; his studies were based exclusively on the ideas and methods of classical physics, which, certainly, made the basis of his theory inadequate for the physical problem he was considering. However, in his works he succeeded in expressing a number of physical concepts which were refined and fully correct qualitatively, and separate details of his approach strikingly anticipated some features of the quantum description.

All of that, in our opinion, shows that Ritz's premature decease undoubtedly deprived physics of a possible active developer of the atomic quantum theory. Exactly this idea was expressed by Sommerfeld in a letter to Ehrenfest on November 16, 1916, concerning quantum problems on which, as is well known, he was actively engaged at that time. In that letter, having expressed deep regret for Ritz's early death, Sommerfeld in wrote particular: '... his rich imagination, his enthusiasm to master the problem, not hampered by a too critical approach, would be very appropriate here' (see Ref. [25], p. 291).

It appears certain that the fundamental works by Ritz on atomic spectra theory deserve to take their proper place in the history of physics.

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†Note that in that article Ref. [5] to Bohr's report (as well as Refs [6] and [7]) were omitted from the list of references.

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