FROM THE HISTORY OF PHYSICS

PACS numbers: **01.65.+g, 32.30.–r**

Grotrian diagrams

S G Rautian, A S Yatsenko

70 years have passed since the publication of a widely renowned book *Graphische Darstellung der Spektren von Atomen und Ionen mit Ein, Zwei und Drei Valentzelektronen* (Graphic Representation of Spectra of Atoms and Ions with One, Two and Three Valence Electrons) by W Grotrian [1], which has played an enviable role in atomic spectroscopy and the quantum mechanics of atomic systems. Grotrian diagrams have long become an habitual and indispensable element of the professional language of physicists and chemists and it is now difficult to perceive how we could obviate the need for them. Meanwhile nearly 15 years had elapsed since the enunciation of the quantum postulates by N Bohr in 1913 [2] and the issue of the 'hero of our narration'. The explanation for such a long period of time is certainly associated with a radical transformation of basic ideas in physics.

By 1913, the spectroscopists had amassed extensive factual data for the frequencies of emission and absorption spectral lines. Summing up "... a 60-year scientific activity resulting in fifteen thousand works" Professor D S Rozhdestvenskiĭ wrote in 1915: "All the elements acquired their own characteristics in the lists of spectral lines..., these lists are nearly concluded, the wavelengths are occasionally measured to an astonishing precision..., empirical relationships between wavelengths of spectral lines have been established" [3].

The wavenumbers of lines are governed by Rydberg's formula to an 'astonishing accuracy' as well:

$$\nu_{21} = T_2(n_2) - T_1(n_1)\,, \quad T(n) = \frac{R}{(n+\alpha+\beta/n^2)^2}\,, \qquad (1)$$

where n is an integer, and R, α and β are constants. The quantity $T(n)$ had been referred to as 'the spectral term', and later, when the etymology of the word was forgotten, simply as 'the term' (using the English word). N Bohr related the term to the energy of an atomic stationary state and relationship (1) was assigned the meaning of the law of conservation of energy for the atomic radiation transition from one stationary state to another.

Since spectral lines can be calculated with the use of terms, the latter are of much more importance in studies of atomic spectra than the former. The variety of lines is much wider than a relatively simple collection of terms, which in fact reflect individual peculiarities of a particular atom. It is extremely complicated, however, to obtain a spectral series (1) on a basis of tables of wavelengths. Professor G S Landsberg wrote in this connection in his review article [4]: "Not without reason Paschen says that your attempts at searching for a series from the examination of tables of spectral lines are hopeless 'if you are not Rydberg". In this situation, the graphical methods of analysis played an important part.

It is a matter of general experience that graphs illustrating a great diversity of functions, for example, the dependence of potential energy on distance, $U(x)$, hold much favour in classical physics. The peculiarities of a graph instantaneously strike our eyes and it is frequently more useful for forming a qualitative picture of the physical processes involved than analysis of the explicit formula describing the behaviour of $U(x)$. The terms 'potential well', 'potential barrier', 'turning point', etc., being obviously thrusted by the geometrical associations (the word composition of the language always reflects the point of the matter!), were not coined without reason.

Schematic diagrams played a fully similar cognitive role in atomic spectroscopy. However, evolution of the graphic version of atomic terms turned out not to be simple due to the unusual and unaccustomed nature of quantum laws and the discrete character of quantity variations. It was N Bohr who first suggested the graphic representation of stationary atomic states, which is illustrated in Fig. 1 (the figure was borrowed from Ref. [2]; here n, k are the principal and orbital quantum numbers). The energy axis is plotted horizontally in this figure, the logic of this approach being that the energy seemed to be the main independent variable setting all the others. For the symbols of stationary atomic states the points were then replaced with short straight-line segments; and the sense of the axis complying with energy growth was also changed. A somewhat different graphic representation was employed by researchers affiliated with St. Petersburg school of spectroscopy. Professor D S Rozhdestvenskiĭ writes in his article [5]: "In order to better unpack and hold all the variety of possible intraatomic processes in memory, it is convenient to represent schematically the system of spectral lines in the following way" and further refers to the figure with a scheme of transitions between Na states (Fig. 2). The emphasis is on the transitions from one atomic state to another and their relative positions on the energy scale (the vertical axis) is only reflected in the sequence of states and is drawn without keeping to the scale.

In 1924, W Grotrian made a highly felicitous and decisive stride forward [6]. His diagrams combined in some sense those of both N Bohr and D Rozhdestvenskiĭ. The energy axis conclusively pointed upwards and the space along horizontal axis was given over to the scheme of classification of states by orbital and spin quantum numbers, as displayed in Fig. 3,

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Received 24 March 1998
Uspekhi Fizicheskikh Nauk **169** (2) 217 – 220 (1999)
Translated by A Radzig; edited by M S Aksent'eva

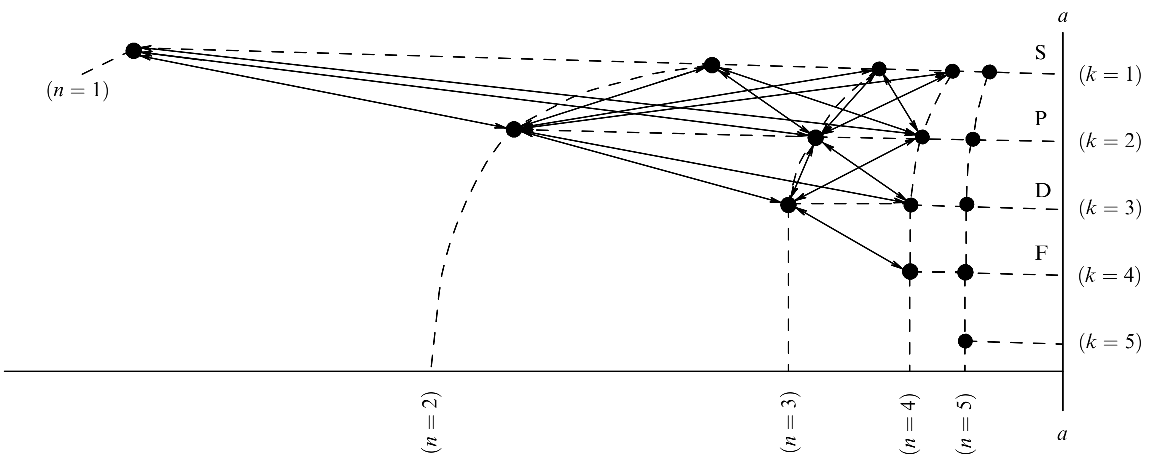

Figure 1. Scheme of electronic terms and serial spectrum of Na due to N Bohr [2].

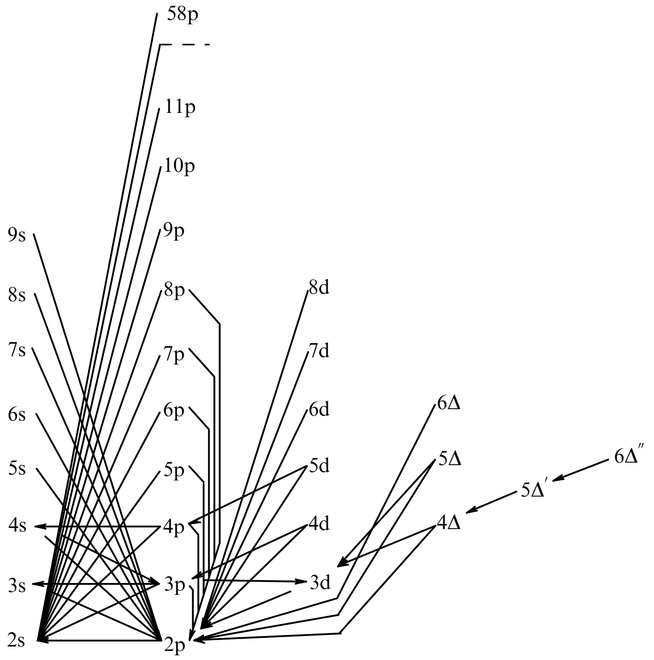

Figure 2. Scheme of electronic terms and radiative transitions of Na due to D Rozhdestvenskiĭ [5].

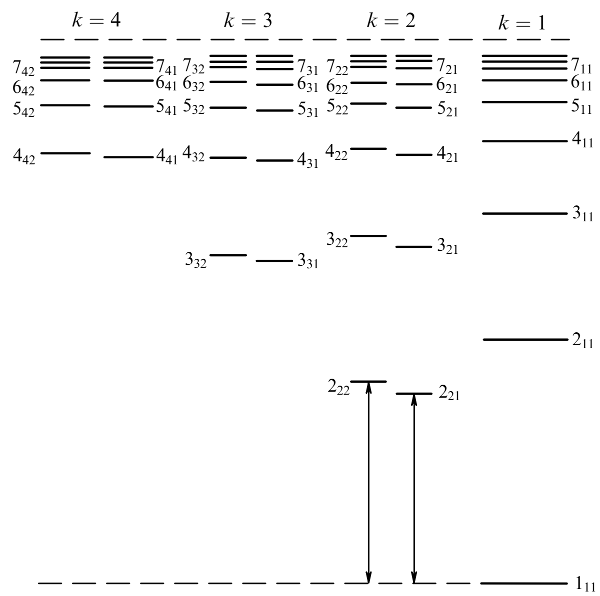

Figure 3. Diagram of the sodium energy levels due to W Grotrian [6] (the notation n_{kj} denotes n — the principal quantum number, k — the orbital quantum number, and $j = 1, 2, \ldots$ — the multiplet components).

taken from Ref. [6]. Without question Grotrian associated the vertical direction of the energy axis with the vector of gravitational force or the energy alteration in the field of gravity. It is appropriate here to give several passages from his article [6]: "... the atomic energy levels between which quantum jumps proceed may be arranged in a single series which will be designated by the energy ladders. However, the interrung distance for each of the ladders does not remain constant as in an ordinary staircase but progressively decreases as we mount the ladder". In the case of multiplet spectra "each rung is decomposed into several adjacent rungs". The multiplet characteristics which proved to be extremely fruitful in analyzing complex spectra are also positioned horizontally on the Grotrian diagrams. After issuing article [6], a book [1] was published, where sequences in the representation of quantum states were standardized and quantitative information about the states and spectra of 23 neutral atoms and 48 ions of various degrees of ionization was brought together. It is of first importance that the allowed radiative transitions on the diagrams displayed in Ref. [1] are marked with lines whose thickness increases with a rise in line intensity and alongside of which the corresponding wavelengths are put down. As a result, the diagram featured on one page gives illustrative, detailed information which is convenient for turning over in one's mind and processing. Comparing Figs 1 – 3 with Fig. 4 on which the diagram for Na involving the scheme of atomic energy levels and transitions between them is illustrated [1], clearly demonstrates the progress made by Grotrian in preparing his famous book [1]. In those cases where the optical transitions are not examined and all attention must be centred on atomic energy levels, Grotrian sketches the states in the form of circles (see Fig. 5 taken from Ref. [1]) as N Bohr proposed.

Spectroscopists instantaneously perceived and appreciated the Grotrian diagrams at their true value and over the years have widely employed them in a full or abridged form

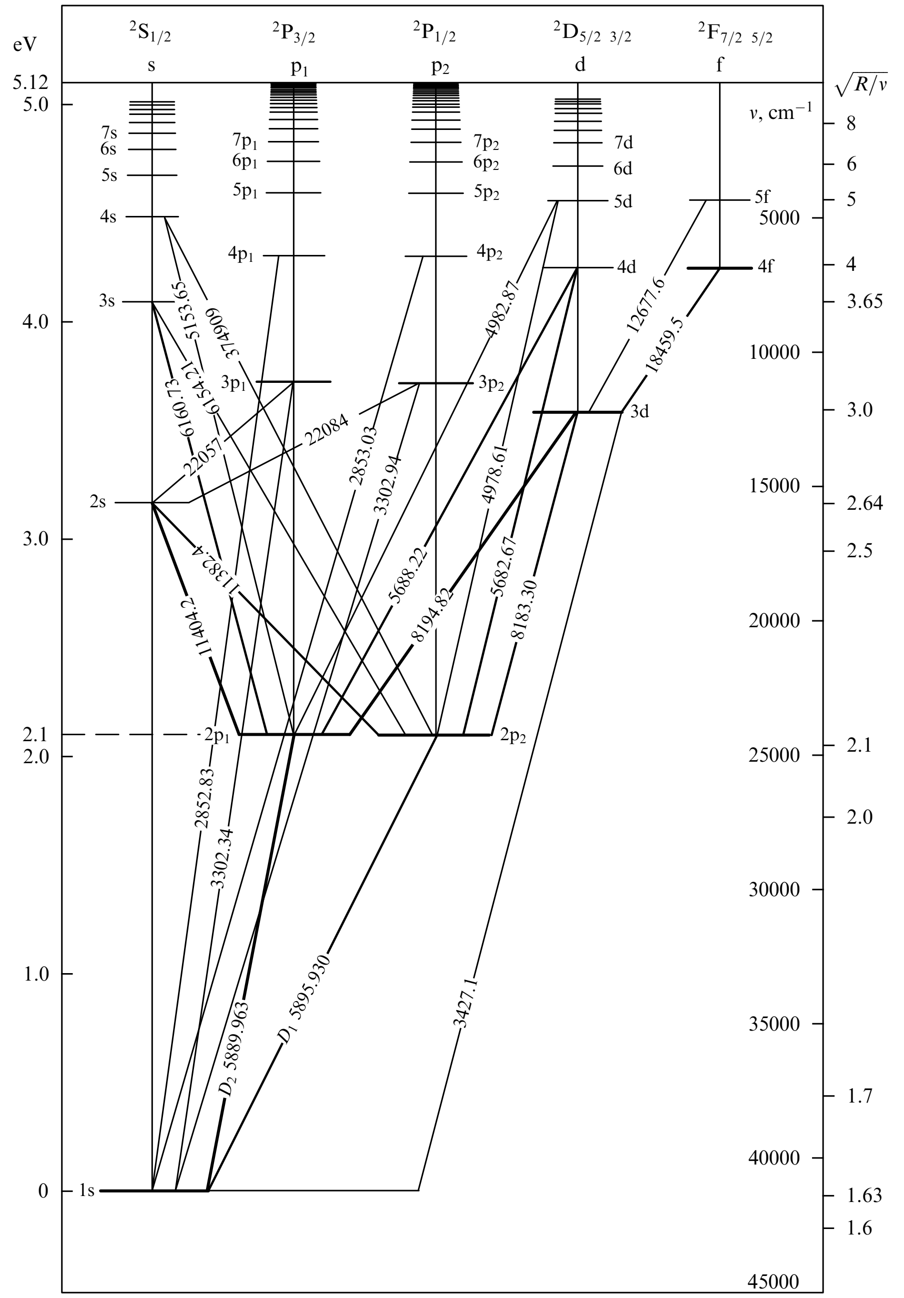

Figure 4. Grotrian diagram of sodium energy levels and spectra [1].

when publishing periodical, monographic and educational literature. One would highlight, for instance, the monographs written by M Born (1933) [7], H Bethe (1933) [8], S Frish (1934) [9], E Condon and G Shortley (1935) [10], G Herzberg (1944) [11], I Sobel'man (1963) [12] and many later publications. At the same time, it is particularly remarkable that courses of quantum mechanics do not included Grotrian diagrams of atomic particles as part of the material discussed. Beginning with the courses written by P Dirac [13], A March [14], and V Fock [15] in the early 1930s and ending with numerous modern textbooks including the many-volumed set by L Landau and E Lifshitz [16], we did not find an exception to this rule. It seems likely that the theory of atoms is expounded in such courses as an illustration of the general quantum theory and thus Grotrian diagrams turn out to be burdened with redundant information from the standpoint of fundamental science. This fact indubitably testifies to the selective, practical trend of the Grotrian idea oriented to close examination of particular atoms and atomic ions.

W Grotrian compiled and published the diagrams of atomic energy levels and spectra for elements from groups I, II, and III of the Periodic Table, i.e. for atomic particles whose electronic structures were carefully examined by 1928. Further progress in spectroscopy and atomic physics demanded replenishment of the characteristics involved, namely, an indication of electron configurations and the states of the atomic core in addition to electronic terms. This situation is strikingly illustrated by the examples of description of the electronic structure and spectrum of rare-earth elements [17, 18] and the elements of the actinide series [19 – 21]. A huge extension of basic and applied spectroscopic

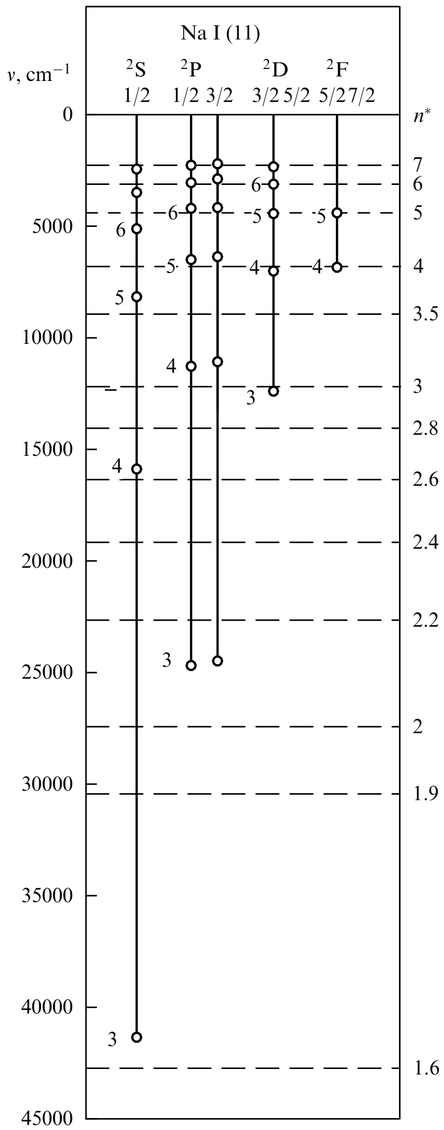

Figure 5. Scheme of sodium energy levels [1]. Horizontal dashed lines indicate positions of hydrogen-like energy levels pertinent to effective principal quantum numbers n^*.

problems over the course of the past 70 years has impelled researchers to elaborate the Grotrian diagrams of all the chemical elements and their ions [22, 23] as well as to compile diagrams of more specific interest, for example, in astrophysics [24] or vacuum ultraviolet investigations [25]. Experience accumulated in constructing diagrams for atomic systems proved to be useful with respect to the form of presentation of spectroscopic data for diatomic molecules [26].

It may be concluded beyond any reasonable doubt that Grotrian's ideas of graphic representation of atomic and ionic states will live a full life as long as physics still survives.

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