Atomic Spectra for the Astrophysicist[1]

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IN THE application of quantum theory to astronomy atomic spectra have played a major role. The discoveries of "regularities" among the wave numbers of spectral lines, of multiplets, of series, and of the Bohr theory are inseparable parts of the intricate picture fitted together by the quantum theory to describe the properties of atoms as we know them today.

Without this theory the astrophysicist was restricted to a qualitative interpretation of astronomical spectra, such as the chemical identifications of spectral lines and the measurement of radial velocities. He is directly dependent upon the quantum theory for the quantitative chemical analysis of celestial spectra—for his knowledge of the physical properties of the stars, such as temperature and pressure; for his interpretation of the many kinds of lines excited in celestial sources. It is not the purpose of this paper to stress the cosmological importance of this development, but to offer some comments regarding the present status of atomic spectra, with special emphasis on astrophysical problems.

In 1946 a program was instituted at the National Bureau of Standards on the compilation of "Atomic Energy Levels as Derived from the Analyses of Optical Spectra." This program entails the critical editing of all analyses of optical spectra and the tabulation of the electron configurations, term designations, energy levels, term intervals, and observed g-values of the individual spectra—all presented in a uniform style and notation. Arrays of predicted terms of the various configurations are also included for each type of spectrum, with similarly arranged arrays of observed terms for the more complex spectra. All levels are listed from the ground state as zero, with the limit and ionization potential appearing in the heading for a given spectrum. A similar project was carried out by Bacher and Goudsmit in 1932. Their classical book on *Atomic Energy States* included atomic energy levels for 231 spectra of 69 elements. At present something is known about the structure of 501 spectra of 84 elements.

Volume I, published in 1949, includes 206 spectra of the elements $_1$H–$_{23}$V (*1*). Volume II will include 152 spectra of the elements $_{24}$Cr–$_{41}$Nb. Of the 152, 131 are in galley proof, 16 more are in press, and 2 additional spectra have been completed, leaving 3 unfinished.

Such a compendium enables one to survey the upper half of the periodic table with regard to the behavior of the outer electrons of the various atoms. The correctness of the interpretation of individual spectra can readily be studied by comparing similar and related spectra. Along the isoelectronic sequences the spectra are similar, although the related lines acquire greater frequencies as the sequence progresses to the spectra of higher ionization. The electronic structure is the same for all members of the sequence, even though the terms are not necessarily in the same order throughout. Spectra in the same stage of ionization, of elements that appear in the same vertical columns of the periodic table, are likewise similar in structure.

The first over-all survey of Volumes I and II, so far as the writer is aware, has come about quite incidentally through the request of Forsythe for a revision of the tables on "Binding Energies," to be included in the forthcoming edition of the *Smithsonian Physical Tables*. These particular tables give the maximum binding energy of the running electrons in first and second spectra. This quantity is determined by converting the absolute value of the lowest energy level assigned to a given running electron into electron volts. Where two limit terms are involved, as, in this instance, for the spectra K I–Zn I, Rb I–Nb I, care must be exercised to refer the level in question to the proper limit. If the two limit terms are handled separately in grouping the binding energies of successive spectra, the runs are regular.

H. N. Russell and the writer have recently prepared two of these tables, one for first, and one for second spectra of the elements $_1$H–$_{41}$Nb, utilizing the data in Volumes I and II of *Atomic Energy Levels*. This survey has revealed some interesting facts. In Si I, for example, a serious discrepancy existed in the binding energy of the $3d$-electron as given in Volume I of *Atomic Energy Levels*. There are two low $^3D^\circ$ terms in Si I, one from $3s\ 3p^3$ and the other from $3s^2\ 3p\,(^2P^\circ)\,3d$. In this volume the lower term, ascribed to the latter configuration, was used to calculate the binding energy. The results run as follows:

Spectrum	$3d$
Na I	1.52
Mg I	1.89
Al I	1.96
Si I	2.54
P I	1.83
S I	1.94

By interchanging the published configurations of these two $^3D^\circ$ terms, the binding energy is determined from $3d\ ^1D^\circ_2$, which lies between the two triplet terms. This gives the improved value 2.28, instead of 2.54, for Si I; and the run compares favorably with

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[1] Based on a paper presented at the Joint Symposium of Sections D and B of the AAAS on "Fifty Years of Quantum Theory in Astronomy," Cleveland, Ohio, December 27, 1950.

that of the elements Li I–O I, which are directly above this group in the periodic table.

The *d*-electrons in Br I also deserve mention. Here the binding energies run as follows:

Spectrum	4*d*	5*d*
Ga I	1.69	0.94
Ge I	1.87	1.02
As I	2.03	—
Se I	1.89	1.03
Br I	0.71	0.47
Kr I	2.00	1.13

The values 0.71 and 0.47 should probably be ascribed to the 6*d* and 7*d* electrons, according to Russell. The terms from 4*d* and 5*d* are evidently not known as yet.

From these general calculations Russell has concluded that it would be advisable to use the *average* value of the energy levels of related terms—triads, pentads, etc.—rather than the lowest level of the group, as has been done in the revised tables. Average values should have been adopted, but the laborious calculations have not been repeated.

The publication of Volume I appears to have stimulated requests for ionization potentials. The literature on this subject is, admittedly, confusing. An attempt is being made to improve the situation (1) by giving the limit for each spectrum referred to the ground state of the ion, (2) by using the same factor throughout to convert the limits to electron volts, and (3) by stating what series have been observed and what series formula has been used to derive the ionization potential.

It has long been known that limits based on series of only two members are too high. Russell has recently restated that a reevaluation of limits is important in such cases: "If but two members are available, serious errors occur if the Ritz correction is ignored." In the course of the work on binding energies, he has revised the limits of the second spectra of the elements of the iron group, utilizing additional series from recent analyses. Good series have been observed in the spectra of Ca II, Mn II, Cu II, and Zn II. He has corrected the Rydberg denominators by an empirical formula that fits these four spectra, and has thus derived revised limits and ionization potentials for the intermediate spectra: Sc II, Ti II, V II, Cr II, Fe II, Co II, and Ni II (*2*). He states that

> This method is familiar, but published estimates have not been made on a uniform system. Such estimates for spark spectra from Ca II to Zn II give ionization potentials differing from a smooth formula by ± 0.02 volt, while the differences in the three cases where the Ritz correction was not applied, average ± 0.39 volt.

Finkelnburg (*3*) has made similar calculations for spectra of many degrees of ionization, by utilizing the regularities in the change of the screening constant.

Other adjustments have resulted from the intercomparison of binding energies. A few selected ones have been mentioned to indicate that this method of approach may prove to be a useful guide in handling the complex spectra to be included in Volumes III, IV, etc., of *Atomic Energy Levels.*

Even though the conditions of excitation in celestial sources have so far not been quite duplicated on earth (fortunately), yet in astrophysics the progress of the astronomer and the spectroscopist go hand in hand. This statement is confirmed by an event that occurred in Cambridge, England, last September, when a Joint Commission for Spectroscopy was formed. The Commission consists of twelve members, six representing the International Union of Pure and Applied Physics, and six the International Astronomical Union. The purpose is to coordinate the work of the spectroscopists and the astronomers with regard to both atomic and molecular spectra. On this occasion three papers were presented at a symposium on spectra: W. F. Meggers described the present state of atomic spectra; R. W. B. Pearse discussed laboratory molecular spectra; and P. Swings reviewed the needs of astronomers in interpreting astronomical spectra of all types. The results were enlightening. Summarized all too briefly, the more urgent needs are as follows:

a) Infrared observations of second spectra of elements in the iron group, especially Fe II. (It would be well to include here also the first spectra of this group of elements.)

b) Laboratory investigations of the third spectra of these elements (the metals in general) over the maximum spectral range. (Only Fe III and Cu III have a Grade A analysis.)

c) More work on spectra of higher ionization. (Fe IV and Fe V, in particular, are badly needed. Forbidden lines are especially important in this group.)

d) More analysis on the spectra of the light elements and more terms of other spectra that are cosmically abundant, even though the present analyses appear to be fairly complete: C I to C IV, N I to N V; O II to O VI, Si III, Si IV.

e) Second and third spectra of rare earths.

Swings' paper left the impression that the study of celestial spectra is only well begun, and that laboratory observations are still inadequate for the solution of many astrophysical puzzles among the spectra of stars all along the sequences—the Wolf-Rayet stars, the B-stars, the giants, the dwarfs, and the cool red stars, peculiar stars—and in the spectra of nebulae, novae, comets, planets, interstellar matter, the night sky, the sun, and the corona. Many hundred unexplained lines over the whole observable range still challenge the spectroscopist.

In 1945 (*4*) a Multiplet Table was prepared expressly to aid in the study of astronomical spectra. The short wave limit of this table was 3,000 A, a limit set by the ozone in the earth's atmosphere, which cuts off observations of celestial spectra near this point. Almost overnight this table became out of date. The shorter ultraviolet solar spectrum was recorded, during the flights of two V-2 rockets, at an altitude above the ozone layer. The leading lines, long anticipated—the Mg II pair at 2,795 A and 2,802 A (analogues of H and K of Ca II), one strong line of

Mg I at 2,852 A, and one of Si I at 2,881 A—stand out on these films conspicuously enough to gratify the solar physicist. The other lines are seriously blended, and the identifications depend on a careful study of ultraviolet multiplets of well-known spectra. The rocket spectra have thus provided the impetus for the preparation of an Ultraviolet Multiplet Table (*5*), which is now being compiled along with the compendia of *Atomic Energy Levels*. This multiplet table includes, also, lines in the short-wave region that are responsible for the forbidden transitions observed in the nebulae, etc. The writer is attempting to include all important ultraviolet lines that may prove to be useful in disentangling complicated astrophysical spectra.

These programs, fortunately, involve much more than writing down in a uniform style the data known on atomic spectra. Every effort has been made to stimulate work on spectrum analysis, with particular emphasis on unknown or incompletely known spectra of astrophysical importance. The result has been rewarding in more than one respect. There has been the most cordial cooperation, national and international. Manuscripts have already been received, in advance of publication, that anticipate some of the needs pointed out by Swings.

One of the fountain sources of material is, naturally, the Spectroscopy Section of the National Bureau of Standards. W. F. Meggers is chiefly responsible for the recent completion of a study of As I. He is progressing rapidly with the analyses of Tc I and Tc II (element 43), which was obtained from Oak Ridge in sufficient quantity for spectroscopic study. He, with Scribner and Bozman, has also observed the Pm spectra (element 61), but the lines of Pm I and Pm II have not been separated as yet. In the same laboratory, C. C. Kiess has furnished extended analyses of the very complex spectra Cr I and Cr II. He now has about 2,800 classified lines of Cr I in the range between 1,988 A and 11,610 A, and 1,400 of Cr II between 1,200 A and 7,300 A. All extra copies of proof giving the energy levels of these two spectra are now in the hands of astronomers. Mn I and Mn III are being completed by M. A. Catalán, of the University of Madrid, who discovered multiplets in 1921 while working in Fowler's laboratory on the spectra of Mn. Mn II has been greatly extended by C. W. Curtis, and Co II by N. E. Hager, Jr., both of Lehigh University. A. G. Shenstone, at Princeton, has given his wholehearted support to this program. He has observed many spectra in the short-wave region (< 2,000 A) and thereby made it possible for others to extend their work—for example, Cr I to Cr IV, Mn I to Mn IV, Co II, As I, etc. In addition, he is working on the analyses of Co III and Ni III and has furnished his recent results on Cu III, and new data on Ni II. F. L. Moore, Jr., who started his spectroscopic work at Princeton, is investigating Cr III, Cr IV, and Mn IV. Extended series in Ge II have been furnished by C. W. Gartlein. W. E. Albertson has supplied additional terms of Ce II. Finally, B. Edlén, of Lund, has contributed provisional unpublished work on the analyses of high ionization spectra in two sequences:

Ni I sequence: Se VII, Br VIII, Rb X, Sr XI, Y XII.
Co I sequence: Br. IX, Rb XI, Sr XII, Y XIII, Zr XIV.

(The missing spectrum in the former group, Kr IX, is being studied by F. W. Paul at Fort Belvoir.) The Joint Commission for Spectroscopy may well feel encouraged by the cooperation and accomplishment demonstrated by this impressive array of unpublished material.

No discussion of quantum theory would be complete without reference to one particular stellar spectrum—that of our nearest star, the sun. Rowland published his classical work on *Solar Spectrum Wave Lengths* in 1895–97, before the quantum theory was known. His observations extended from 2,975 A to 7,330 A. Excluding the ultraviolet rocket spectra mentioned above, there are now some 26,000 lines recorded in the solar spectrum in the photographic range 2,950 A–13,495 A. In certain regions atmospheric lines mask the real solar spectrum, but they constitute a relatively small percentage of the total number. As laboratory spectra become better known, it is possible to revise and extend the identifications of solar lines.

In 1928 (*6*) Charles E. St. John and others at Mount Wilson revised Rowland's original table of solar spectrum wavelengths and reported 57 elements present in the sun, as against 39 found in Rowland's *Table*. At that time some 1,700 lines were included beyond the red limit of the Rowland *Table*—i.e., 7,330 A–10,218 A. In 1918 Meggers had observed the infrared spectrum as far as 9,000 A. It was well known that the sensitivity of Rowland's plates decreased rapidly from 6,600 A to longer waves. When red-sensitive plates were improved, the solar spectrum was, therefore, observed from 6,600 A to 13,495 A at Mount Wilson, and more than 7,400 lines were recorded in this region. The new data were published by H. D. Babcock and the writer in 1947 (*7*). At that time 66 elements were listed as identified in the sun.

Meanwhile, Minnaert, Mulders, and Houtgast, at the Utrecht Observatory, prepared a *Photometric Atlas of the Solar Spectrum* (*8*) that extends from 3,332 A to 8,771 A, utilizing plates taken at Mount Wilson. This is no ordinary atlas. It consists of 173 pages 12″ × 17″, each containing two uniformly calibrated microphotometer tracings on millimeter paper, the scale being 1 A/20 mm. One can literally read the solar spectrum from these tracings. The staff at Utrecht is now engaged in measuring the equivalent widths of all the solar lines in this atlas, to replace Rowland's visual estimates of intensity used in the 1928 edition, and perpetuated in the 1947 publication.

The International Astronomical Union, at the General Assembly in Zurich in 1948, placed on its agenda the second revision of Rowland's *Table of Solar Spectrum Wave Lengths*. Active work on this project is now in progress. In the second revision the wavelengths will be corrected to the IAU standards of 1928 (1922 standards having been previously used for Rowland's lines). The wavelength range will be 2,950 A–

TABLE 1

ELEMENTS IN THE SUN

Present—no special comment	H, He, Be, C, N, O, Na, Mg, Al, Si, P, S, K Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge Sr, Y, Zr, Cb, Mo, Ru, Rh, Pd, Ag, Sn, Sb, Ba, La Ce, Pr, Nd, Sm, Eu, Gd, Dy, Tm, Yb, Lu, Hf, W, Os Ir, Pt, Pb	55	
Evidence from sunspot spectrum	Li, Rb, In	3	
Present in compounds only (BH, MgF, SrF)	B, F	2	
Only one line present	A,* Cd, Au, Th	4	
Present with a question	Tb, Er, Ta	3	
Total number present			67
Indeterminate	As, Tc	2	
Insufficient laboratory data	Pm, Ho	2	
			4
Total number absent†			15
Ultimate lines accessible	0.0 0.0 0.0 0.0 0.0 0.0 Cs Re Tl Bi Ra U	6	
Ultimate lines inaccessible	4.9 5.5 6.0 6.9 7.8 8.3 8.9 9.9 11.5 16.6 Hg Te Se I Br Xe Cl Kr A† Ne	9	
Not to be expected	Po, At, Rn, Fa, Ra§, Ac, Pa, Np, Pu, Am, Cm, Bk, Cf	12	

* Forbidden line identified in spectrum of corona as [A x].

† The low excitation potential of the accessible lines is entered above the chemical symbol for the absent elements.

§ Entered also in group with ultimate lines accessible.

13,495 A, with the recent Mount Wilson observations (*9*) replacing Rowland's between 2,950 A and 3,060 A. Revised identifications and the Utrecht equivalent widths will be given. For atomic lines the revisions in identifications will be based on the data being assembled for the Atomic Energy Level program. The low excitation potential will be entered for atomic lines, and in the same column of the table, band spectrum data for molecular lines.

At present about 30 per cent of the lines observed in the solar spectrum still remain unidentified. As Russell has pointed out, many of these are doubtless of molecular origin, solar or terrestrial. As work on analysis of atomic spectra progresses in the laboratory, however, so does the solar spectrum keep revealing secrets. For example, almost every line of Fe I that has been observed in the laboratory is present in the solar spectrum. From the energy levels, the positions of many additional lines can be predicted. Many of these predicted lines are unquestionably present in the sun, thus indicating that the sun is a favorable source for faint lines of Fe I. Systematic laboratory observation of this complex spectrum over the entire range, with a source suitable for exciting the weakest lines, would undoubtedly provide many additional solar identifications. In fact, a number of predicted Fe I lines found in the sun have already been confirmed in the laboratory (*10*).

With respect to the solar spectrum in the far infrared region, where observations have been made by means of improved detectors, the work of Adel, Migeotte, McMath, Goldberg, Mohler, Chapman, Shaw, and others emphasizes the need of laboratory atomic spectra of the more abundant elements. In spite of the numerous atmospheric bands, a number of lines of the more abundant elements, predicted from the Atomic Energy Levels, have been identified, the most notable being, perhaps, Fe I and Si I. The laboratory data are seriously inadequate for future work in this region. R. Fisher, at Northwestern University, is now extending the analysis of Fe I from observations in the far infrared. C. J. Humphreys is doing similar work on Si I, Ca I, and Sr I at the National Bureau of Standards. It is hoped that suitable detectors will be developed in the near future for exploring other infrared atomic spectra as well.

The present status of the knowledge of elements in the sun is summarized briefly in Table 1. The elements marked "present" have been discussed in the literature and require no comment. Argon, however, deserves special mention. It is added as present on the strength of Edlén's identification of one coronal line at 5,536 A (*11*) as due to a forbidden transition of argon atoms that have lost 9 electrons, namely, [A X]. This brings the total number of elements identified in the sun to 67.

The ultimate lines of B I, Tc II, and Hg I, and the low-level lines of As I lie between 2,288 A and 2,647 A. The existing rocket spectra that cover this region are of such low dispersion that all lines are badly blended and therefore do not provide a test as to whether these particular lines are present. Since boron is present in compounds, its ultimate atomic lines should be present. It would also be interesting to hunt for the Hg I line.

The two elements As and Tc are labeled "indeterminate" for widely different reasons. The accessible lines of As I are so blended or masked by other elements known to be present in the sun that it appears impossible to decide definitely about its presence, although it may reasonably be expected. The three strongest accessible lines of Tc II are all accounted for in the sun—one as a blend with Co I, one as masked by Fe I, and one as possibly present and unblended. This may furnish evidence of the presence of element 43, but the most stable known isotope, ^{99}Tc, has a half-life of less than a million years, which is a relatively short time compared with the age of the sun. This casts doubt on the evidence. One wonders whether Tc is as rare in nature as is at present supposed.

There are many more astrophysical problems than the three special topics that have been emphasized here—atomic energy levels, the ultraviolet multiplet table, and the second revision of *Rowland's Table of Solar Spectrum Wave Lengths.* Our knowledge of forbidden lines is probably far from complete. The quantitative determination of cosmical abundances of the chemical elements will continue to attract its full share of attention as one of the most important problems. The measurement of line intensities in laboratory and stellar spectra is also of prime importance to both astronomers and physicists. Our study of atomic spectra may be well begun, but who can guess how many secrets will be revealed by the atom in the next fifty years?

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Technical Papers

In Vitro and *In Vivo* Production of a Ceroidlike Substance from Erythrocytes and Certain Lipids[1]

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Ceroid, an orange-brown pigmented deposit which is insoluble in alcohol, xylol, and ether, sudanophilic, and acid-fast (*1*), is found in fibrous trabeculae of cirrhotic livers of rats which have been fed a diet low in choline and its precursors. Pathological accumulation of fat in hepatic parenchyma, which always precedes and accompanies this type of fibrosis, is greatest in centrolobular regions (*2*), which are also the sites of initial fibrosis (*3*) and ceroid deposition. The same lobular area is the locus for formation of pathological fatty cysts. These atrophy and become surrounded by bands of connective tissue, so that fibrotic replacement of atrophied cysts appears to be the mechanism by which the cirrhotic lesions develop (*4*). Degeneration of a cyst may frequently be initiated by a small hemorrhage into its lumen, in which erythrocytes and lipid become intimately mixed (*5*). These red cells neither become thrombosed nor disintegrate to form hemosiderin, but it is noteworthy that it is in these regions ceroid is deposited. Furthermore, the only animals in which hemosiderin deposits in the livers could be demonstrated belonged to a special group of cirrhotic rats[2] which were largely free of ceroid. These observations suggested that, under favorable conditions, some types of lipid might react with some component of red blood cells to produce ceroid in a manner that at the same time prevented the formation of hemosiderin from the altered erythrocytes. It had been noted that some granules of ceroid resembled erythrocytes in shape and size. The possibility of making ceroid from red cells and fat was therefore attempted *in vitro* and *in vivo.*

Cod liver oil was mixed in a test tube with one tenth the volume of heparinized, washed red cells of an adult rat of the Wistar strain, and incubated for 5 days at 37° C with manual agitation at frequent intervals. The centrifuged sediment was washed repeatedly with ethyl alcohol, xylol, and ether to remove all traces of cod liver oil, affixed to gelatinized microslides, stained by a variety of methods, and examined microscopically. Many erythrocytes, although deformed, exhibited the normal staining reaction to Light Green (Color Index No. 670) and failed to show any trace of sudanophilia. Groups of others, which were often crenated, clumped, and granular, no longer stained with Light Green and were strongly sudanophilic. Aggregates of red cells altered in this

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[1] This work was supported by grants from the National Cancer Institute of Canada and from the National Research Council of Canada.

[2] These animals were fed a basal choline-deficient diet supplemented with 10 mg of α-tocopherol acetate per 10 g of food mixture. The diet contained 57.5% sucrose, 12% fat, 22% protein (arachin 12%, gelatin 6%, casein 3%, fibrin 1%), with a supplement of 0.5% cystine, 1% vitamin powder (*6*), a cod liver oil concentrate, and 5% salt mixture.