

LINE SPECTRA AND THE PERIODIC ARRANGEMENT OF THE ELEMENTS

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INTRODUCTION

The conception of the periodic system is the most important generalization in the whole domain of chemistry. It is recognized now, as a result of the work of Rutherford, Moseley, Aston, and others, that the properties of the elements are periodic functions, not of the atomic weight (as was believed for so many years) but of the atomic number (N). Since the atomic number corresponds to the charge on the nucleus, and since the number of electrons external to the nucleus must be equal to the nuclear charge, it would seem to be a logical consequence to correlate the periodic properties of the elements with periodic variations in the distribution of electrons in the various atoms.

Such a correspondence has actually been derived, as a result of the Bohr theory, from the study of atomic spectra, both in the visible and x-ray region. While the work of the early spectroscopists had led chemists to use spectra merely as a qualitative guide towards the identification of elements, and physicists had previously found it impossible to formulate an atomic model by which to account for the origin of spectra, Bohr's conception of energy "levels" and electronic orbits has paved the way for a well-nigh complete revelation of the structure of the atom in all its complexity. It is true that there are still a great many problems regarding atomic structure which remain unanswered, the whole conception of electronic orbits is being viewed askance by a large and influential group of physicists, and the wave mechanics bids fair to outlaw the "naïve" idea (as one physicist has designated it) of orbits. But nevertheless, the most essential concept in Bohr's theory—that of the correspondence between so-called

energy levels in the atom and spectral "terms"—remains unaltered and provides the guiding principle in correlating the periodic properties of the elements with their spectra.

BOHR THEORY, ENERGY LEVELS

In order to understand the method of interpreting spectra in terms of the arrangement of electrons in atoms it is necessary to recapitulate briefly the essential features of the Bohr theory.

The assumption on which Bohr bases his theory of the origin of spectra has been stated by him in the following form (1).

Postulate A.

An atomic system can, and can only, exist permanently in a certain series of states corresponding to a discontinuous series of values for its energy, and consequently any change of the energy of the system, including emission and absorption of electromagnetic radiation, must take place by a complete transition between two such states. These states will be denoted as the "stationary states" of the system.

Postulate B. That the radiation absorbed or emitted during a transition between two stationary states is *monochromatic* and possesses a frequency ν , given by the relation

$$h\nu = E_i - E_f \quad (1)$$

where E_i and E_f designate the energy values corresponding to initial and final states respectively, and h is Planck's constant.

In order to determine the individual energy values of the different stationary states Bohr assumed that the angular momentum of the electron in its orbit is an integral multiple of $h/2\pi$. It was shown later by Wilson and Sommerfeld that this assumption could be replaced by a more generalized one which is based on classical mechanics and states that for each degree of freedom of an atomic system

$$\oint pdq = nh \quad (2)$$

where q is a generalized Lagrangian coordinate, and p is the corresponding momentum, and the integral is taken over a

complete period of the motion. The integer n is known as the quantum number for the particular degree of freedom concerned.

Representing the hydrogen atom as constituted of an electron rotating in a Keplerian orbit around a nucleus of unit positive charge, Bohr derived the following relation for the energy of the atom in any state of quantum number n .

$$E_n = -Rch/n^2 \quad (3)$$

where c = velocity of light and R = a universal constant.

Hence, in accordance with equation (1), the frequency of any line in the spectrum of atomic hydrogen should be represented by a relation of the form

$$\nu = Rc \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \quad (4)$$

where m and n are the quantum numbers of initial and final states respectively.

Now this is exactly the type of equation which Balmer had found a long time ago to apply to a series of lines in the visible portion of the hydrogen spectrum, and slightly modified forms of this equation (with the same constant R) had been used by Ritz and Rydberg to represent certain series observed in the spectra of the alkalis, alkaline earths, and some of the other elements. Thus Bohr gave a theoretical interpretation of a conclusion which had been empirically derived by spectroscopists, that the frequency of a line is to be represented as a difference between two terms, one of which (that corresponding to n in the above equation) remains constant for all the members of the same series, while the other (corresponding to m) varies by unity for successive members of the series.

However, Bohr went one step further and actually found that from his model of the hydrogen atom the value of the Rydberg constant, R , could be calculated from fundamental constants by the relation

$$R = \frac{2\pi^2e^4m_0}{ch^3} = 109,737 \text{ cm}^{-1}$$

where e = charge, and m_0 = mass of electron.

Bohr also pointed out the manner in which the value of this constant must be modified slightly for different values of the atomic mass.

For a "hydrogen-like" atom consisting of a positive nucleus of charge Ze and an electron rotating about this nucleus, the energy corresponding to the orbit of quantum number n is given by

$$E_n = - \frac{RchZ^2}{n^2} \quad (5)$$

Physically, the expression Z^2Rch/n^2 is to be interpreted as the amount of energy required to remove the electron from the particular orbit to infinity. Since this energy may be determined experimentally, in the case of the normal atom, by bombarding the latter with electrons possessing a definite velocity, it is usually expressed in volts, (energy = Ve) and is known as the *ionizing potential* (V_i). Similarly the energy corresponding to the removal of the electron from its normal orbit to that of the first excited state is known as the *resonance potential* (V_r).

In the case of the hydrogen atom

$$V_{i,e} = Rch/1^2$$

since $n = 1$, $m = \infty$.

Substituting the known values of R , c , h and e , it is found that $V_i = 13.54$ volts.

Similarly, $V_{r,e} = Rch \left[\frac{1}{1^2} - \frac{1}{2^2} \right]$, and $V_r = 10.16$ volts.

In the case of other elements, these critical potentials (as they are known) have been determined either by direct measurement (2) or from the values of the lowest energy levels. The discussion of the data thus obtained is, however, best deferred for a subsequent section.

SPECTRAL SERIES. QUANTUM NUMBER, h

While in the case of the hydrogen atom the different spectral terms may be designated (to a very high degree of approximation) by integral values of a single quantum number, this is no longer

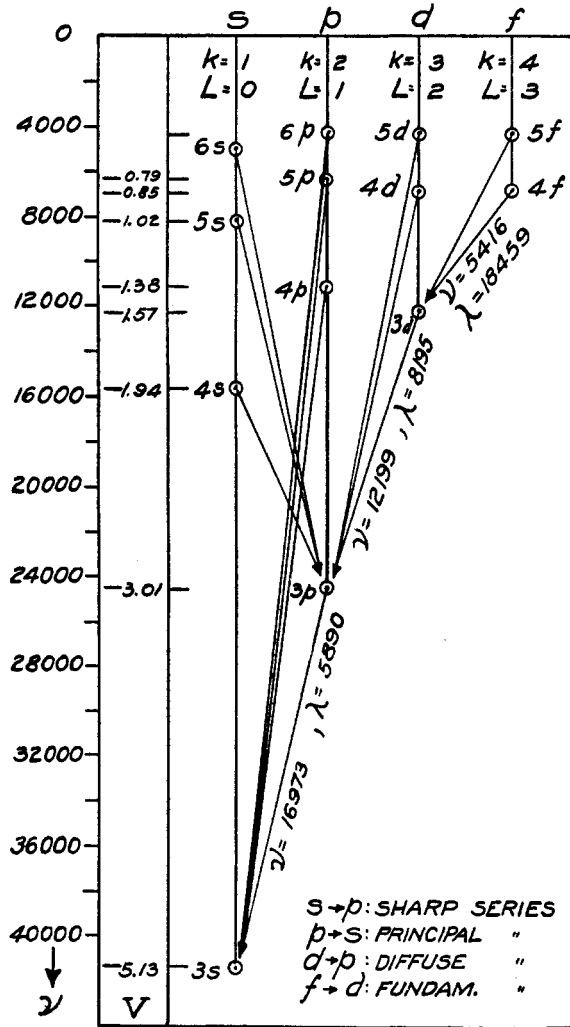


FIG. 1. ENERGY LEVELS FOR SODIUM

possible in the case of the other elements. In fact, in order to account for the spectral structures observed for the latter and also for the behavior of their lines in magnetic fields, it has been found necessary to introduce at least three other quantum numbers by which each term is defined. Before, however, discussing this, it is essential to describe some of the main features of spectroscopic nomenclature.

As a typical spectrum we may consider that of sodium. Here it is found that the observed lines group themselves into four different series and must, therefore, be regarded as due to transitions between four different sets of terms or corresponding energy levels in the atomic system. Figure 1 gives a diagrammatic representation of these levels. These four series of terms are designated by the letters s , p , d and f respectively. Now it will be observed that transitions occur only between neighboring series of levels, but *never* from one level in any one series to another level in the same series. This is due to the existence of a "selection principle" which forbids transitions between orbits for which the value of a second quantum number k is the same, and permits only those transitions to occur for which the value of k changes by $+1$ or -1 . Physically k has been regarded as a measure of the angular momentum of the electron in its orbit in terms of multiples of $h/2\pi$ and is known as the azimuthal quantum number. Thus the level $3s$ has the total quantum number 3 and electronic angular momentum of value $h/2\pi$ ($k = 1$), while the level $4d$ has the total quantum number 4 and electronic angular momentum of value $3h/2\pi$ ($k = 3$).

It will be observed that the maximum value of k is given by the relation $k \leq n$.

The figures in the first column on the left hand side of figure 1 give the value of the spectral terms in wave-numbers ($\nu = 1/\lambda$ in cm^{-1}). Hence the wave-number of any line in the spectrum is given by the difference between the wave-numbers of the initial and final terms (or "levels"). Values of ν are shown for three of the lines, with the corresponding values of λ in Ångströms.¹

¹ $1 \text{ \AA} = 10^{-8} \text{ cm}$. Thus $\lambda = 10^8/\nu$. The corresponding frequency of radiation is given by the relation, $\nu^* = 3 \times 10^{10}\nu$. The symbol ν is used in the following discussion to designate *wave-number*.

The second column in the diagram gives the corresponding value of the energy levels in volts (V), where

$$V = \frac{\nu}{8100}$$

Thus the ionizing potential for Na, $V_i = 5.13$ volts, and the first resonance potential, $V_r = 5.13 - 3.01 = 2.12$ volts.

RYDBERG-RITZ FORMULAS FOR SPECTRAL SERIES (3) (4) (5) (6)

For the spectral series of the alkali metals (and also of the alkaline earth metals) it was observed by Rydberg, Ritz and others that the terms in the series could be represented by expressions which will be recognized as modifications of equation (4). Thus the expression derived by Rydberg is of the form

$$\nu_m = \frac{R}{(m + \alpha)^2} \quad (6)$$

where R denotes the Rydberg constant,² and α is a constant (or approximately so) for all members of the same series, while m assumes successive integral values for the different members of the same series. The values of m assigned in accordance with this relation by spectroscopists are for most series (as will be shown subsequently) less than the values of the total quantum numbers which it has been found necessary to assign to these terms in accordance with Bohr's theory of electronic configurations in atoms. Since the values of n and k are the significant ones from the standpoint of Bohr's theory, it has also become customary to replace the above equation by the expression

$$\nu_n = \frac{R}{(n - \alpha_K)^2} \quad (7a)$$

$$= R/(n_{\text{eff}})^2 \quad (7b)$$

² As mentioned already the value of this constant varies slightly for different atoms. The exact relation is given by $R = R_\infty (1 - m_0/M)$ where m_0/M = ratio of mass of electron to that of the atom, and $R_\infty = 109,737.1$. For He, $R = 109,722.1$ and for H, $R = 109,677.7$.

where n is the total quantum number, and α_K is a constant for each term which depends upon the value of k for the series. The expression $n - \alpha_K$ has also been designated as the "effective" quantum number, n_{eff} , while α_K is known as the "quantum defect."

If now we calculate the values of n_{eff} , for the lowest terms in the four spectral series of the alkali metals and compare these

TABLE 1

ATOM		s	p	d	f
H	n	1.00	2.00	3.00	4.00
Li	n	2.00	2.00	3.00	4.00
	n_{eff}	1.59	1.96	3.00	4.00
	α_K	0.41	0.04	0.00	0.00
Na	n	3.00	3.00	3.00	4.00
	n_{eff}	1.63	2.12	2.99	4.00
	α_K	1.37	0.88	0.01	0.00
K	n	4.00	4.00	3.00	4.00
	n_{eff}	1.77	2.23	2.85	3.99
	α_K	2.23	1.77	0.15	0.01
Rb	n	5.00	5.00	3.00	4.00
	n_{eff}	1.80	2.28	2.77	3.99
	α_K	3.20	2.72	0.23	0.01
Cs	n	6.00	6.00	3.00	4.00
	n_{eff}	1.87	2.33	2.55	3.98
	α_K	4.13	3.67	0.45	0.02

values with those of n as derived from considerations of electronic distribution (see subsequent section) we obtain the results shown in table 1 (4) (7). In accordance with (7b) the values of n_{eff} , have been obtained from the wave-numbers of the terms by the relation

$$n_{\text{eff.}} = \sqrt{109,722/\nu}$$

It will be observed that the differences between the two values of n are less for p than for s and become still smaller for d and f

terms. This observation led Bohr to the interpretation that s orbits penetrate much closer to the nucleus than p orbits, and the latter penetrate nearer than d or f orbits. In fact, in the case of the latter it was considered that the orbit of the valence electron is so far outside the orbits of the other electrons in the atom that the whole system may be regarded as "hydrogen-like." This is evident from the fact that n_{eff} , for lowest d and f terms in all the alkali spectra have practically the same values as those observed in the case of H .

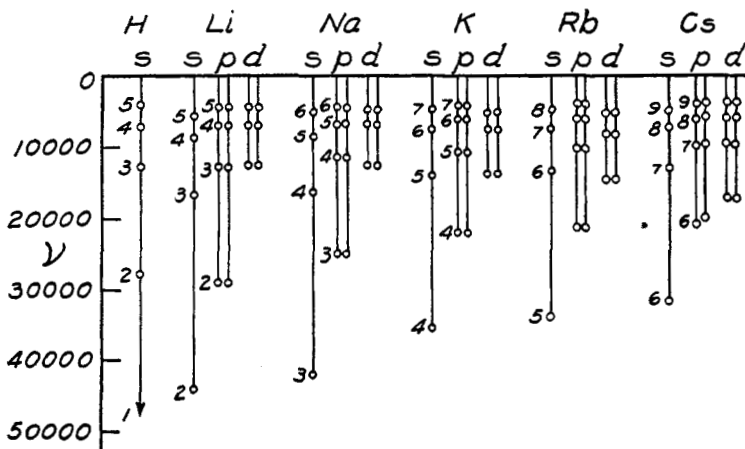


FIG. 2. ENERGY LEVELS FOR ALKALIES COMPARED WITH THOSE FOR HYDROGEN

Figure 2, taken from Hund's book (4) shows graphically the various terms in the spectra of the alkali metals compared with those for H . The numbers attached to each term give the corresponding value of n , while the value of n_{eff} may be obtained from that value of n for H which has the same value of ν .³

MULTIPLY LEVELS

A closer examination of the spectrum of sodium and the other alkali metals shows, however, that the p , d , f levels are really of a

³ The diagram shows the doublet p levels which are mentioned in the next section.

doublet nature. The level indicated as $3 p$ in the diagram (figure 1) consists actually of two levels, designated as $3 p_1$ and $3 p_2$ respectively, with the respective wave-numbers 24492.8 and 24475.65. The transitions between these levels and the normal ($3 S$) level give rise to the two lines of the well-known sodium doublet $\lambda 5889.96$ and $\lambda 5895.93$.

In the case of calcium and other metals of group II, it has been found that there are two separate systems of s , p , d , f levels. In one system, the p , d , f levels are triplets, while in the other they are singlets.

As we proceed in the periodic table, from group I to group VIII, it has been observed that the spectral terms exhibit periodic variations such as shown in table 2 for the elements from K ($N = 19$) to Ni ($N = 28$).

It will be observed that firstly, the multiplicity alternates between even and odd, and, secondly, the complexity increases to a maximum in the case of Mn and then decreases. It is the presence of these multiplet levels that gives rise to the extremely complex nature of a large number of spectra, such as those of Ti, Cr, Mn, Fe and other elements. For instance, H. N. Russell has analyzed the spectrum of titanium and finds that it consists of seventeen series divided between singlet, triplet and quintet systems.

Formally the existence of these multiplets may be correlated with the assignment of a *third*, or so-called *inner quantum* number j , which differs for each component of the multiplet term, and which has been interpreted physically as designating the number of units of angular momentum (in terms of $h/2\pi$) of the atom as a whole about an axis of symmetry. According to the older theory it was furthermore assumed that this angular momentum is to be regarded as a resultant of the angular momentum of the orbit and that of the rest of the atom (or kernel).

This led to difficulties in the interpretation not only of the effect of magnetic fields on spectral lines, but also of multiplet terms with more than two components.

The hypothesis of the spinning electron introduced by G. E. Uhlenbeck and S. Goudsmit (11) has, however, served to remove

TABLE 2

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Doublets	Singlets Triplets	Doublets Quartets	Singlets Triplets Quintets	Doublets Quartets Sextets	Triplets Quintets Septets	Quartets Sextets Octets	Triplets Quintets Septets	Doublets Quartets Sextets	Singlets Triplets Quintets

TABLE 3

	SINGLET	DOUBLETS	TRIPLETS	QUARTETS
s	0	1/2	1	3/2
p	1	1/2, 3/2	0, 1, 2	1/2, 3/2, 5/2
d	2	3/2, 5/2	1, 2, 3	1/2, 3/2, 5/2, 7/2
f	3	5/2, 7/2	2, 3, 4	3/2, 5/2, 7/2, 9/2
g	4	7/2, 9/2	4, 5, 6	5/2, 7/2, 9/2, 11/2
	QUINTETS	SEXTETS	SEPTETS	OCTETS
s	2		3	
p	1, 2, 3	5/2	2, 3, 4	7/2
d	0, 1, 2, 3, 4	3/2, 5/2, 7/2	1, 2, 3, 4, 5	5/2, 7/2, 9/2
f	1, 2, 3, 4, 5	1/2, 3/2, 5/2, 7/2, 9/2, 11/2	0, 1, 2, 3, 4, 5, 6	3/2, 5/2, 7/2, 9/2, 11/2
g	2, 3, 4, 5, 6	3/2, 5/2, 7/2, 9/2, 11/2, 13/2	1, 2, 3, 4, 5, 6, 7	1/2, 3/2, 5/2, 7/2, 9/2, 11/2, 13/2, 15/2

most of these difficulties. According to this theory, each electron in the atom possesses an angular momentum of magnitude $1/2$ ($h/2\pi$). It is, therefore, assigned a quantum number, $s = 1/2$, giving the number of units of angular momentum (in terms of $h/2\pi$).

In the case of the alkali atoms where only one electron is present in the "valence shell," the vector representing the angular momentum of the atom as a whole, j , is the resultant of the vector, s , for the electron, and a vector $l = k - 1$ for the electron in its orbit. Since $s = 1/2$, j can have only the two values $l + 1/2$, and $l - 1/2$. This conclusion is in accordance with the observations on the spectroscopic nature of the normal term for the atoms of the rare gases.

The fact that s has to be assumed as equal to $1/2$ and not to an integral value is necessitated by the existence of doublets in the alkali spectra. For the behavior of the rare gas atoms leads to the conclusion that j for these atoms must be zero. Now if we assume that an electron has $s = 1$, then the resultant values of j for the alkali atom would be $k + 1$, k , and $k - 1$ (i.e., 2, 1, and 0 for the s -state). But the alkali atoms have *no* triplet levels. In fact triplet levels occur in atoms which have an *even* number of valence electrons.

Furthermore, in the s -state of the alkali atoms we have only *one* level. Therefore, the angular momentum of the electron in the orbit cannot be 1, since this would lead to the values $1/2$ and $3/2$ for the resultant value of j (assuming $s = 1/2$). Thus the observed multiplicities are best correlated by assuming that $s = 1/2$, and $l = 0$ for the s -state, $l = 1$ for the p -state, etc., where l designates the number of units of angular momentum for the *electronic orbit*, and takes the place of the quantum number k introduced previously.

On this basis, the j -values assigned to the different component levels in the spectra of the alkali metals are those given in table 3 for a doublet system.

As in the case of the quantum number, k , (or l in the new system) a *selection principle* also governs transitions between different multiplet levels. Not only must we have Δk (or Δl)

= ±1, but also Δ*j* = ±1 or 0, with the added condition that no transitions can occur from *j* = 0 to *j* = 0.

Denoting the components by the corresponding *j*- values as subscripts, we find the following transitions:

*p*_{1/2} → *s*_{1/2}; *p*_{3/2} → *s*_{1/2}..... two lines
*d*_{5/2} → *p*_{3/2}; *d*_{3/2} → *p*_{3/2}; *d*_{3/2} → *p*_{1/2}..... three lines
*f*_{7/2} → *d*_{5/2}; *f*_{5/2} → *d*_{5/2}; *f*_{5/2} → *d*_{3/2}..... three lines

The *D*- lines in sodium correspond to the two *p*→*s* transitions. Since the energy levels corresponding to *d*_{5/2} and *d*_{3/2} are much closer than those corresponding to *p*_{3/2} and *p*_{1/2}, the two lines ending on the *p*_{3/2} level are usually merged into one, so that the resulting spectral lines are ordinarily seen as two lines very close together.

For singlet systems and higher degrees of multiplicity than two the values of *j* for the various component terms are those given in table 3. While the reasons for assigning these values of *j* to the different terms will be discussed in a subsequent section, it should be noted in the present connection that the following empirical relations may be deduced.

1. The *s*- level is always single. Denoting the *degree of multiplicity* by *r* (*r* = 1 for singlets, *r* = 2 for doublets, etc.) and the value of *j* for this level by *j*_s.

$$j_s = \frac{r - 1}{2}$$

2. For other levels, the possible values of *j* are given by the series

$$j_s + l, j_s + l - 1, \dots, |j_s - l|$$

where $|j_s - l|$ indicates the absolute difference between the two values. In other words, the values of *j* are the resultants of *l* and *j*_s treated as vectors.

SPECTRAL TERMS AND ELECTRONIC LEVELS

It is very important in this connection to emphasize the difference between spectral terms and electronic levels. In the case

of the alkali metals where we are dealing with transitions of a *single electron* between different orbits, the quantum numbers n, k, j for the orbits are the same as those of the spectral terms. But as will be shown in a subsequent section, when there are two or more electrons present in the valence shell (as in case of *Be, B, C*, etc.) the spectral term is the resultant of interactions between the different electrons, each of which is in a different orbit or level. Thus the interactions of two electrons similar to the valence electron in the alkali metals give rise to singlet and triplet terms in the spectra of the alkaline earth metals. In a similar manner the higher degrees of multiplets arise from the interaction of several electrons.

The spectral notation adopted in accordance with these ideas is that first suggested by Russell and Saunders (8) which is as follows:

The *series* is denoted by the capital letters *S, P, D, F, H, I* ; the *system* by an index at the upper left hand, giving the *multiplicity*, and the *component* of a multiple term by a subscript on the right, giving the inner quantum number. In the case of terms due to a single electron or where the several electrons all have the same total quantum number, the latter is denoted by an integer prefixed to the main symbol.

For example, in the Na spectrum the 3 p_2 component of the doublet level is designated on the new basis as $3^2P_{3/2}$. However, in order to avoid writing fractional subscripts it is more usual to write the symbol as 3^2P_2 , thus writing $j + \frac{1}{2}$ instead of j in the case of doublets, quartets, sextets, octets, etc. Similarly, in the case of Hg, the lowest level is a singlet ($^1S_0, \nu = 84178.5$). The next higher level is a triplet, and the three component levels are designated as $^3P_2, \nu = 40138.3$, $^3P_1, \nu = 44768.9$, and $^3P_0, \nu = 46536.2$. The well known line in the ultra-violet, $\lambda, 2536.52$, originates in a transition from the 3P_1 level to the 1S_0 and is therefore designated as $^1S_0 - ^3P_1$. It will be observed that the integer corresponding to total quantum number has been omitted in the symbols for these levels. As pointed out by Russell and Saunders, the particular value of n used depends in a number of cases (as will be shown subsequently) on the particular arrangement of

electronic orbits assumed for the model of the atom, and may therefore be modified as a result of further investigation. On the other hand, the behavior of the line λ 2536.5 in magnetic fields (Zeeman effect) and other observations leave no doubt that this line represents a transition from the triplet to a singlet level as indicated above. Furthermore, as is evident from an inspection of the energy diagram for Na, the total quantum number, n , has no bearing on the possibility or impossibility of a transition between two given levels.

NORMAL AND ANOMALOUS ZEEMAN EFFECTS (4) (5) (9) (10)

In 1896 Zeeman discovered that the lines of series spectra are influenced by magnetic means. In the simplest case there appear instead of one line, when viewed longitudinally, that is, when the ray is in the direction of the magnetic lines of force, two lines (Zeeman doublet, longitudinal effect), but when viewed transversely, that is, when the ray is perpendicular to the magnetic lines of force, instead of one line, three lines are observed (Zeeman triplet, transverse effect). Of the latter three lines one occupies the position of the original unresolved line, and the other two are displaced by equal amounts to greater or smaller wave-lengths, and occupy the same position in the spectrum as the two lines of the doublet in the longitudinal effect. The displacement amounts to

$$\Delta \nu_n = \frac{e}{2m_0c} \cdot \frac{H}{2\pi} \quad (8)$$

$$= 1.41 \times 10^6 H$$

where $\Delta \nu_n$ = change in frequency

e/m_0 = ratio of charge to mass of electron in e. s. u.

H = intensity of field in gauss (37).

The resolution into three components with separation given by the above equation is known as the *normal* Zeeman effect. The magnetic field in this case leads to a change in the energy level by an amount

$$\pm h \cdot \Delta \nu_n = \pm \frac{eH}{2m_0c} \cdot \frac{h}{2\pi} = \pm o \quad (9)$$

where ω is known as the "Larmor precession," since the change in frequency is interpreted physically as a frequency of precession of the orbit about the direction of the magnetic lines of force.

Most spectral lines, however, exhibit a much more complex resolution in magnetic field. Instead of three components in a transverse magnetic field there are observed a larger number, and the separations from the original position may in all cases be represented by rational multiples (not necessarily integral) of the normal value, $\Delta\nu_n$. This is known as the *anomalous Zeeman effect*.

In accordance with Bohr's point of view we must assume that the magnetic field affects both the initial and final levels involved in the origin of any given line, but the effect on each level depends upon the values of the two quantum numbers, j and k of the particular orbit (or level). In presence of a magnetic field, an atomic system having the resultant angular momentum $j \cdot h/2\pi$ can orient itself with respect to the magnetic field only in certain definite positions (space quantization in a magnetic field), and to each of these positions there corresponds a definite magnetic moment of the atomic system.

MAGNETIC QUANTUM NUMBER, m

The development of this point of view leads to the conclusion that for a level of inner quantum number, j , in presence of a magnetic field there exists a magnetic moment, m , and that the resultant change in the value of the energy level is given by $mg \cdot \omega$, where $m = j, j-1, \dots, -(j-1), -j$.

The constant, g is known as the "splitting-up" factor, since it gives the *distance* in multiples of $\Delta\nu_n$ between the different components into which the energy level is resolved in the magnetic field, while the number of components is obviously equal to the total number of different values which m may assume. The negative values are due to the fact that the magnetic moment of the orbit may orient itself either with the field or in the opposite direction.

The value of g is determined by the values of k and j of the level. From these considerations there readily follow the various

generalizations regarding the Zeeman effect which were observed previously to the development of the theory as sketched above. The most important of these is that the Zeeman effect is similar for lines which correspond to transitions between levels of the same initial quantum numbers, k_i and j_i , and the same final quantum numbers, k_f and j_f . Thus lines belonging to the same spectral series show similar values of m and g . Consequently it is possible *from an investigation of the behavior of spectral lines in magnetic fields, to determine the values of k and j (i.e. the series type and multiplet component) for the corresponding energy levels.* This conclusion has been of greatest importance in revealing the nature of the terms in the case of the more complex spectra, such as these of Mn, Cr and Ru.

TABLE 4

SPECTRAL LEVEL	k	l	j	CORRESPONDING VALUES OF m	TOTAL NUMBER OF LEVELS IN MAGNETIC FIELD
S	1	0	$\frac{1}{2}$	$\pm \frac{1}{2}$	2
P	2	1	$\frac{1}{2}; \frac{3}{2}$	$\pm \frac{1}{2}; \pm \frac{3}{2}; \pm \frac{3}{2}$	6
D	3	2	$\frac{3}{2}; \frac{5}{2}$	$\pm \frac{1}{2}; \pm \frac{3}{2}; \pm \frac{5}{2}$	10
F	4	3	$\frac{5}{2}; \frac{7}{2}; \frac{9}{2}; \frac{11}{2}$	$\pm \frac{1}{2}; \pm \frac{3}{2}; \pm \frac{5}{2}; \pm \frac{7}{2}; \pm \frac{9}{2}; \pm \frac{11}{2}$	14

The existence of the anomalous Zeeman effect has been most satisfactorily interpreted physically by the hypothesis of the spinning electron, which has been mentioned in a previous section, together with an additional hypothesis, also introduced by Uhlenbeck and Goudsmit, that the magnetic moment corresponding to the spin vector, $s = 1/2$, is *not* $1/2 \left(\frac{e}{2m_0c} \right) \left(\frac{h}{2\pi} \right)$ as would follow from Larmor's theory, but *double* this quantity, that is equal to $2s$ in units $\left(\frac{e}{2m_0c} \right) \left(\frac{h}{2\pi} \right)$. It is the presence of this factor 2 that leads to the "anomalous" effect.

Since the magnetic moment of the electron may be in the same

direction as, or opposed to, the direction of the external magnetic field, it is obvious that the term ${}^2S_{\frac{1}{2}}$ will yield two terms in presence of a magnetic field. In the case of the doublet P terms, one term, 2P_1 , has $j = 1/2$, while the other, 2P_2 has $j = 3/2$. Hence in presence of a magnetic field, the values of m due to $j = 1/2$ are $m = 1/2, -1/2$, while those due to $j = 3/2$ are $m = 3/2, 1/2, -1/2, -3/2$. Thus the two P -levels give rise to six levels in a magnetic field. Similar considerations lead to the values given in table 4 for the total number of terms or levels which are due to different values of l in presence of a magnetic field.

Thus the total number of possible states of an atomic system for given value of l , in a weak magnetic field, is equal to $2(2l+1)$.

PASCHEN-BACK EFFECT (4) (9) (10)

In weak magnetic fields the number of orientations is determined by first obtaining the resultant momentum, j , (in units $h/2\pi$) of the momenta l and s and then assigning to the vector j all the possible integral values ranging from j to $-j$.

This procedure is logical only when the magnetic field is so weak that it does not affect the constraining forces between the valence or "optical" electron (that is, the electron which is passing from one orbit to another) and the rest of the atom ("Rumpf"). But in stronger magnetic fields these constraining forces are loosened, and finally, in very strong fields, the vectors l and s will no longer influence each other. The stationary states of the atomic system will then correspond to states of the model in which l and s are oriented separately, so that the component m_s of s is either parallel or antiparallel with the field, while the component m_l of l will orient itself so that $m_l = l, l-1, \dots, -(l-1), -l$. Taking into account that the magnetic moment due to s , the angular momentum of spin of the electron, is equal to $2s$, while that due to l is m_l (both moments being measured in units $\left(\frac{e}{2m_0c} \cdot \frac{h}{2\pi}\right)$, the magnetic quantum number in very strong is given by $m' = m_l + 2m_s$.

This is the explanation of the phenomenon observed by Paschen and Back (9) that in strong magnetic fields both the number and spacing of the components of a given term are different from those obtained in weak magnetic fields.

STONER'S AND MAIN SMITH'S SCHEME OF ELECTRON DISTRIBUTION

As shown in table 4 the total number of orbits in a magnetic field for an electron of serial quantum number l is given by $2(2l+1)$. Now corresponding to any given value of n , values of l may range from $n-1$ to 0. Hence the number of orbits (or levels) for any

TABLE 5

n	VALUE OF l	SPECTRAL DESIGNATION	NUMBER OF LEVELS IN MAGNETIC FIELD
1	0	1s	2
2	0	2s	2
	1	2p	6
3	0	3s	2
	1	3p	6
	2	3d	10
4	0	4s	2
	1	4p	6
	2	4d	10
	3	4f	14

given value of n will also be limited in accordance with the following scheme (table 5) which may be extended for larger values of n .

Thus the maximum number of levels for a 1s, 2s, 3s or ns electron are 2, while for an nf electron (where n denotes the total quantum number and f the particular series type) the maximum number of levels is 14.

Now according to E. C. Stoner (12) and Main-Smith (13) the numbers given in the last column of table 5 must also represent the *maximum number of electrons of that spectral type which an atomic system can possess*. As will be shown in a subsequent section a real basis for this hypothesis is furnished by Pauli's

principle. However, it is possible, even without discussing this principle, to follow up the logical consequences of the hypothesis in its application to the problem of electron distribution in atoms.

The electron in the atom of H is in orbit of type $1s$. To form the atom of He we add a second electron (and, of course, increase the charge on the nucleus by one unit of positive electricity). Since two electrons of type $1s$ may exist in an atom, the second electron is also of this type. Table 6 shows the type of orbit formed by each electron as it is added in succession to build up the atoms of higher atomic number.

With the addition of a third electron we enter upon the second period (Li-Ne), and the first 2 electrons belong to the $2s$ group. Since this represents the maximum number for a $2s$ group the third electron will be of type $2p$, and this last group will be filled with the eighth electron (Ne = 10).

The eleventh electron, corresponding to Na ($N = 11$) and the twelfth (Mg, $N = 12$) form the $3s$ group, while A ($N = 18$) completes the $3p$ group, and thus resembles Ne in the configuration of the external group of eight electrons.

When we come to K ($N = 19$) the analogy with Na and Li leads to the conclusion that the added electron must enter a $4s$ group. Much more important, however, in the case of this and the other atoms is a criterion which points definitely to the same conclusion and which may be stated as follows: During the process of formation of the atoms by addition of successive electrons the *last bound electron always assumes that orbit for which the energy of the atomic system is a minimum*. Thus in the case of K the spectrum shows that an electron in a $3d$ orbit has a higher energy value than in a $4s$. The same holds true for Ca, but in the case of Sc ($N = 21$), the energy in a $3d$ is lower than that in a $4p$ level (since the $4s$ level is already filled). Consequently we begin, with this element, to fill up the $3d$ group, which can contain 10 electrons as a maximum. As shown in table 6 this group is completed in Cu, and the $4p$ group is completed in Kr.

Proceeding to still larger values of N we find that there is a constant tendency for electrons to shift between levels such as $4d$ and $5s$, $4f$, $5d$ and $6s$, etc. To understand the reasons for

LINE SPECTRA AND PERIODIC ARRANGEMENT OF ELEMENTS 129

TABLE 6

ELEMENT	N	K			L			M			N		NORMAL TERM	V _i	
		1s	2s	2p	3s	3p	3d	4s	4p						
H	1	1										² S ₁	13.54		
He	2	2										¹ S ₀	24.48		
Li	3	2	1									² S ₁	5.37		
Be	4	2	2									¹ S ₀	9.48		
B	5	2	2	1								² P ₁	8.4		
C	6	2	2	2								³ P ₀	11.24		
N	7	2	2	3								⁴ S ₂	12.2		
O	8	2	2	4								³ P ₂	13.56		
F	9	2	2	5								² P ₂	18.6		
Ne	10	2	2	6								¹ S ₀	21.5		
Na	11	Neon "Shell"			1							² S ₁	5.12		
Mg	12				2									¹ S ₀	7.61
Al	13				2	1								² P ₁	5.96
Si	14				2	2								³ P ₀	10.19
P	15				2	3								⁴ S ₂	13.3
S	16				2	4								³ P ₂	10.20
Cl	17				2	5								² P ₂	13.0
A	18				2	6								¹ S ₀	15.48
K	19	Argon "Shell"							1			² S ₁	4.32		
Ca	20										2			¹ S ₀	6.09
Sc	21									1	2			² D ₂	6.57
Ti	22									2	2			³ F ₂	6.80
V	23									3	2			⁴ F ₂	6.76
Cr	24									5	1			⁷ S ₃	6.74
Mn	25									5	2			⁶ S ₃	7.40
Fe	26									6	2			⁵ D ₄	7.83
CO	27									7	2			⁴ F ₅	7.81
Ni	28									8	2			³ F ₄	7.64
Cu	29	Argon "Shell"						10	1			² S ₁	7.69		
Zn	30									10	2			¹ S ₀	9.35
Ga	31									10	2	1		² P ₁	5.97
Ge	32									10	2	2		³ P ₀	
As	33									10	2	3		⁴ S ₂	11.5
Se	34									10	2	4		³ P ₂	12.7
Br	35									10	2	5		² P ₂	
Kr	36									10	2	6		¹ S ₁	13.3

TABLE 6—Continued

ELEMENT	N	NUMBER IN INNER SHELLS	N		O			P	NORMAL TERM	V _i
			4d	4f	5s	5p	5d	6s		
Rb	37	Krypton Shell			1				² S ₁	4.16
Sr	38				2				¹ S ₀	5.67
Y	39		1		2				² D ₂	
Zr	40		2		2				³ F ₂	
Cb	41		4		1				⁶ D ₁	
Mo	42		5		1				⁷ S ₃	7.35
Ma	43		6		1				⁶ D ₅	
Ru	44		7		1				⁵ F ₅	7.7
Rh	45		8		1				⁴ F ₃	7.7
Pd	46		10						¹ S ₀	8.5
Ag	47	Palladium "Shell"			1				² S ₁	7.54
Cd	48				2				¹ S ₀	8.95
In	49				2	1			² P ₁	5.76
Sn	50				2	2			³ P ₀	7.37
Sb	51				2	3			⁴ S ₂	8.5
Te	52				2	4			³ P ₂	
I	53				2	5			² P ₂	
Xe	54				2	6			¹ S ₀	11.5
Cs	55		(1s-4d = 46)						1	² S ₁
Ba	56							2	¹ S ₀	5.19
La	57				(5s-5p = 8)		1	2	² D ₂	
Ce	58			1			1	2	³ H ₄	
Pr	59			2			1	2	⁴ K ₆	
Nd	60			3			1	2	⁵ L ₆	
Il	61			4			1	2	⁶ L ₆	
Sa	62			5			1	2	⁷ K ₄	
Eu	63			6			1	2	⁸ H ₂	
Gd	64			7			1	2	⁹ D ₂	
Tb	65			8			1	2	⁸ H ₉	
Ds	66			9			1	2	⁷ K ₁₀	
Ho	67			10			1	2	⁶ L ₁₀	
Er	68			11			1	2	⁵ L ₁₀	
Tu	69		12			1	2	⁴ K ₉		
Yb	70		13			1	2	³ H ₆		
Lu	71		14			1	2	² D ₂		

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TABLE 6—Concluded

ELEMENT	N	NUMBER IN INNER SHELLS	O		P			Q	NORMAL TERM	V _i	
			5d	5f	6s	6p	6d	7s			
Hf	72	(1s-5p = 68)	2		2				³ F ₂		
Ta	73		3		2				⁴ F ₂		
W	74		4		2				⁵ D ₀		
Re	75		5		2				⁶ S ₃		
Os	76		6		1				⁶ D ₅		
			6		2				⁵ D ₄		
Ir	77		7		1				⁵ F ₅		
			7		2				⁴ F ₅		
Pt	78		8		1				⁴ F ₅		
			8		2				³ F ₄		
		9		1				³ D ₃			
		10						¹ S ₀			
Au	79	(1s-5d = 78)			1				² S ₁	9.20	
Hg	80				2				¹ S ₀	10.39	
Tl	81				2	1			² P ₁	6.08	
Pb	82				2	2			³ P ₀	7.39	
Bi	83				2	3			⁴ S ₂	8.0	
Po	84				2	4			³ P ₂		
85					2	5			² P ₂		
Rn	86				2	6			¹ S ₀		
Ra	87		(1s-5d = 78)					1		² S ₁	
88						(6s-6p = 8)		2	¹ S ₀		
Ac	89						1	2	² D ₂		
Th	90			1			1	2	³ H ₄		
							2	2	³ F ₂		
Ux	91			2			1	2	⁴ K ₆		
							3	2	⁴ F ₂		
Ur	92			3			1	2	⁵ L ₆		
							4	2	⁵ D ₀		

adopting the particular distribution assigned to each element it has been necessary to investigate not only the ordinary or optical spectra, but also the x-ray spectra. We must therefore digress in this connection to a discussion of the important deductions which have been derived from investigations of spectra of this class.

X-RAY SPECTRA. *K, L, M, N, O* LEVELS (5) (14)

Since x-ray spectra may be considered as indicating the process by which an atom undergoes reorganization after a disturbance in its interior, it is evident that a study of the corresponding energy levels must lead to information about the distribution of electrons in the interior of atoms. A detailed study of x-ray spectra from the point of view of the Bohr theory has thus led to the identification of a number of different sets of levels which are listed in table 7, together with the corresponding values of n , l , and j . The last line gives the analogous levels in the optical spectra of the alkali metals.

TABLE 7
Classification of x-ray levels

LEVEL.....	K	L			M				
		L _I	L _{II}	L _{III}	M _I	M _{II}	M _{III}	M _{IV}	M _V
n.....	1	2	2	2	3	3	3	3	3
l.....	0	0	1	1	0	1	1	2	2
j.....	1	1/2	1/2	3/2	1/2	1/2	3/2	3/2	5/2
Optical analog.....	1S	2S	2P ₁	2P ₂	3S	3P ₁	3P ₂	3D ₂	3D ₃

In the elements of higher atomic number, there are also present seven *N* levels ($n = 4$, $l = 0, 1, 2, 3$) and five *O* levels ($n = 5$, $l = 0, 1, 2$).

Figure 3 taken from the paper by Bohr and Coster (14) shows the values of $\sqrt{\nu/R}$ ($\nu =$ wave-number; $R =$ Rydberg constant) for the different levels plotted against the corresponding values of N . It will be observed that for any given type of level the value of $\sqrt{\nu/R}$ varies approximately linearly with N (Moseley's law), so that $\sqrt{\frac{\nu}{R}} = \frac{N - \sigma}{n}$, where σ is a "screening" constant, and n the total quantum number corresponding to the level. Applying this relation to the curves shown in Fig. 3, it is found that as a first approximation $n = 1$ for the *K* levels, $n = 2$ for the *L* levels and $n = 3$ for the *M* levels. By analogy with the optical levels in hydrogen it has therefore been concluded

that the values of n for K , L and M levels must be 1, 2 and 3 respectively. In fact, it has been shown by Millikan that the

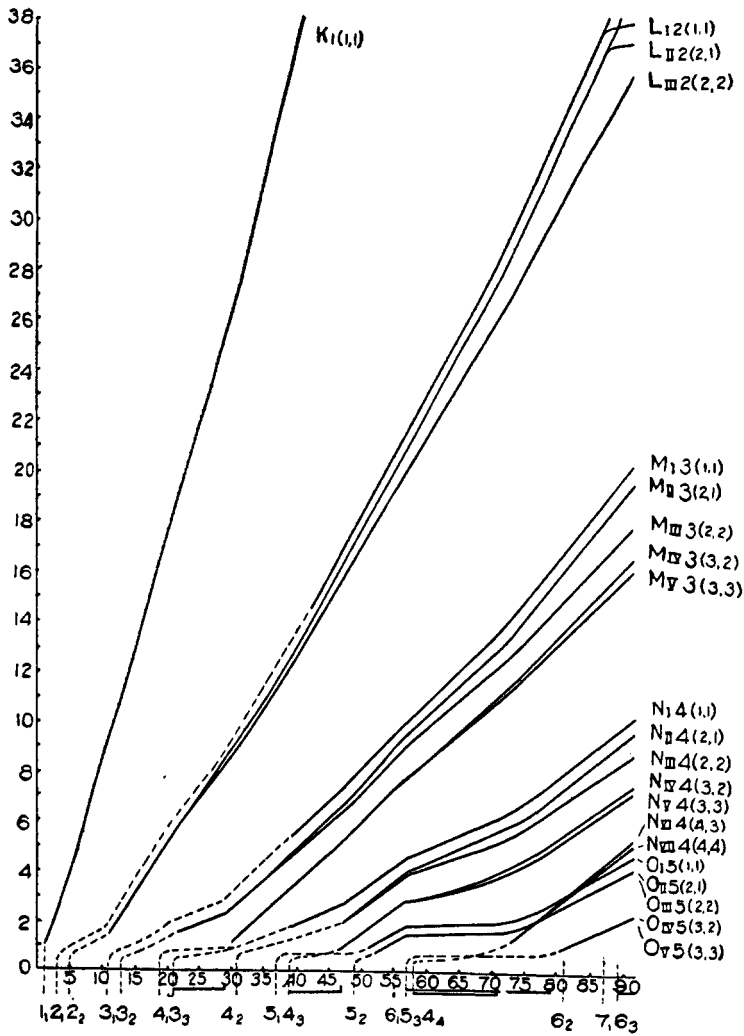


FIG. 3. MOSELEY DIAGRAM FOR X-RAY LEVELS

limiting wave-number in the Lyman series for H (corresponding to the normal level in H) forms an extension of the K level.

The regular increase in $\sqrt{\nu/R}$ with N for any one series of levels, so noticeable in the diagram, and first observed by Moseley, is obviously different from that observed for say S levels in optical spectra. The reason for this difference is due to the difference in origin of x-ray lines and optical lines. While the latter are due to transitions from *virtual* orbits external to the outermost normal orbits of the electrons in the atom, x-ray lines indicate a re-arrangement of electrons in the interior of the atom. Thus the K_α , K_β and K_γ lines are due to a transition of an electron from L , M and N levels respectively to the K level.

The fact that the values of the x-ray energy levels correspond to total quantum numbers—1, 2, 3 for K , L and M levels respectively lends strong support to Bohr's conception of the mode of formation of atoms by addition of electrons in successive levels of higher energy value. Furthermore, a closer study of the values of N at which certain x-ray levels begin to appear, furnishes evidence regarding the stages at which a re-arrangement occurs in the external electrons between such levels as $3d$ and $4s$ or $4f$ and $5d$.

This conception of Bohr's regarding the mode of formation of atoms may now be described in more detail. In the H atom the electron is normally in an orbit for which $n = 1, l = 0, j = 1/2$, but in excited states the electron may be raised to any one of the other (*virtual*) levels corresponding to higher values of n and the accompanying possible values of l and j ($l = n - 1, n - 2, \dots, 1, 0; j = l \pm 1/2$) as shown in table 5 for the values $n = 1, 2, 3$, and 4. The optical spectrum of H results from transitions between these levels as well as the normal level. As more electrons are added these enter in succession the higher (virtual) levels for H , and the number of electrons which can enter each of these levels is given by Stoner's rule. Owing to the increased nuclear charge the energy for these levels is, of course, greater than that for the same level in the H atom. X-ray spectra are produced, as stated already, by reorganization of the electrons in completed levels, while optical spectra are produced by removal of an electron from one of the external levels to a still higher virtual level.

Figure 4, also taken from the paper by Bohr and Coster, shows the energy levels for the rare gas radon ($N = 86$), as deduced from

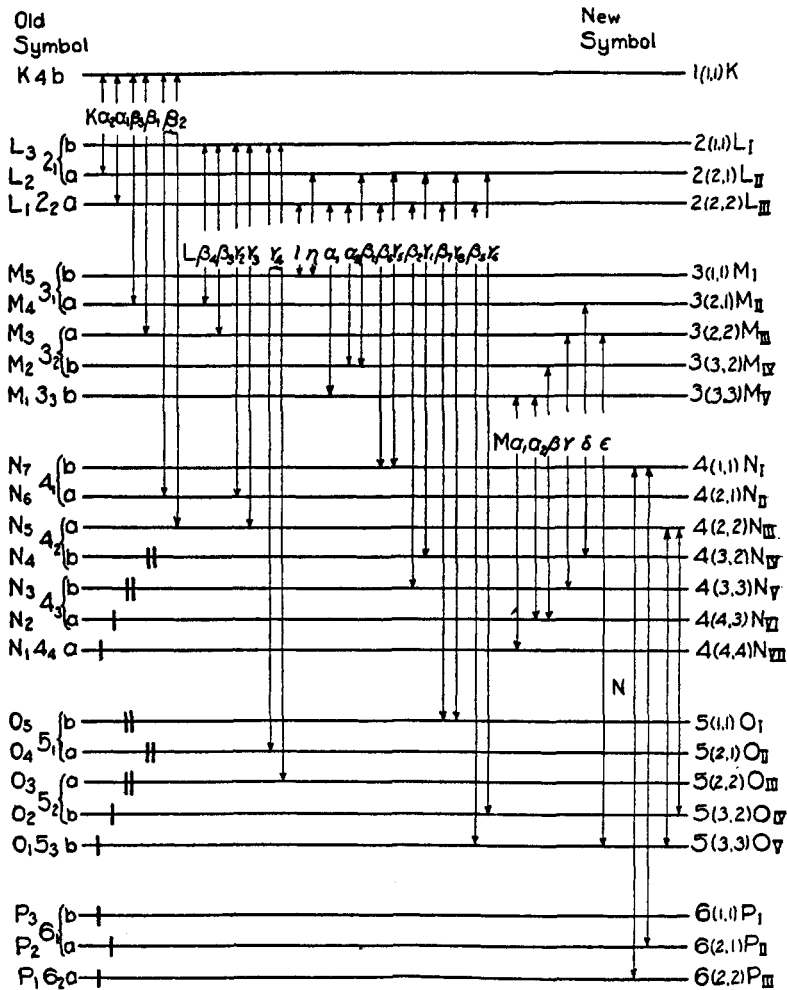


FIG. 4. X-RAY LEVELS IN RADON

x-ray absorption data for elements of high atomic number. The symbols suggested by Bohr and Coster are given on the right hand side together with the values of n, k , and $j + 1/2$, while the

older nomenclature is given on the left. The arrows indicate possible transitions and correspond therefore to observed lines in the x-ray spectra. For elements of lower atomic number the number of levels obviously decreases. For instance, in the case of Cs ($N = 55$) the L and M levels are present and N_I to N_V as well as O_I , O_{II} and O_{III} . The valence electron occupies the $6s$ level. In the case of K, the K and L levels are filled, and the M_I , M_{II} and M_{III} ($3s$, $3p_1$, and $3p_2$ respectively) while the valence electron occupies the N_I or $4s$ level. For the latter atom all the other levels indicated in the diagram are *virtual* levels to which the valence electron may be raised, thus leading to the formation of lines in the optical region when the electron returns to the $4s$ level.

DISTRIBUTION OF ELECTRONS IN ATOMS

We can now consider in further detail the electron distribution for the different atoms as shown in table 6. It is evident that the periodic recurrence of atoms with similar physical and chemical properties is correlated with similar energy levels for the external electrons. The gases of Group O exhibit the arrangement of eight outer electrons of which two are in s levels and six in p levels. A convenient notation for this, also adopted in recent papers, is s^2p^6 , the power index indicating the number of electrons in the particular level. Similarly we can write for the electrons external to the rare gas "shell" the following symbols for different groups:

Group I	Li, Na, K, Rb, Cs.....	s
Group IIa	Be, Mg, Ca, Sr, Ba, Ra.....	s^2
Group IIb	Zn, Cd, Hg.....	$d^{10}s^2$
Group IIIa	B, Al, Ga, In, Tl.....	s^2p
Group IIIb	Sc, Y, La, Ac.....	d^5s^2
Group VII	F, Cl, Br, I.....	s^2p^5

The rather anomalous properties of the Ni, Pd and Pt groups, as well as the properties of the elements immediately following them (Cu, Ag and Au) are to be interpreted by the fact that in the first-named elements a d level either becomes completed or tends to be completed, (and in a great many respects the elements

immediately following a completed level behave like those which follow the elements of Group O). We shall however discuss this point again in connection with magnetic and spectroscopic properties of the atoms.

The position and number of the 14 rare earth elements Ce to Lu is of special interest. Firstly, this arrangement shows that there cannot exist more or less than 14 such similar elements. Secondly the fact that the added elements from Ce to Lu enter into a $4f$ level while the $5d$ and $6s$ levels remain unaltered, is in agreement with the well-known fact that all these 14 elements are strikingly similar in all their chemical and physical properties. It is indeed remarkable that both La, which precedes Ce, and Hf which follows Lu are so much more definite in their characteristic properties that there can be no question as to which elements they each resemble. Thus La falls naturally in the Sc, Y group, while Hf belongs just as naturally with Ti and Zr.

There is some doubt regarding the exact distribution of electrons in the elements beyond Hf and in table 6 there have been incorporated the various arrangements suggested for each atom by J. S. McLennan, A. B. McLay and H. G. Smith (15). Further investigation is necessary before a definite decision on these questions can be reached. Thus, depending upon whether Pt resembles Ni or Pd, the distribution in $5d$ and $6s$ levels of the last three electrons will vary from d^8s^2 (Ni) to d^{10} (Pd).

Again, in the case of Th, and the next two elements, it is doubtful whether the added electrons enter the $5d$ level (in analogy with Ti and Zr etc.) or $5f$ level (in analogy with Ce, etc.).

DISTRIBUTION OF ELECTRONS IN SUB-LEVELS

One more point remains to be mentioned in connection with the arrangement of electrons in atoms shown in table 6. According to the evidence obtained from x-ray spectra (see Table 7 and figure 3) the levels which we have designated as p , d , f , etc. in table 6 are each to be regarded as doublet levels, corresponding to two different values of j , the inner quantum number. Table 7 shows the analogy (discussed more fully in a subsequent section) between these sub-levels derived from x-ray data with the optical sub-levels in the spectra of the alkali metals.

Now, as has been pointed out in connection with table 4, the number of electrons in each completed level is equal to $2(2l+1) = 2\sum(j + \frac{1}{2})$, that is, to the sum of the two values of $j + \frac{1}{2}$ for each of the levels p , d , and f . Stoner (12) has accordingly suggested that the number of electrons associated with each sub-level separately is also equal to $2(j + \frac{1}{2})$. In support of this assumption he points out that this number represents the observed term multiplicity in a weak magnetic field. That is, as shown in table 4, the number of different values of m is equivalent to $2(j + \frac{1}{2})$ and therefore these states of the atomic system are "always

TABLE 8

LEVEL	SPECTRAL NOTATION	SUB-LEVEL			CORRESPONDING X-RAY DESIGNATION	TOTAL NUMBER OF ELECTRONS IN SUB-LEVEL
		n_{kj}	l	j		
s.....	${}^2S_{\frac{1}{2}}$	n_{11}	0	$\frac{1}{2}$	$K_I L_I M_I N_I O_I P_I$	2
p.....	${}^2P_{\frac{3}{2}}$	n_{21}	1	$\frac{1}{2}$	$L_{II} M_{II} N_{II} O_{II} P_{II}$	2 4
	${}^2P_{\frac{1}{2}}$	n_{22}	1	$\frac{3}{2}$	$L_{III} M_{III} N_{III} O_{III}$	
d.....	${}^2D_{\frac{3}{2}}$	n_{32}	2	$\frac{3}{2}$	$M_{IV} N_{IV} O_{IV}$	4 6
	${}^2D_{\frac{5}{2}}$	n_{33}	2	$\frac{5}{2}$	$M_V N_V O_V$	
f.....	${}^2F_{\frac{5}{2}}$	n_{43}	3	$\frac{5}{2}$	N_{VI}	6 8
	${}^2F_{\frac{7}{2}}$	n_{44}	3	$\frac{7}{2}$	N_{VII}	

possible and equally probable, but only manifest themselves separately in the presence of the external field. Electrons can enter a group until all possible orbits are occupied, when the atom will possess a symmetrical structure."

According to this view therefore the maximum number of electrons in each of the sub-levels would be as shown in table 8.

Only those levels have been mentioned in this table, which are actually found completed in the periodic arrangement. While the numbers given in the last column of table 8 undoubtedly represent the distribution of electrons in the atoms of Group O, there is still considerable discussion regarding the exact distribu-

tion between each sub-level for a large number of the elements. This is specially true of the elements in Groups V, VI and VII and VIII as well as the rare earth group. Under these circumstances it has been considered advisable to defer discussion of this topic to a subsequent section of the paper.

SIMULTANEOUS TRANSITIONS OF TWO OR MORE ELECTRONS

In a previous section the origin of doublet levels in the spectra of the alkali metals was accounted for by assuming an interaction

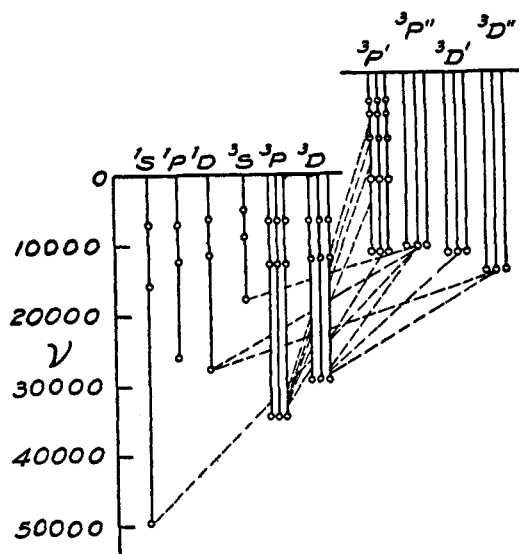


FIG. 5. NORMAL AND NEGATIVE TERMS FOR CALCIUM

between the angular momentum of the spin of the electron ($s = \frac{1}{2}$) and the angular momentum l of the electronic orbit. In this manner the values of j , the resultant momentum, given in table 4, were obtained. Evidently the assumption that the spectral terms are due to changes in the nature of the orbit of a single electron is not adequate to account for higher multiplet levels than the doublet. In other words, transitions of a single valence or "optical" electron between different levels does not explain the mode of formation of more complex spectra. Although

Heisenberg, Landé and others had formerly derived certain rules by which they could calculate the nature of the multiplet levels formed by successive addition of electrons, there existed, as mentioned previously, certain theoretical difficulties in the whole scheme. While the conception of the spinning electron has served to remove some of these difficulties, the evidence brought forward by Russell and Saunders (8) for the simultaneous transition of two electrons has helped materially in clarifying the whole problem of complex spectra.

It had been known for some time that in the spectrum of Ca there exist not only the two systems of singlet and triplet levels mentioned already, but also an anomalous group of levels for which the limiting terms (corresponding to the ionizing potential in the normal spectra of alkali and alkaline earth metals) have *negative* values. Figure 5 (4) which gives the energy diagram for Ca illustrates what is meant by negative terms. The S , 3S and other normal terms converge to the term marked 0 which corresponds to the ionizing potential. On the other hand there exist a group of terms such as $^3P'$, $^3P''$, etc., which converge to a higher term than that corresponding to the ionizing potential, so that some of the terms are negative (with reference to the convergence limit for the normal terms.)

The clue to the nature of this phenomenon is afforded by the observation that the difference between the limit of the normal term and that of the anomalous terms is equal to the difference between the lowest and next highest terms in the spectrum of ionized Ca (Ca^+ or CaII). The latter spectrum resembles that of K , since the atom has the same total number of electrons, external to the nucleus, in both cases. Thus the anomalous terms must obviously be due to *simultaneous transitions* of one of the two valence electrons from the $4s$ to a $3d$ level and of the other electron from the $4s$ to any other level. When *both electrons* return to lower levels a *monochromatic radiation* is emitted just as in the case of the transitions of a single electron.

Formally the observed phenomena may be accounted for on the following basis, which forms an extension of the vector-model used in interpreting the relations between l and s for the terms in the spectra of the alkalis.

The l -vectors of the two electrons interact to form a resultant L -vector, similarly the s -vectors combine to form an S -vector, and the resultant of L and S gives rise to a j -vector for the particular term. As an illustration of the application of this method of procedure, let us consider the case where $l_1 = 0$, and $l_2 = 2$ (as in that of Ca, where one of the electrons is in a $4s$ and the other may be in a $3d$ level). The resultant level has $L = 2$ (D term) while $S = 1$ or 0 , corresponding to a singlet or triplet level. Thus we obtain ${}^1D'$ and ${}^3D'$ terms. Similarly when $l_1 = 1$ and $l_2 = 2$, it may be shown that the resultant terms are ${}^3F'$, ${}^3D'$, ${}^1D'$ and ${}^1S'$. The dashes on the upper right hand side of the letters indicate that these terms are "anomalous."

DERIVATION OF TERMS IN COMPLEX SPECTRA

On the basis of these considerations it is now possible to discuss briefly the method developed by F. Hund (4) (16), for deriving the types of spectral terms which may result from the interaction of more than one electron in an atom. Before proceeding with this it is well to summarize briefly the discussion in the previous sections regarding quantum numbers. Following Russell's notation we distinguish the *state of a single electron* in an atom from the *state of the atomic system which corresponds to a definite spectral term*.

1. The state of a *single* electron is ordinarily designated by *four* quantum numbers: (a) n , the principal or total quantum number, which determines to a first approximation the energy of the state; (b) l , the "serial" quantum number, since it serves to designate the system to which the state belongs (s , p , d , f , etc.); (c) m_l , the magnetic quantum number which designates the orientation of the orbit in a magnetic field; (d) m_s , the magnetic quantum number which designates the direction of spin in a magnetic field.

It is to be observed, furthermore, that

$$\begin{aligned} l &= n - 1, n - 2, \dots 0 \\ m_l &= l, l - 1, \dots -(l - 1), -l \\ m_s &= \pm 1/2 \end{aligned}$$

and

$$m = m_l + m_s$$

in weak magnetic fields.

2. The *state of an atomic system* is defined by three numbers: (a) the "serial" quantum number, L , which is the resultant of the l -vectors for the individual electrons, and which designates the type of system (S, P, D, F , etc.); (b) the spin quantum number S which corresponds to the resultant of the spin vectors of the individual electrons, and (c) the inner quantum number, j , which represents the total number of units of angular momentum of the atomic system for the given state, and which is the resultant (vectorially) of L and S .

The value of S determines the multiplicity, r , of the system which is given by the relation

$$r = 2S + 1.$$

Hence $r = 1$ (singlets) for $S = 0$; $r = 2$ (doublets) for $S = 1/2$, and so forth.

As mentioned previously, the multiplicity is indicated by an index at the upper left hand corner of the symbol for the series; while the value of j is shown by an index at the lower right hand corner.

According to the method used by Hund, the values of L , S and j for the different possible terms resulting from the interaction of two or more electrons are determined as follows: Forming the sums of the different combinations of values of m_l for the individual electrons, we obtain values of $\Sigma m_l = m_L$; similarly values of $\Sigma m_s = m_S$ are obtained for each different combination. From these the values of $m = m_L + m_S$ are derived and these, in turn, are used to deduce the possible values of j , since corresponding to a given value of the latter in a spectral term, the magnetic quantum numbers, m , are given by the series of values $j, j-1, \dots -j$. Similarly corresponding to a given value of L in the spectral terms, the values of m_L are given by $L, L-1, \dots -L$, and corresponding to given value of S , the values of m_S are given by $S, S-1, \dots -S$.

Hund furthermore assumes that of all the possible spectral terms thus obtained, the *normal term*, or term corresponding to the lowest energy state of the atomic system is determined in accordance with the following two rules:

(1) The normal term corresponds to the highest value of the multiplicity, r .

(2) For regular multiplets the lowest value, $j = L - S$, and for inverted multiplets the highest value, $j = L + S$, is chosen.

From table 4 it follows that in case of levels which contain their maximum number of electrons, $\Sigma m = 0$. Consequently

TABLE 9
 $n_2 = n_1 = 3; l_1 = l_2 = 2$

m_{l_1}	m_{l_2}	m_{s_1}	m_{s_2}	m_L	m_S	m
2	2	$+\frac{1}{2}$	$-\frac{1}{2}$	4	0	4
	1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	3	100-1	4332
	0	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	2	100-1	3221
	-1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	1	100-1	2110
	-2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	0	100-1	100-1
1	1	$+\frac{1}{2}$	$-\frac{1}{2}$	2	0	2
	0	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	1	100-1	2110
	-1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	0	100-1	100-1
	-2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	-1	100-1	0-1-1-2
0	0	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	0
0	-1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	-1	100-1	0-1-1-2
0	-2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	-2	100-1	-1-2-2-3
-1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	-2	0	-2
-1	-2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	-3	100-1	-2-3-3-4
-2	-2	$+\frac{1}{2}$	$-\frac{1}{2}$	-4	0	-4

$j = 0$, and the interaction of all these electrons in the *completed level* must lead to a term having the designation 1S_0 . In table 6 the second last column gives the *lowest* or *normal term* in the spectrum of the element, and it will be observed that the 1S_0 term is characteristic of all those elements in which a level becomes completely filled, such as Ne; Mg, Pd and analogous elements.

The method of determining the spectral terms which may result from the interaction of two or more electrons may be illustrated by considering a case, such as that of Ti, in which two ($3d$) elec-

trons are added to the two (4s) electrons already present in the shell external to that of argon. Since the two (4s) electrons represent a completed level, $j = m = 0$ for these and therefore they contribute no angular momentum to the resultant angular momentum of the two (3d) electrons. Designating one of the latter electrons by subscript 1 and the other by subscript 2, we obtain the values of n, l, m_l, m_s given in table 9.

The values of m correspond to $j = 4$ (two terms), $j = 3$ (one term), $j = 2$ (three terms), $j = 1$ (one term) $j = 0$ (two terms). Altogether there result nine terms. The values of $m_s = 0$ indicate singlet terms, while $m_s = 1, 0, -1$ correspond to triplet terms. Also since the maximum value of m_L is 4, we may expect terms in G, F, D, P and S levels. Distributing the nine terms among these levels we obtain the spectral terms ${}^1S_0, {}^1D_2, {}^1G_4; {}^3P_2, {}^3P_1, {}^3P_0, {}^3F_4, {}^3F_3, {}^3F_2$. In accordance with the rules given by Hund, the normal term must be of type 3F_2 , the lowest value of j being used since the number of electrons is less than half that corresponding to a completed (3 d) level.

It will be observed that for the cases $m_{l_1} = m_{l_2}$ only the values $m_{s_1} = \frac{1}{2}$ and $m_{s_2} = -\frac{1}{2}$ have been used. The reason for excluding other combinations of m_s is based on a rule which is known as "Pauli's Principle of Restriction of Quantum Numbers," and which may be enunciated as follows:

In any one atom there cannot exist two electrons having the four quantum numbers, (n, l, m_s and m_l) respectively the same in both.

That is, if for two electrons $n_1 = n_2; l_1 = l_2; m_{l_1} = m_{l_2}$, then m_{s_1} cannot be equal to m_{s_2} . Furthermore it is obvious that in the case illustrated above, $m_{l_1} = 2, m_{l_2} = 1$ is identical with $m_{l_1} = 1$ and $m_{l_2} = 2$, and so forth.

It will be recognized that Pauli's principle is essentially the real justification for Stoner's theory of electron distribution in levels; since, for instance, putting more than 6 electrons in a p level would be in contradiction with this principle.

On the basis of these considerations it is possible to derive, as has been shown by Hund, the different spectral terms which may be obtained from the interaction of two or more electrons having the same values of n and l respectively. The results of these

calculations are given in table 10 for the case $l = 1$ (p - electrons).

Since $\Sigma m_l = \Sigma m_s = \Sigma m = 0$ for all the electrons in a completed level, it follows that 4 equivalent electrons give the same spectral terms as 2, and 5 the same as 1. The only difference occurs in the order of the multiplet levels. While in the case of the first three electrons, the lowest multiplet level corresponds to the least value of j , the order is reversed in the case of the last three, as is shown in the last column of table 10 which gives the multiplet level of lowest energy content and therefore corresponds to the "normal" term.

It will be observed that in table 10 the multiplicity $r = 2$ for one electron changes to $r + 1$ and $r - 1$ on addition of a second

TABLE 10
Terms for equivalent p-electrons

NUMBER OF ELECTRONS	TERMS	LOWEST MULTIPLET
1	2P	$^2P_{1/2}$
2	1S_0 1D_2 3P	3P_0
3	2P 2D 4S	$^4S_{3/2}$
4	1S_0 1D_2 3P	3P_2
5	2P	$^2P_{3/2}$
6	1S_0	1S_0

electron, and the same result is reproduced on addition of a third electron. Then the multiplicities decrease in reverse order as the last three electrons are added. In Table 1 a similar set of observations were shown for the elements of the first long period. A given multiplicity r in any one atom becomes altered to $r + 1$ and $r - 1$ in the succeeding atom in the periodic arrangement. (Heisenberg's "branching" rule.) This leads to increasing complexity in the degree of multiplicity until the number of electrons added corresponds to half of the maximum number possible for the given level, and then the complexity decreases in reverse order. Thus in the $3d$ level the complexity reaches a maximum with Cr. In all cases the maximum occurs in that case for which the number of added p or d electrons is one half the maximum possible number for the completed shell.

On the basis of Hund's theory this phenomenon is accounted for readily since for every added electron, the value of S , the resultant spin vector is decreased or increased by $1/2$, and consequently the multiplicity must be decreased or increased by 1. Furthermore, the occurrence of maximum complexity in the middle of the series corresponding to a given level is due to the same cause as the repetition of spectral terms in the second half of the series which has been mentioned above, i.e., Pauli's exclusion principle.

PERIODIC VARIATIONS IN NATURE OF NORMAL TERM

Table 6 gives the normal term for each of the 92 elements (15) (16). In certain cases (such as Cr, Cu, Ni and Pd) the nature of the normal terms as derived from the Zeeman effect has led to the conclusion that the electron distribution must be that given in the table. In other cases, such as the rare earth group and a large number of the elements of higher atomic number, detailed investigation of the spectra still remains to be carried out before a final decision can be reached regarding the exact electron distribution. However, Hund's theory of the relation between spectral terms and electron arrangement as outlined above, has been so singularly confirmed in such a large number of cases that no doubt exists in regard to its validity.

The periodic variation in spectral terms with increasing atomic number is evident from table 6. Atoms which have a similar arrangement of electrons in the "valence" or outer levels, have identical spectral terms. In accordance with the rules enunciated in a previous section, it is observed that the term corresponding to $m - \chi$ electrons in a level is the same as that for χ electrons, where m denotes the *maximum number* of electrons for the completed level; the only difference which occurs is that in the second half of the group of m atoms, the component of the multiplet level which has the lowest energy value is that corresponding to the highest value of j , ("reversed multiplets") as contrasted with "regular multiplets" at the beginning of the group.

Thus Ti with $(3d)^2$ electrons and Ni with $(3d)^8$ electrons exhibit 3F terms; V with $(3d)^3$ and Co with $(3d)^7$ have 4F terms, and simi-

larly for other elements in the group, Sc to Ni. The only exception is Cu for which the expected electron distribution $(3d)^9(4s)^2$ does not apparently possess as low an energy content as that corresponding to $(3d)^{10}(4s)$. Hence the latter yields a normal term which is different from that of Sc.

The rare earth group is an illustration of the case for which the completed $4f$ level should contain 14 electrons, and it will be observed that the normal term for $14 - \chi$ electrons is of the same nature (except as regards the particular value of j) as that for χ electrons ($\chi = 1$ to 6). The spectral terms given in table 6 are derived on the assumption that the electron configuration corresponds to $(4f)^n(5d)(6s)^2$ where n is the number of electrons in $4f$ level. On the other hand, Hund has suggested the alternative possibility $(4f)^n(5d)^2(6s)$ in which case the normal terms would be of still higher degree of complexity. Thus for Gd ($N = 64$) the normal term would be of type ${}^{11}F$ instead of 9D as given in the table, and for all the other atoms of the group the normal level would be altered to that corresponding to the next higher value of L with an increase in degree of multiplicity by 2.

In the case of Os, Ir, Pt and some of the other elements more than one distribution is possible and the normal terms have been given for each of these, as calculated by McLennan, McLay and Smith (15). In a recent paper, A. C. Hausmann (18) has, however, reached the conclusion, from an examination of the Zeeman effect on the terms in the arc spectrum of Pt, that the normal term is of type 3D_3 corresponding to the configuration d^9s .

ENHANCED SPECTRA

We shall now consider types of spectra which are of considerable importance inasmuch as they furnish experimental evidence for Bohr's general conception of the building up of atoms by addition of successive electrons. It has already been stated that according to Bohr's theory the energy of an atomic system consisting of a nucleus of charge Ne and a single electron is given by

$$E_n = - \frac{RchN^2}{n^2} \quad (5)$$

where E_n denotes the energy for the state corresponding to total quantum number n .

As a consequence of this relation it was shown by Bohr that certain lines previously ascribed to hydrogen really belong to ionized helium, since in this case $N = 2$. It is evident that for an ionized atom, the number of electrons is one less ($N - 1$) than the charge on the nucleus, and, therefore, for orbits of large quantum number the force between the "optical" electron and the rest of the atom will approximate that of a nucleus for which $N = 2$, acting on a single electron. Thus the spectra of singly ionized atoms will possess terms in which the Rydberg constant, R , obtained in ordinary spectra, is to be replaced by $4R$. Now such spectra had been observed and were known as "*spark spectra*" in contradistinction to the more usual *arc spectra*."

Bohr's theory, however, led to the conclusion that it should also be possible to observe spectra due to atoms in which two or more electrons have been removed, and for these "*enhanced*" spectra the value of the Rydberg constant would have to be replaced by $4R$, $9R$ or p^2R according as one, two or $(p - 1)$ electrons have been removed from the neutral atom. It has become conventional to designate such a "stripped" atom by the symbol of the element to which is attached at the lower right hand corner a Roman numeral whose value is equal to that of p . Thus we speak of the spectrum of F_{VII} and signify by this symbol the spectrum emitted by a fluorine atom which has been stripped of *six* external electrons and therefore actually has the same number of electrons as the Li atom.

As an important corollary from the remarks made in connection with Hund's theory of the formation of spectral terms it follows that the first spark spectrum of any element ought to exhibit the same multiplet structures as the arc spectrum of the element preceding it in the periodic table. (Kossell-Sommerfeld's displacement law.) Furthermore, the enhanced spectrum of an element of atomic number N from which p electrons have been removed should resemble the ordinary spectrum of an element of atomic number $N - p$. (But, of course, the coefficient of the Rydberg constant in the case of the enhanced terms would be $(p + 1)^2$.)

A very interesting illustration of these considerations is furnished by the spectra of the series Na_I , Mg_{II} , Al_{III} , Si_{IV} , which have been investigated by Paschen, Foote and Fowler (19), and P_V , S_{VI} , and Cl_{VII} investigated by Millikan and Bowen (20). All these spectra exhibit doublet levels, but owing to the effect of in-

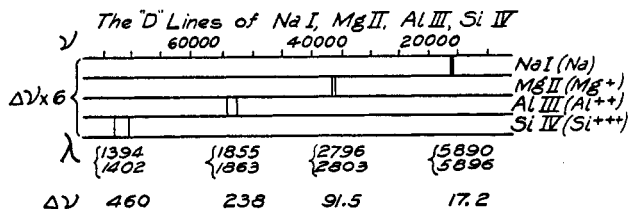


FIG. 6. "D" LINES IN ENHANCED SPECTRA OF SODIUM-LIKE ATOMS

creasing net nuclear charge, the wave lengths of similar lines (i.e., corresponding to transitions between levels of same spectral designation) become shorter as the number of electrons removed from the atom increase. Thus figure 6 (20), (21) shows the "D" lines in the spectra of the first four atoms.

TABLE 11
Comparison of frequencies of series terms for stripped atoms Na_I to S_{VI}

	3S	3P	3D	4F
H.....	12192.8	12192.8	12192.8	6858.4
Na/1.....	41449.0	24475.7	12276.2	6860.4
Mg/4.....	30316.9	21376.6	12444.3	6866.8
Al/9.....	25494.9	19504.0	12611.0	6871.3
Si/16.....	22756.8	18272.6	12733.7	6874.2
P/25.....	20979.7	17401.9	12811.8	6876.4
S/36.....	19729.6	16753.6	12856.6	6878.1

Table 11 (20) gives a comparison of the lowest series terms for these spectra. In accordance with equation (5) the observed values of ν have been divided by p^2 where $p-1$ designates the number of electrons removed from the neutral atom. The values of ν for the corresponding levels in H are given at the top. Here again it is observed that the values of D and F levels are approximately the same as those of similar levels in H , (thus indicating

that the corresponding orbits are completely external to the rest of the atom) while owing to the deeper penetration of the s and p orbits the corresponding energy values (as measured by the values of ν) are greater. Consequently the quantum defect ($\alpha_K = n - n_{eff}$) decreases as we pass from Na_I to S_{VI} .

Millikan and Bowen have also obtained the spectra of the series Li_I to F_{VII} and these show variation in the frequencies of series terms similar to those observed for the series Na_I to Cl_{VII} .

While these spectra all resemble those of the alkali metal group in exhibiting doublet levels, Millikan and Bowen have also found spectra of stripped atoms which resemble the metals of Group II in exhibiting singlet and triplet levels. Such are the series:

$$\begin{array}{l} Be_I, B_{II}, C_{III}, N_{IV}, O_V, F_{VI} \\ Mg_I, Al_{II}, Si_{III}, P_{IV}, S_V, Cl_{VI} \end{array}$$

In fact the spectra of all these atoms have been obtained in all the various states of enhancement. Thus, series, such as P_I to P_V ; Si_I to Si_{IV} ; N_I to N_V , have been observed spectroscopically and in each case the expectations based on Hund's theory have been signally confirmed (22). Similar results have been obtained by Russell for the enhanced spectra of Ti (23).

MULTIPLY LEVELS IN STRIPPED ATOMS

In a previous section it was stated that an investigation of x-ray spectra has led to the identification of a number of different sets of levels, which are listed in table 7. Millikan and Bowen (24) pointed out in 1924 that the relations observed for the separations between certain pairs of these levels could be applied to analogous levels in optical spectra. These observations have since been extended to multiplet levels in stripped atoms and furnish additional evidence for the periodic variation in the structure of spectral terms with variation in atomic number.

Now in the case of the L_{II} L_{III} levels it had been shown by A. Sommerfeld (5) that the separation

$$\Delta\nu = 0.365 (N - \sigma)^4 \tag{10}$$

where N = atomic number, and σ denotes the "screening" constant. Similarly for the M_{II} M_{III} levels:

$$\Delta\nu = 0.108 (N - \sigma)^4 \tag{11}$$

These levels constitute what are known as "relativity" or regular doublets and as may be seen from an inspection of figure 3 the separation, $\Delta\nu$, increases rapidly with increase in N . On the other hand, the levels, $L_I, L_{II}; M_I M_{II}$ from the so-called

TABLE 12

	$2P_1 - 2P_2$			$2S - 2P_1$	
	$\Delta\nu$	$\sqrt[4]{\Delta\nu/365}$	σ	$\Delta\nu$	$\sqrt{\nu_S} - \sqrt{\nu_{P_1}}$
Li_I	0.34	0.981	2.019	14903.8	39.470
Be_{II}	6.61	2.063	1.937	31927.6	44.297
B_{III}	34.4	3.116	1.884	48358.7	45.594
C_{IV}	107.4	4.142	1.858	64481.2	46.068
N_V	259.1	5.162	1.939	80455.1	46.276
O_{VI}	533.8	6.184	1.816	96367.8	
	$3P_1 - 3P_2$			$3S - 3P_1$	
	$\Delta\nu$	$\sqrt[4]{\Delta\nu/108}$	σ	$\Delta\nu$	Diff.
Na_I	17.18	3.550	7.450	16956.17	
Mg_{II}	91.55	5.394	6.606	35669.42	18713.25
Al_{III}	234.00	6.820	6.180	53681.53	18012.11
Si_{IV}	461.84	8.084	5.916	71285.49	17603.96
P_V	794.82	9.259	5.741	88649.42	17363.93
S_{VI}	1267.10	10.404	5.596	105866.04	17216.62
Cl_{VII}	1889.5	11.496	5.504	123001.23	17135.19

"irregular" or "screening" doublets. For these levels the values of the differences, $\sqrt{\nu_{L_I}} - \sqrt{\nu_{L_{II}}}$ and $\sqrt{\nu_{M_I}} - \sqrt{\nu_{M_{II}}}$ increase only slightly with increase in N , as shown in figure 3.

According to Hertz this relation indicates that the difference between the values of σ , the screening constant, for the L_I (or $2s$) and L_{II} (or $2p_I$) levels is practically constant for all the atoms.

As a result of recent developments in the theory of wave mechanics Sommerfeld's physical interpretation of the difference, $\Delta\nu$, between the wave numbers of the two levels L_{II}, L_I , etc. has been discarded (25) and it has been shown that the observed

differences must be regarded as due to differences in direction of spin of the electron for the two levels whose inner quantum numbers are $j = l + 1/2$ and $j = l - 1/2$ respectively. But it is of interest that the relation derived on the basis of this theory is identical in the case of doublet levels with Sommerfeld's equations (10) and (11).

Table 12⁴ gives the values of $\Delta\nu$ and σ for doublet terms in the spectra of stripped atoms of types Li_I and Na_I .

Thus the levels $2P_2$ and $2P_1$ are analogous to L_{II} and L_{III} respectively; $3P_2$ and $3P_1$ to M_{II} and M_{III} respectively, while $2S$

TABLE 13
Analogous levels

X-RAY LEVEL	OPTICAL LEVEL	X-RAY LEVEL	OPTICAL LEVEL
K	$1S$	$\{N_I$	$4S$
$\{L_I$	$2S$	$\{N_{II}\}$	$4P_1$
$\{L_{II}\}$	$2P_1$	$\{N_{III}\}$	$4P_2$
$\{L_{III}\}$	$2P_2$	$\{N_{IV}\}$	$4D_2$
$\{M_I$	$3S$	$\{N_V$	$4D_3$
$\{M_{II}\}$	$3P_1$	$\{N_{VI}\}$	$4F_3$
$\{M_{III}\}$	$3P_2$	$\{N_{VII}\}$	$4F_4$
$\{M_{IV}\}$	$3D_2$	$\{O_I$	$5S$
$\{M_V$	$3D_3$	$\{O_{II}\}$	$5P_1$
		$\{O_{III}\}$	$5P_2$

and $3S$ are analogous to L_I and M_I respectively. The analogy has been found to extend over the whole range of x-ray and optical levels as shown in table 13.

Irregular doublet levels are shown bracketted on the left hand side, while regular doublet levels are bracketted on the right.

The analogy is best illustrated by the Moseley diagram shown in figure 7 taken from the paper by Bowen and Millikan (20).

Their remarks in this connection are worth quoting. They state:

This whole comparison may be very beautifully made graphic in precisely the way in which Moseley first exhibited the relations

⁴ The subscripts to the P levels are those to be assigned on the basis of the j values and are the reverse of those used formerly by spectroscopists.

between atomic numbers and x-ray spectra. Indeed, no more striking demonstration of the fact that x-ray laws hold throughout the *optical* region as well can be made than is found in figure 7. In this figure we have plotted all our stripped atom levels, corresponding to the second row of the periodic table, in a Moseley diagram. That these optical levels follow the *Moseley law* is exhibited by the linear relation everywhere found between $\sqrt{\nu}/R$ and atomic number. That they follow the irregular doublet law is shown by the parallelism of the 3s, 3p and 3d lines, all of which have constant screening differences,

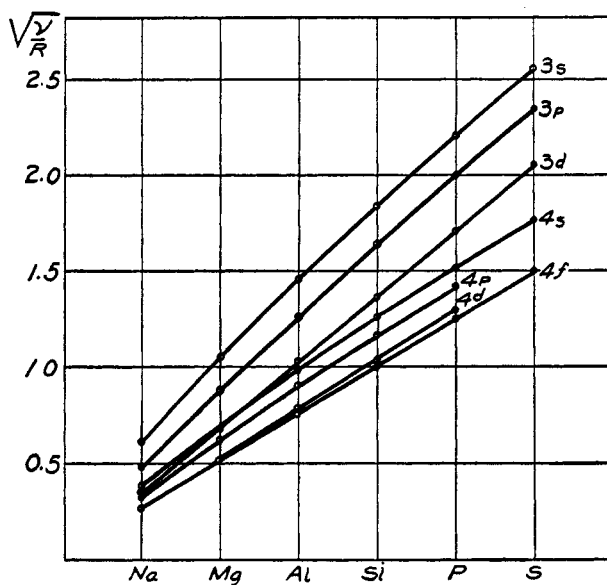


FIG. 7. MOSELEY DIAGRAM FOR OPTICAL LEVELS IN SODIUM-LIKE ATOMS

corresponding as they do to 3_1 , 3_2 and 3_3 orbits,⁵ respectively. Quite similarly, the irregular doublet law appears in the near parallelism of the 4s, 4p, 4d and 4f lines, which correspond to 4_1 , 4_2 , 4_3 , and 4_4 orbits, respectively. . . . The diagram thus furnishes a very satisfactory graphical illustration of the extension of two of the three x-ray laws, namely, the Moseley law and the irregular doublet law, into the field of optics. That it fails to illustrate the extension of the third, or regular doublet law, is merely due to the fact that the regular

⁵ The subscripts here refer to the values of $k = l + 1$ for the orbits.

doublet separations are so small as not to be visible at all upon a drawing of this scale.

As shown in table 12 the value of the screening constant, σ , is approximately 2 for the series Li_I to O_{VI} , which corresponds to the number of electrons in the K shell, and thus represents the residual number of electrons after the L electrons are removed. In the case of the series Na_I to Cl_{VII} , the value of σ is approximately 6, instead of the expected value 10, which is interpreted as due to

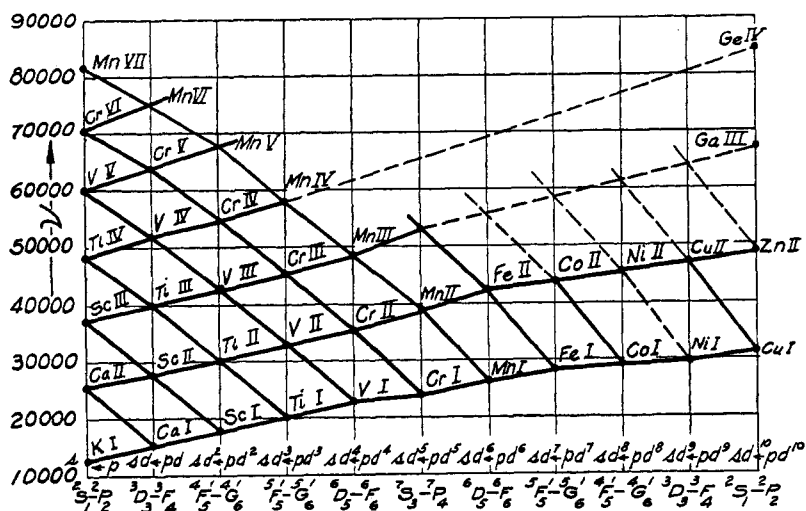


FIG. 8. ANALOGOUS LINES IN ENHANCED SPECTRA OF ELEMENTS OF FIRST LONG PERIOD

a penetration of the $3P$ orbits within the L shell, and, indeed, when σ is calculated from the doublet separations $3D_2 - 3D_3$ and $4F_3 - 4F_4$, the value obtained is approximately 10.

R. C. Gibbs and H. E. White have investigated, in a similar manner to Bowen and Millikan, the relations existing for doublets of stripped atoms of the potassium, rubidium, and caesium types (26). The irregular and regular doublet laws were found to be also applicable to these atoms. Figure 8 taken from a more recent paper (27) shows the regular displacement of multiplets for the elements in the first long period. Vertical lines represent atoms having the same number of external electrons⁶ ("iso-elec-

⁶ A very apt term used, as far as the writer knows, only by Gibbs and White.

tronic systems"). The ordinates give the values of ν for the spectral lines indicated at the bottom of the figure. Thus, along the first vertical column are given the frequencies of the line $4^2S_1 - 4^2P_1$ (first line of the principal series) for the potassium-like atoms K_I to Mn_{VII} , which have only one valence electron. The second vertical line corresponds to the calcium-like atoms, Ca_I to Mn_{VI} , which are two electron systems, and the ordinates give the frequencies of the spectral line whose initial level is the 3F_4 level (corresponding to a combination of one electron in a p level and the other in a d level) and final level is the 3D_3 level (whose origin is one electron in an s level and the other in a p level). Above the spectral designation of each line are given the combinations of electrons which give rise to the corresponding levels.

It will be observed, as has been mentioned previously, that the multiplicity alternates between even and odd values as we pass from K-like to Cu-like atoms, and also that the degree of this multiplicity passes through a maximum (seven) for the atoms for which the number of electrons and their distribution are the same as that of Cr_I . This variation in multiplicity is in agreement with the fact that as we pass from K-like to Cu-like atoms the number of electrons in the atomic system external to the argon shell increases from one at the beginning to eleven at the end, and, as is to be expected on the basis of Hund's theory, atomic systems having the same number and distribution of electrons external to the next lower rare gas exhibit the same spectral structure. In fact, this figure illustrates beautifully all that has been stated in the previous discussion in regard to the conclusions which can be drawn from Hund's theory.

As a further illustration it is of interest to refer briefly to the various spectra of Ti which have been investigated in detail by Russell (23). The systems of terms present in the successive spark spectra have been found by him to be as follows:

	T^i_I	T^i_{II}	T^i_{III}	T^i_{IV}
Systems present in spectrum.....	Quintets Triplets Singlets	Quartets Doublets	Triplets Singlets	Doublets
Electron configurations..	$(3d)^2 (4s)^2$	$(3d)^2 (4s)$	$(3d)^2$	$(3d)$

IONIZING POTENTIALS OF NEUTRAL ATOMS

The ionizing potential has already been defined as the energy required to remove one of the external electrons completely from the rest of the atomic system, thus leaving the latter in the state of a singly ionized atom. Hence the ionizing potential may ordinarily be calculated from the wave-number of the lowest energy level by the relation

$$V_i = \frac{\nu}{8100}$$

H. N. Russell (28) has, however, pointed out that in an atomic system in which there are two or more valence electrons (as in Groups II to VIII) there should be more than one ionizing potential corresponding to different processes for the removal of the electron.

As an illustration he considers the elements of the first long period (K to Ni). If we designate the number of electrons outside the "argon shell" by n , the normal state of the atom corresponds to the configuration s in the case of K and $d^{n-2}s^2$ in all the other cases (except Cr for which the normal configuration is d^5s).

Now, as is evident from table 2 the degree of multiplicity, r , changes by $+1$ or -1 as we pass from one element to the next in the periodic arrangement (Heisenberg's "branching" rule.) Therefore, in the removal of one of the $4s$ electrons from the configuration $d^{n-2}s$ the resulting ion may have a greater or less multiplicity than the neutral atom. Corresponding to these two possibilities we have two different ionizing potentials:

$$\begin{aligned} A: & d^{n-2}s^2 \text{ to } d^{n-2}s \text{ (greater multiplicity)} \\ B: & d^{n-2}s^2 \text{ to } d^{n-2}s \text{ (smaller multiplicity)} \end{aligned}$$

Thus in the case of Ca the normal level is of type 1S_0 . On ionization there results a potassium-like ion, in which the lowest term is of greater multiplicity, i.e., of type 2S_1 . On the other hand, the ionization may be accompanied by the simultaneous transition of the second electron from the $4s$ to the $3d$ level, and

again the multiplicity may be either increased or decreased, with the corresponding two possible ionizing potentials:

$$C: d^n - 2s^2 \text{ to } d^{n-1} \text{ (greater multiplicity)}$$

$$D: d^n - 2s^2 \text{ to } d^{n-1} \text{ (smaller multiplicity)}$$

Russell therefore defines the *principal ionizing potential* as that which represents the difference in energy between the normal states of the atom and that of the ion. He furthermore accounts for the difference between the four ionizing potentials *A*, *B*, *C* and *D* as follows:

The differences between the ionization potentials *A* and *B*, or *C* and *D* admit of a simple explanation: The reverse process for the transition *C* and *D*, whether in the arc or the spark, consists of adding a 4s electron to a partially completed shell of 3 *d* electrons. In case *C*, the multiplicity is increased, that is, the added electron is *spinning in the same direction* as the resultant spin of those already present. In case *D*, it is spinning in the opposite direction. Now, as Hund has pointed out, the magnetic interaction produces attraction in the first case, and repulsion in the second, so that the energy of binding is greater for *C* than for *D*.

Thus the principal ionizing potentials for Ca, Sc, Ti, Mn, Fe and Zn correspond to a transition of type *A*; while those for K, Cr and Cu correspond to a transition of type *B*. For V, Co and Ni the transition involving the least energy change is of type *C*.

In the last column in table 6 the ionizing potentials have been given for all the elements for which reliable data are available (29). As far as possible the principal ionizing potentials, as defined by Russell, have been given. Figure 9 shows the values plotted as a function of the atomic number, and as in the case of other properties it is observed that the ionizing potential is to a large extent distinctly a periodic function of *N*.

Thus the inert gases occupy the highest places, while the chemically very active alkali metals are located at minimum points on the curve. The extremely electronegative elements F and Cl also have values of V_i which are relatively close to those of group O. In a general way, the ionizing potential tends to increase as the number of electrons in any given level is increased, and reaches

a maximum value when the particular level is completely filled. This is illustrated by the relative values of V_i for the triads Li, Be, B; Na, Mg, Al; Zn, Ga, Ge; Ag, Cd, In; and Au, Hg, Tl. In each case the element in the middle corresponds to the completion of an s level and with the last named element electrons begin to enter a p level. On the other hand, it is difficult to interpret the fact that V_i for sulfur is less than for either of the neighboring elements.

The similar appearance of the two sections of the graph corresponding to the K-Zn series on the one hand and to the Rb-Cd

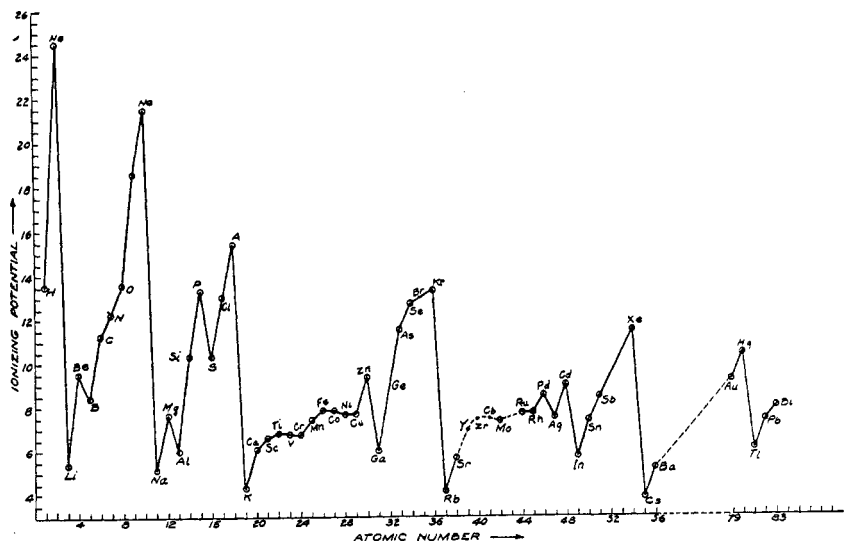


FIG. 9. PLOT OF IONIZATION POTENTIAL AS FUNCTION OF ATOMIC NUMBER

series on the other is quite evident. Also it will be observed that for elements belonging to the same group, V_i decreases as N increases. In a general way it is possible to prophesy from these data the ionizing potentials for the other elements of the periodic arrangement. The graph shows the interpolated values for Y, Zr and Cb which have been located by analogy with the corresponding points for Sc, Ti and V, and undoubtedly, La, Ce and the rare earth elements will occupy similar positions with respect to Ba, with values of V_i ranging between 7 and 8, reaching a low

TABLE 14
 Ionizing energy of stripped atoms⁷

ELEMENT	N	ELECTRON DISTRIBU- TION IN VALENCE SHELL	ENERGY OF REMOVAL OF OUTER ELECTRON FORM						
			M	M ⁺	M ²⁺	M ³⁺	M ⁴⁺	M ⁵⁺	M ⁶⁺
H	1	s	1.00	∞					
He	2	s ²	1.80	4.00	∞				
Li	3	s	0.40	5.60	9.00	∞			
Be	4	s ²	0.70	1.34	11.4	16.0	∞		
B	5	s ² p	0.62	1.79	2.80	19.3	25.0	∞	
C	6	s ² p ²	0.83	1.79	3.36	4.74	29.0		
N	7	s ² p ³	1.07	2.18	3.49	5.43	7.19		
O	8	s ² p ⁴	1.00	2.58	4.05	5.69	8.07	10.14	
F	9	s ² p ⁵	1.25	2.39	4.62	6.40	7.56	(11.0) ⁸	13.60
Ne	10	s ² p ⁶	1.59	2.70					
Na	11	s	0.38	3.50					
Mg	12	s ²	0.56	1.11	5.98				
Al	13	s ² p	0.44	1.34	2.09	9.00			
Si	14	s ² p ²	0.76	1.20	2.34	3.32	12.47		
P	15	s ² p ³	0.98	1.46	2.22	3.53	4.78		
S	16	s ² p ⁴	0.76	1.74	2.37	3.48	4.93	6.47	
Cl	17	s ² p ⁵	0.96	1.66	2.76	3.50	5.00	(6.8) ⁸	8.40
A	18	s ² p ⁶	1.16	2.12 ⁹					
K	19	s	0.32	2.34					
Ca	20	s ²	0.45	0.87	3.76				
Sc	21	s ² d	0.49	0.95	1.82	5.33			
Ti	22	s ² d ²	0.50	1.00	2.04	3.18	7.07		

⁷ The energy is expressed as a multiple of 13.54 V (= 312,368 cal. per gram atom; = 109,678 cm⁻¹).

⁸ Values obtained by interpolation on log-log plot. The values 7.56 for F and 3.50 for Cl are apparently low.

⁹ The value for A⁺ is from a paper by Compton, Russell and Boyce, Proc. Nat. Acad. (in print).

maximum value at Hf and then decreasing to W with another pronounced maximum at about 10 volts in Pt.

IONIZING POTENTIALS OF STRIPPED ATOMS

As a result of the work of Millikan and Bowen, A. Fowler, H. N. Russell and others, our knowledge of the nature and energy values of levels in enhanced spectra has been increased enormously in the past three years. While certain results of these investigations have been discussed in previous sections, we shall consider in the present connection a number of interesting observations which have been made on the relations between the ionizing potentials of atoms from which one or more electrons have been removed.

Table 14, taken with slight modification from a recent paper by A. A. Noyes and A. O. Beckman (29.4), gives the relative values of the energy of ionization for the neutral stripped atoms of the first two series and part of the third in the periodic arrangement. The energy is given in terms of ν/R , where ν represents the wave number of the lowest level, and is therefore expressed as a *multiple of that required to ionize the H atom*, i.e., 13.54 volts (= 109,678 cm.⁻¹; = 312,368 calories per gram atom).

MOSELEY'S LAW FOR IONIZING POTENTIALS

The most striking feature about these data is the observation that if we plot the square roots (that is, $\sqrt{\nu/R}$ or $\sqrt{V_i}$) of the values corresponding to stripped atoms which are iso-electronic, against N , approximately straight lines are obtained. Figure 10 shows a series of such lines plotted for the series Li to Ne in all the states of ionization. Values for O_{VI} and F_{VII} have been obtained from published data by Millikan and Bowen. The regularity of the lines furnishes a beautiful illustration of the validity of Moseley's law for isoelectronic systems. As a matter of fact, the Moseley diagram in figure 7 for the 3s level in the series Na_I to S_{VI} represents a plot of the same data, since in the case of these one-electron systems this level is the lowest, and therefore corresponds to the ionizing energy. Furthermore, a comparison with the slope of

the line for which $\frac{\Delta\sqrt{\nu/R}}{\Delta N} = 1/2$, is evidence, as in the case of the K levels, for elements of high atomic number, that the total quantum number for these levels is equal to 2.

In table 14 a stair-like line has been drawn to the right of those values which correspond to the complete removal of the electrons in the valence shell. Thus in the case of Be it requires 0.70 units to remove the first s electron, 1.34 more units to remove the second (total = 2.04 to remove both valence electrons), but as the third electron belongs to the He "shell," the energy required to remove this one is considerably greater (11.4 units) and to remove the fourth one requires 16.0 units more. A better conception of the actual amounts of energy required for these various processes is obtained by converting these results into gram calories per gram atom.

Energy in kgm. calories per gram atom for removal of electrons in Be

ELECTRONS REMOVED	ENERGY	TOTAL ENERGY
1	218.7	218.7
2	418.6	637.3
3	3561	4198
4	4998	9198

The last column gives the *total energy* required for the removal of 1, 2, 3 or 4 electrons respectively. Comparing with these values the chemical energy of formation of BeCl_2 , 155 kgm. cal. per gram mol, it is seen that in general the energy of removal of one electron from the valence shell is of the same order of magnitude as chemical heats of formation, while that required for the removal of two or more electrons is usually larger than any chemical energy of formation. But the energy required to remove electrons from the rare gas shells underneath the valence shells is of a much different order of magnitude.

Now it is very interesting that the Moseley line shown in figure 10 for the series He_I , Li_{II} , Be_{III} , B_{IV} , and C_V (in all of which the electron removed belongs to the He shell) has a slope which is exactly *twice that for the series Li_I to O_{VI}* . (In the diagram the

slopes actually appear the same because the values of $(1/2)\sqrt{v/R}$ have been plotted.) This again is in agreement with the conclusion that in these atoms the electrons are in the $1s$ level.

Passing to the series Na-A, we find relations between the different ionizing energies similar to those observed for the first series. The Moseley diagrams for iso-electronic systems are shown in figure 11. The slope is not as well defined, but is

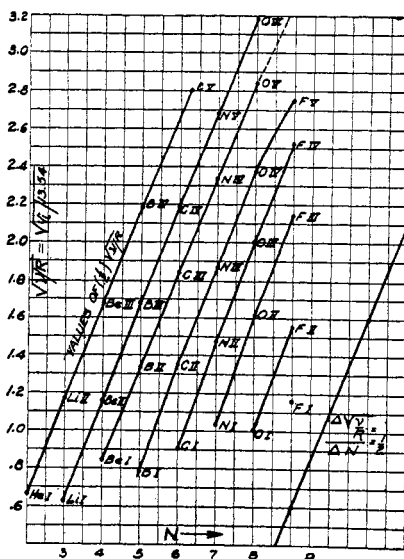


FIG. 10

FIG. 10. MOSELEY DIAGRAM OF IONIZATION POTENTIALS OF "STRIPPED" ATOMS OF SERIES Li to F

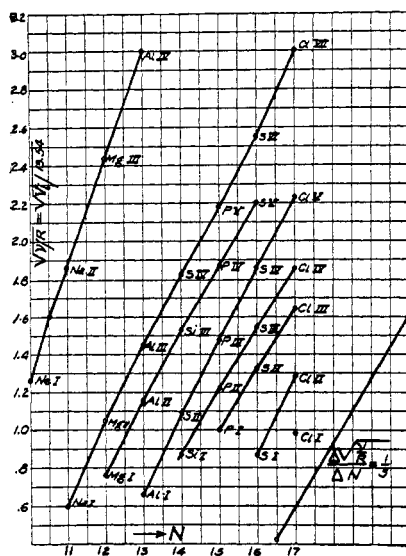


FIG. 11

FIG. 11. MOSELEY DIAGRAM OF IONIZATION POTENTIALS OF "STRIPPED" ATOMS OF SERIES Na to Cl

approximately $1/3$, and here it is also observed that the values for the series Ne_I to Al_{IV} (which is analogous to the series He_I to C_V) shows the slope $1/2$, indicating that the electrons in these systems are in levels for which the total quantum number is 2, while in the systems $Na_I - Cl_{VII}$, etc., the electrons are in $3s$ levels.

For any one atomic system the value of the total energy for the removal of n electrons varies approximately linearly with n^2

(at least for larger values of n). Thus in the case of Ti, the values of n^2 and the corresponding values of the total energy (in the units used in table 14) are as follows:

n^2	1	4	9	16
Total energy.....	0.50	1.50	3.54	6.72
Ratio.....	0.50	0.38	0.39	0.42

There are other interesting relations which may be deduced from the data in table 14 but as a result of the discussion already given in this and previous sections it is evident that from a study of the energy terms in the spectra of stripped atoms it is possible to derive conclusions regarding the processes by which atoms are formed by the addition of successive electrons. We thus see in the spectra of these ionized atoms a process which is the reverse of that observed in x-ray spectra. But it is equally worthy of note that both lines of evidence lead to similar conclusions regarding the nature and distribution of electrons in the various atoms.

MAGNETIC PROPERTIES IN RELATION TO SPECTRAL TYPE

In view of the effect of magnetic fields on spectral terms it is natural to look for some relation between magnetic properties of atoms and the corresponding electron distribution. While it is not intended in the present connection to discuss this topic at great length, there are certain special points which may be mentioned briefly since they bear a direct relation to the conclusions based on investigations of spectral terms.

The fact that $\Sigma m = 0$ for all the electrons in a completed level is obviously in agreement with the observed diamagnetic properties of the rare gas elements. Also the experiments of Gerlach and Stern on the deflections of atomic beams in magnetic fields have served to throw additional light on the values of m for the atoms tested in their experiments. Finally Sommerfeld, Hund and Bose have attempted to develop theories of ionic paramagnetism on the basis of the electronic distributions assigned to the atoms in table 6.

In order to understand these theoretical considerations it is necessary, however, to refer briefly to the discussion of the Zeeman effect given previously. According to Larmor's theory, the magnetic moment due to an angular momentum of quantum number l is given by $\frac{e}{2m_0c} \cdot \frac{h}{2\pi} l$. The unit magnetic moment, $\frac{eh}{4\pi m_0c} = \mu_B$, is known as a Bohr *magneton* and corresponds to a magnetic moment per gram atom of $M_B = 6.06 \times 10^{23} \cdot \mu_B = 5584$ gauss. For an atomic system of quantum number, j , the magnetic moment, μ , is given by $\mu = \mu_B \cdot jg$ where g is Landé's factor. As mentioned previously, g gives the difference in energy between the different orientations in a magnetic field, and depends upon the values of L and j for the particular atomic state. Thus for a 2S_1 term in a weak magnetic field, $g = 2$, and hence $gj = 1$. Consequently the atoms of group I in the normal state possess *one* Bohr magneton.

MAGNETIC DEVIATION OF ATOMIC RAYS

Confirmation of this conclusion regarding the magnetic moments of the alkali atoms has been obtained by Gerlach and Stern in experiments which they have carried out at Frankfurt since 1921. As Stoner has stated (10):

In these investigations possible magnetic moments of atoms in the field direction are determined; the beauty of the experiments themselves, and the theoretical significance of the results, combine to make the research one of outstanding interest and fundamental importance.

In the experiments the element under investigation is heated in a small oven, and the evaporating atoms escape through an aperture; by means of a suitable system of slits a narrow unidirectional stream of atoms is produced, the velocity of the atoms depending on the oven temperature. The stream passes through a region in which a non-homogeneous (magnetic) field may be applied, the field and its gradient being at right angles to the stream, and the atoms impinge on a glass plate, forming a thin deposit, which can be rendered visible; from the traces obtained (giving the cross-section of the stream) with and without field the deviation produced by the field may be determined.

In the case of an atom for which the magnetic moment is one magneton two spots should be obtained in a magnetic field at equal distances from the zero position, corresponding to the two possible orientations of the magneton in a magnetic field, and actually this result was obtained for Cu, Ag and Au for each of which as shown in table 6 the normal term is 2S_1 .

No effect was observed for the vapors of Zn, Cd and Hg, which again is in accordance with the predictions based on the type of the normal term (1S_0), since for $j = 0$, the atom possesses no magnetic moment. Similar results were obtained for Sn and Pb for which $j = 0$. In the case of Ni and Fe, the results obtained by Gerlach and Stern are not so readily interpreted but indicate magnetic moments which are not those expected from the j -values for the normal terms.

PARAMAGNETISM OF IONS IN RELATION TO SPECTRAL TYPE

For an ionized atom the number of Bohr magnetons may be calculated from the electron distribution in the same manner as for the neutral atoms, that is, by the relation $\mu = \mu_B g j$ where j is the inner quantum number for the normal term in the ionized atom. Thus for Ca^+ and Sc^{++} the magnetic moment is one magneton, the same as for K . In the case of other elements of the second long period the first stage in the process of ionization consists in the removal of the two $4s$ electrons. Hence the normal terms for Ti^{++} and Fe^{++} are 3F_2 and 5D_4 respectively, while for Fe^{+++} , for which the electron configuration is $(3d)^5$, the normal term is 6S_3 .

Assuming that the same electron configurations are valid for the ions in solution it should be possible as was first pointed out by Sommerfeld (30), to calculate the magnetic moments from the j -values of the corresponding spectral terms. Hund (31) has applied these considerations to the calculation of the magnetic moments of the trivalent ions of the rare earths in solution and finds that the theoretical results are in very good agreement with the experimentally observed magnetic susceptibilities.

On the other hand, in the case of divalent and trivalent ions of the series Sc-Zn, the agreement is not so good. In explanation

it has been suggested by Hund that for these ions the different terms corresponding to any given electron configuration have energy values that are so near each other that probably the discrepancy is due to lack of knowledge of the particular value of j which should be used in the calculation of μ . It is true that Sommerfeld obtained good agreement by assuming that the ions are in an S state, for which, independently of the value of r , the number of magnetons is 1. However, this assumption cannot be justified on the basis of spectral terms.

In a recent paper, D. M. Bose (32) has brought forward the suggestion that in the case of the paramagnetic ions of the iron group only the magnetic moment due to the spin of the electrons is effective. This is, at first glance, the same hypothesis as that of Sommerfeld's since it corresponds to the assumption that the spectral term is of type $L = 0$ (that is, an S term). According to Bose, however, the difference between the two points of view is as follows:

According to Sommerfeld the magnetic moment of an atom or ion is an unalterable magnitude, $\mu = n \cdot \mu_B$ (where n = number of Bohr magnetons) and in a magnetic field the atom can orient itself as a whole along certain discrete directions with respect to the field. . . . According to the view here presented (Bose's), μ is no longer a fixed magnitude and there is no definite orientation for the atom as a whole in a magnetic field. The magnetic moment is made up of the algebraic sum of the spin moments of the individual electrons in an uncompleted shell, some of which are oriented parallel and the rest anti-parallel to the direction of the field.

The agreement between the calculated values based on this theory and experimental observations is found to be satisfactory for trivalent and divalent ions of the elements Ti to Cu. But when the same theory is applied by Bose to the case of the trivalent ions of the rare earths, no agreement at all is found, whereas Hund's calculations, as mentioned previously, led to concordant results.

On the whole, therefore, we must regard this problem of correlation between magnetic moments and electron configurations as still in a developmental stage, and further investigations of a

theoretical nature are necessary before all the observed phenomena can be accounted for satisfactorily.

SPECTROSCOPIC TERMS AND VALENCE OF ATOMS

Naturally the chemist will seek for some connection between electronic configuration in the valence shell (or what is equivalent to this, viz., the spectral term) and valence bonds. In the light of present knowledge of atomic structure the essential elements in the conclusions deduced by Langmuir and Lewis over ten years ago regarding the mode of formation of polar and non-polar compounds still remain valid. In fact Langmuir's suggestions regarding electron distribution in the molecules of N_2 , CO and NO have received remarkable confirmation in the results obtained by R. S. Mulliken from an examination of energy levels in the band spectra of these molecules.

However, a number of papers have appeared in the past few years, in which attempts have been made to correlate more intimately the valence and co-valence relations of atoms with the electronic configurations as given in table 6. While it is intended to discuss the views of these writers at greater length in another paper, it may not be out of place to mention rather briefly some of these in the present connection.

Thus H. A. Grimm and A. Sommerfeld (33) have pointed out that the valence is intimately connected with the electronic configuration in the incompleting level, but their remarks are really a re-statement, in terms of Stoner's classification, of relations which Langmuir had derived on the basis of the octet theory.

In a previous section mention was made of Stoner's suggestion that the p , d and f levels really consist each of two sub-groups, which may be designated in accordance with the corresponding j values as p_1 , p_2 ; d_2 , d_3 ; f_3 and f_4 respectively. The principal argument for this sub-division is the existence of corresponding x-ray levels as indicated in table 7 and figure 4. Stoner assumed that in the gradual completion of, say, the p level, the p_1 level would be completed first with 2 electrons and then the p_2 level with 4 electrons. Similarly the d_2 and d_3 sub-levels require 4 and 6 electrons respectively to complete them, while the f_3 and f_4 sub-levels require 6 and 8 electrons respectively.

In a series of papers published during the past two years, H. Lessheim and R. Samuel (34) have suggested that the valence relations of atoms are governed by the distribution of the valence electrons in these sub-levels. In arriving at this distribution they have modified Hund's method for deriving spectral terms in this respect that they add vectorially the angular momenta corresponding to the quantum numbers $m = j, j-1, \dots -j$, and $\mu = l - j$, for the case $m \leq l-s$, or $\mu = m - (j-s)$ for the case $m \geq l-s$. As a result they obtain for the normal term, the same result as Hund for the atoms in the first half of any level, but obtain the term with *lowest value* of j for the atoms in the second half (instead of highest value of j which Hund derives).

The method thus involves as a preliminary step the assignment of j values to the different electrons, that is, a division of the electrons in any one level into sub-levels with corresponding values of j . For instance, according to this point of view the distribution of electrons in the two p -levels for the atoms B to Ne (and similarly for the atoms Al to A) is as follows:

	p_1	p_2	NORMAL TERM]	NORMAL TERM (HUND)
B	1		$^2P_{1/2}$	$^2P_{1/2}$
C	2		3P_0	3P_0
N	3		$^4S_{3/2}$	$^4S_{3/2}$
O		4	3P_0	3P_2
F	1	4	$^2P_{1/2}$	$^2P_{3/2}$
Ne	2	4	1S_0	1S_0

The last two columns give the normal terms as derived by Lessheim and Samuel and compared with these, those derived by Hund. The fact that the latter is in agreement with spectroscopic observation would argue strongly against the view suggested by the former. Furthermore, it would appear meaningless to assign a j value to any one electron in a group of electrons since physically this quantum number can only apply to the atom as a whole and, therefore, to the resultant of the l 's and s 's for the individual electrons.

Obviously, with a distribution of electrons in two subgroups it

is easier to correlate these with observed valences. For example, in the case of S, $(s)^2(p)^4$, valences of 2, 4 and 6 are readily explained, while in that of Cl, for which the configuration is $(s)^2(p_1)(p_2)^4$, valences of 1, 3, 4, 5 and 7 are to be expected.

However, it would seem to the present writer that the arguments for assigning these distributions in sub-levels are not very sound, and a great many of the conclusions derived by Lessheim and Samuel can be derived without any recourse to assumptions such as they have made.

The problem of co-valency has been treated from the point of view of Bohr's earlier classification of electron levels by R. H. Fowler (35) and N. V. Sidgwick (36). The former suggests that in coördination compounds of Co, Fe, Pt, etc., we may have 12 electrons shared just as in Langmuir's theory, 8 electrons are shared. This would account for a co-valency of 6. Similarly Sidgwick concludes that in the acetyl acetone compounds of elements of higher atomic weight, a co-valency of 8 exists because of the tendency to share 16 electrons.

CONCLUDING REMARKS

While the details regarding spectral terms of a large number of atoms still remain to be investigated, the framework into which these details must fit has been constructed. We can now obtain a perspective, as it were, not only of the manner in which atoms are built up by the addition of successive electrons, but also of interactions between these electrons, compared to which the "harmony of the celestial spheres" is a very simple phenomenon.

Once more the periodic arrangement appears as the most significant guiding principle in the whole of physical science; but where Mendeljeff and Newman saw only certain chemical aspects and atomic weights, the work of the spectroscopists, interpreted along the lines first suggested by Bohr, has led to a revelation that beyond the gross properties of atoms there exist as governing factors a nuclear charge and electrons in definite configurations.

The next great advance in chemistry is going to consist in developing the relations between the energy levels in atoms and those in the molecules which result from their combination. A

beginning has already been made by investigators like R. S. Mulliken, R. T. Birge, J. Franck and others, in the study of energy levels in molecules from band spectra and the correlation of heats of dissociation with observations on absorption limits in these band spectra. But a great deal remains to be accomplished and more and more the physical chemist will find in the investigations of the spectroscopic phenomena of molecules guidance to the ultimate understanding of the hitherto illusive conception of chemical bonds.

In conclusion, the writer wishes to express his appreciation of the help which he has received towards an understanding of Hund's ideas from Professor Russell's published papers and personal correspondence with him on some of the difficulties.

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