

Ordering of the excited-state energy levels of various atoms and their isoelectronic ions*

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In a previous paper, the quantum number $k \equiv n + l$ was considered as an energy-ordering quantum number for the excited states of the alkali-metal atoms and the singly ionized alkaline-earth atoms. It was shown that the energy levels of the valence electron in these cases of a single electron outside a core of closed shells are energy ordered according to the values of k and, moreover, within each k group, there is a definite constant sequence of l values for each atom or ion as the electronic energy is increased; this sequence has been called the " l pattern." In the present work, these considerations are extended to 33 additional spectra of atoms and their isoelectronic ions, which possess a single (n_0s or n_0p) electron or two electrons [$(n_0s)^2$] outside of closed shells in their ground states. An additional 852 energy levels are investigated which exhibit k ordering with very few exceptions. In addition, these spectra possess constant l patterns, which are generally independent of k . Thus the statistics in favor of the k ordering and the l patterns now comprise a total of 1155 levels (including the 303 levels previously investigated). Also discussed are the regions of validity of k ordering and hydrogenic ordering as a function of the atomic number Z and the degree of ionization $Z-N$.

I. INTRODUCTION

In a previous paper,¹ we introduced the concept of the quantum number

$$k \equiv n + l \quad (1)$$

as an energy-ordering quantum number for the excited-state energy levels of the neutral alkali-metal atoms (i.e., Na, K, Rb, and Cs) and the singly ionized alkaline-earth atoms (i.e., Mg⁺, Ca⁺, Sr⁺, Ba⁺, and Ra⁺). In Eq. (1), the usual notation is used, i.e., n is the principal quantum number and l is the azimuthal quantum number of the one-electron state considered (single electron outside closed shells). It should be noted that the sum $n + l$ had been previously considered by Madelung² and by several other workers (see Refs. 2-10 and 12-14 in Ref. 1), in connection with the order in which the successive electron shells are filled for the ground states of the atoms of the Periodic Table of the chemical elements.

We have also considered the difference

$$q \equiv n - l \quad (2)$$

in connection with the ratio of the quadrupole shielding (or antishielding) factors³ R for two states of both copper ($3d$ and $4p$) and terbium ($4f$ and $5d$).^{4,5} From Eqs. (1) and (2), it follows that

$$q = k - 2l, \quad (3)$$

which shows at once that the possible values of q increase in steps of two units. Thus, for even k we have

$$q = 2, 4, \dots, k - 2, k, \quad (4)$$

and for odd k , we have

$$q = 1, 3, \dots, k - 2, k. \quad (5)$$

The value $q = 0$ is excluded since $q = n - l \geq 1$. The quantum number q has been referred to as the "radial-node quantum number," since $n - l - 1 = q - 1$ is the number of nodes of the (nonrelativistic) radial wave function of the state nl . A description of the successive filling of electron shells as the atomic number Z is increased, in terms of k and q , has been given in Table I of Ref. 1. We note that this table predicts that the first h state (namely, $6h$) will occur in the vicinity of $Z_{6h} = 221$, and the first i state (namely, $7i$) will be found in the vicinity of $Z_{7i} = 365$, if such superheavy elements can actually be produced at some future time. It is of interest that these results are in good agreement with the values obtained by Abrahamson,⁶ namely, $Z_{6h} = 222$ and $Z_{7i} = 367$.

The extensive evidence for the relevance of the quantum number k to the energy-level structure of the alkali-metal atoms and the alkaline-earth ions has been verified by means of the extensive tables of Moore.⁷ The spectral energy values [averaged over the j states $j = l + \frac{1}{2}$, $j = l - \frac{1}{2}$, using the weighting factor $(2j + 1)$] for the alkali-metal atoms Na, K, Rb, and Cs have been given in Tables II-V of Ref. 1. The corresponding average spectral energy values for the alkaline-earth ions Mg⁺, Ca⁺, Sr⁺, Ba⁺, and Ra⁺ have been listed in Tables XI-XV. From these tables, it is seen that the levels with the same value of k (but different values of n and l) are grouped together if the levels are listed in order of increasing energy. This phenomenon has been referred to as " k ordering" in Ref. 1. In addition, levels with a given constant value of k are energy ordered according to a definite sequence of

l values, which has been called the " l pattern," and which is in general independent of k . The l pattern is characteristic of a given atom (alkali-metal atom) or ion (alkaline-earth ion). Occasionally a level with a given value of k , namely, k_0 , lies in the region occupied by levels with $k = k_0 + \lambda$, where λ is generally +1 or -1. These so-called $(k + \lambda)$ exceptions have been clearly marked in the tables of Ref. 1.

The statistics in favor of k ordering are considerable, as shown in Table XVI of Ref. 1. Thus a total of 303 levels have been considered for the nine spectra investigated, and the total number of $(k + \lambda)$ "exceptions" is only 39. The possible implications of the k ordering and the constant l patterns have been discussed in Sec. IV of Ref. 1, and we will present additional considerations on these questions in Sec. III of the present paper.

Since the k ordering is so prevalent for atoms with one electron outside closed shells, as discussed in Ref. 1, we have been led to make a more thorough investigation of the extensive and very valuable tables of Moore,⁷ in order to list systematically all of the spectra of neutral atoms and their isoelectronic ions, which contain a single (ns or np) electron outside closed shells in their ground states. In addition, a large number of excited states of the alkaline-earths (Mg, Ca, Sr, Ba, and Ra) have been considered, which belong to the configuration n_0s, nl , where $(n_0s)^2$ is the ground-state configuration, and therefore a single electron has been excited from n_0s to the excited state nl . (Thus $n_0 = 3$ for Mg, $n_0 = 4$ for Ca, etc.) We believe that we have thus included essentially all spectra which exhibit pure k ordering, with relatively very few exceptions of the type $(k + \lambda)$, as discussed above. Moreover, along with the extensive k ordering, we have found constant l patterns in the overwhelming majority of the cases (i.e., l patterns independent of k). However, in a few cases, the l pattern changes somewhat as k is increased.

In Sec. II, we will discuss these additional cases of k ordering, and we will present the tables of the j -averaged energy values for some representative cases. Altogether we have investigated an additional 852 levels, which involve only 81 exceptions of the type $(k + \lambda)$, so that the total statistics in favor of k ordering (including the 303 levels of Ref. 1) consist presently of 1155 levels, with only 120 exceptions. Altogether 33 additional spectra have been investigated, giving a total of 42 spectra (including the nine spectra of Ref. 1). These results permit us in turn to make some general statements about the relative frequencies of different l patterns, which will be discussed at the end of Sec. II.

As already noted, in Sec. III, we will discuss the

general implications of the present results, when combined with those of Ref. 1.

II. EVIDENCE FOR k -ORDERING FROM THE SPECTRA OF THE GROUP IB, IIA, IIB, AND IIA ELEMENTS OF THE PERIODIC TABLE AND THEIR ISOELECTRONIC IONS

In considering additional cases of effective "one-electron" spectra, we were first led to consider whether the excited states of the group IIIA elements exhibit k ordering, i.e., the excited states of the Al, Ga, In, and Tl atoms which possess a single p electron outside closed shells. The answer is definitely positive, if we exclude the very few cases in which one of the electrons of the closed n_0s^2 shell is excited. We have also included in this study the ions which are isoelectronic with Al, Ga, In, and Tl, and whose ionicity $Z - N$ (N is the number of electrons) is not too large. The reason is that, as has been discussed extensively in Ref. 1, if $Z - N$ is too large (generally >2), the ordering of the energy levels rapidly becomes hydrogenic, i.e., levels with the same value of n are grouped together, with a small increase of the energy within each n group as l is increased.

The spectra which have been investigated are listed in Table I. Here we have employed the usual spectroscopic notation, e.g., AsIII means As^{2+} , and in general element ZM signifies the element Z in the ionization state $(M - 1)^+$, i.e., $Z^{(M-1)+}$. Table I lists the number N_L of levels included, the number N_E of exceptions of the type $(k + \lambda)$, the ratio N_E/N_L , and the l pattern. It is seen that while for 10 out of 11 spectra, the l pattern is independent of k , for the case of InI, the pattern changes from $pdsf$ for $k = 6, 7, 8$ to $dpsf$ for $k \geq 9$. This means, of course, simply that the energy difference $E_{kd} - E_{kp}$ decreases from positive values for $k = 7, 8$ to negative values for $k \geq 9$. (This can also be seen in detail from Table IV which lists the energy levels for InI.) It is more remarkable that some spectra (SiII, GeII) show only two exceptions ($N_E = 2$), and for five spectra, namely AsIII, SnII, SbIII, PbII, and BiIII, there is no $k + \lambda$ exception, i.e., the k ordering is perfect. The most striking example among these five spectra is that of PbII, which shows no "exception" in a total of 50 observed levels.

In order not to lengthen the paper excessively, we have shown only six (out of the eleven) spectra, namely those of GaI, GeII, InI, SnII, TlI, and PbII in Tables II-VII, respectively. For each level, we have listed the value of k and the energy E_{nl} above the ground state, which is $n_0p_{1/2}$ ($n_0 = 4$ for Ga, $n_0 = 5$ for In, and $n_0 = 6$ for Tl). The reason why there is nevertheless a listing for n_0p is that the $(2j + 1)$ average was taken, i.e.,

TABLE I. Spectra of group IIIA elements and their isoelectronic ions, having a single n_0p electron in the ground state, outside a core of closed shells. The number of levels included in the spectrum is denoted by N_L , while N_E denotes the number of "exceptions" of the type $k + \lambda$, as explained in the text. The last two columns list the values of the ratio N_E/N_L and the l pattern associated with the spectrum. For In I, two different l patterns are found, corresponding to the k regions $k \leq 8$ and $k \geq 9$, respectively. Representative spectra of group IIIA elements and their isoelectronic ions are listed in Tables II–VII for Ga I, Ge II, In I, Sn II, Tl I, and Pb II, respectively.

Spectrum	N_L	N_E	N_E/N_L	l pattern
Al I	18	5	0.278	<i>fdps</i>
Si II	13	2	0.154	<i>fdps</i>
Ga I	23	4	0.174	<i>pdsf</i>
Ge II	27	2	0.074	<i>gdjfs</i>
As III	7	0	0	<i>fdps</i>
In I	49	9	0.184	$\left\{ \begin{array}{l} \textit{pdsf} \text{ for } k=6-8 \\ \textit{dpsf} \text{ for } k \geq 9 \end{array} \right.$
Sn II	25	0	0	<i>gdpsf</i>
Sb III	8	0	0	<i>dpfs</i>
Tl I	27	4	0.148	<i>pdsf</i>
Pb II	50	0	0	<i>dpjfs</i>
Bi III	17	0	0	<i>dpjfs</i>
Total ⁽¹⁾ p	264	26	0.098	

$$\begin{aligned}
 E(n_0p) &= \frac{1}{3} E(n_0p_{\frac{1}{2}}) + \frac{2}{3} E(n_0p_{\frac{3}{2}}) \\
 &= \frac{2}{3} E(n_0p_{\frac{3}{2}}) \\
 &= \frac{2}{3} \Delta\nu_{n_0p}, \tag{6}
 \end{aligned}$$

where $\Delta\nu_{n_0p}$ is the fine-structure splitting for the ground state of the atom or ion. In Moore's tables and therefore in Eq. (6), $E(n_0p_{\frac{1}{2}})$ is taken as the zero of energy for the spectrum.

TABLE II. Excitation energies E_{nl} (above the ground state $4p_{1/2}$) for the excited states of the neutral gallium atom, corresponding to the spectrum Ga I. The weighted averages over the states $j=l+\frac{1}{2}$ and $j=l-\frac{1}{2}$ (with respective weighting factors $2j+1$) are listed. Thus the entry for $4p$ represents $\frac{2}{3}E(4p_{3/2})$, with $E(4p_{1/2})$ taken as the zero of energy [see Eq. (6)]. The superscript (+1) or (+2) after the value of E_{nl} indicates the value of λ , i.e., the level with the listed value of $k=n+l$ lies in the region occupied by most (or all) of the levels contained in the group $k+\lambda$. The convention with respect to the superscript (λ) is the same for similar tables which follow, namely III, IV, VI, XI, and XIII. The comment with respect to the ground state holds also for the lowest states E_{n_0p} in Tables III–VII. The level listed below the ionization limit (last row) corresponds to the excitation of one of the two $4s$ electrons to give the configuration $4s4p^2$. The l pattern is *pdsf*. The energy values for the various J states in this and the following tables (Tables III–VII and X–XIII) were obtained from the tables of Moore (Ref. 7).

nl	$k=n+l$	$E_{nl}(\text{cm}^{-1})$	nl	$k=n+l$	$E_{nl}(\text{cm}^{-1})$
$4p$	5	551	$8d$	10	45971
$5s$	5	24789	$5f$	8	46131 ⁽⁺²⁾
$5p$	6	33118	$10s$	10	46274
$4d$	6	34786	$9d$	11	46549
$6s$	6	37585	$6f$	9	46661 ⁽⁺²⁾
$6p$	7	40404	$11s$	11	46758
$5d$	7	40808	$10d$	12	46942
$7s$	7	42158	$7f$	10	47022 ⁽⁺²⁾
$7p$	8	43455	$12s$	12	47093
$6d$	8	43579	Limit		48380
$4f$	7	43955 ⁽⁺¹⁾	$4s4p^2$		49213
$8s$	8	44332			
$7d$	9	45074			
$9s$	9	45537			

TABLE III. Excitation energies E_{nl} (above the ground state $4p_{1/2}$) for the excited states of the germanium ion, corresponding to the spectrum Ge II. The convention with respect to the superscript (λ) is explained in Table II. The l pattern is $gdffs$. Below the value of the ionization limit, we have listed the j -weighted averaged energy values of three configurations which correspond to excitation of the $4s^2$ configuration, namely $4s4p^2$, $4s4p5s$, and $4p^3$. Since these are not one-electron excitations, no k values can be assigned to them.

nl	$k=n+l$	$E_{nl}(\text{cm}^{-1})$	nl	k	$E_{nl}(\text{cm}^{-1})$
4p	5	1178	8d	10	119342
5s	5	62402	7f	10	119373
5p	6	79246	7g	11	119521 ⁽⁻¹⁾
4d	6	80942	10s	10	120976
6s	6	94784	9d	11	121513
5d	7	100114	8f	11	121531
4f	7	100317	10d	12	122996
6p	7	101243	9f	12	123007
7s	7	107935	11d	13	124054
6d	8	110389	10f	13	124062
5f	8	110504	Limit		128518
7p	8	111016	4s4p ²		66866
8s	8	114638	4s4p5s		123534
7d	9	115983	4p ³ (⁴ S)		136237
6f	9	116041			
6g	10	116266 ⁽⁻¹⁾			
9s	9	118522			

At the bottom of each spectrum, we have listed the ionization limit, and below the limit, for comparison, the energy of the $(2j+1)$ -weighted average of the levels of the configuration $n_0s(n_0p)^2$, corresponding to the excitation of one of the n_0s electrons. Also some additional average energies are listed for GeII and SnII. These energy values are not directly relevant to the k ordering, since they do not correspond to a single nl electron outside a closed n_0s^2 configuration.

The ground states of the group IB elements, i.e., the noble metals: Cu, Ag, and Au, and their isoelectronic ions have a single s electron outside a closed nd^{10} configuration. The majority of the excited states have the configuration $nd^{10}n'l'$, i.e., the nd shell remains closed. However, in some cases an nd electron is excited, so that the configuration becomes $nd^9n'l'n''l''$. If we exclude these levels as not being "single particle" levels, we obtain the results of Table VIII, which gives the statistics for 192 levels, with only $10(k+\lambda)$ exceptions, in a total of nine spectra. Of these nine spectra, only one exhibits a change of the l pattern (CuI). Especially remarkable are the four spectra: CuI, CdII, HgII, and TlIII, which show perfect k ordering [no $(k+\lambda)$ "exceptions"].

The remaining systems which have been investigated constitute the group of 13 atoms and ions for which the statistics and patterns are listed in Table IX. The first five spectra, namely, MgI, CaI,

SrI, BaI, and RaI, correspond to the neutral alkaline-earth atoms (group IIA elements). The overwhelming majority of their excited levels correspond to the configuration n_0s, nl , which can be considered to be effectively a one-electron excitation, in the approximation in which the spherical n_0s electron distribution is considered to be a part of the core. The statistics, as far as the k ordering is concerned, are quite good, in particular for CaI, which has no $(k+\lambda)$ exception in a total of 42 levels investigated. However, it is perhaps not coincidental that the l patterns change with k for three out of five cases (CaI, BaI, and RaI).

As an illustration of these alkaline-earth spectra, we have listed the weighted average energy levels for the CaI and SrI spectra in Tables X and XI, respectively. We note that below the ionization limit, we have also listed the weighted energy values for a few levels in which both ns electrons are excited. It may be noted that for two nonequivalent electrons n_1l_1, n_2l_2 , the sum of all of the $(2j+1)$ weights is given by

$$\sum_j (2j+1) = 4(2l_1+1)(2l_2+1). \quad (7)$$

The right-hand side can be interpreted as the total number of spin states (4) times the total number of angular momentum states. In the left-hand side, the sum must be taken over all Russell-Saunders coupling configurations.

Concerning Tables X and XI (and also Tables XII and XIII below), it may be remarked that since there is no fine structure in the ground state $(n_0s)^2$, the ground-state energy E_{n_0} is zero, as indicated.

The remaining entries of Table IX pertain to the Group IIB atoms, namely Zn, Cd, and Hg, and their isoelectronic ions. The configurations n_0s, n_1l are one-electron excitations in the same sense as for the alkaline-earth atoms, which have been the subject of the preceding discussion. The representative spectra of ZnI and InII are given in Tables XII and XIII, respectively. The ratio N_E/N_L of exceptions to number of levels is about the same as for the group IIA atoms discussed above, but it may be significant that for the group IIB cases, the l patterns are completely independent of k for all of the spectra, as contrasted to the situation for three of the group IIA atoms.

The lower part of Table IX summarizes the statistics concerning the k ordering, for all of the ca-

ses which have been investigated up to now, including those of Ref. 1. Concerning the notation, "Total^{(2)s}" refers to the cases of Table IX, in which two s electrons are outside closed shells in the ground state [configuration $(n_0s)^2$]; "Total^{(1)p}" refers to the cases of Table I (group IB) in which a single s electron is outside a closed d shell in the ground state.

The last two rows of the table include the totals from Ref. 1 (alkali-metal atoms and alkaline-earth ions), and finally the "Grand Total" for all levels included in the present paper and in Ref. 1. Altogether 42 spectra have been included in the present investigation, so that the average number of levels per spectrum is $1155/42 = 27.5$, and the average number of $(k + \lambda)$ exceptions is $120/42 = 2.86$.

In Table XIV, we have listed the seven different l patterns ($l_1l_2l_3l_4$) which have been encountered, the spectra in which they occur, the frequency of each pattern N_p , and the minimum and maximum

TABLE IV. Excitation energies E_{n_1} (above the ground state $5p_{1/2}$) for the excited states of the neutral indium atom, corresponding to the spectrum In 1. The l pattern is $pdsf$ for $k = 6$ to 8, and $dp sf$ for $k \geq 9$. The state $5s5p^2$ (in the last row) corresponds to an excitation of the closed $5s$ shell, i.e., of $5s^2$.

n_1l	$k = n_1 + l$	$E_{n_1}(\text{cm}^{-1})$	n_1l	k	$E_{n_1}(\text{cm}^{-1})$
5p	6	1475	12d	14	45499
6s	6	24373	10f	13	45564 ⁽⁺¹⁾
6p	7	32016	14s	14	45630
5d	7	32906	13d	15	45706
7s	7	36302	11f	14	45757 ⁽⁺¹⁾
7p	8	38936	15s	15	45807
6d	8	39078	14d	16	45863
4f	7	39708 ⁽⁺¹⁾	12f	15	45903 ⁽⁺¹⁾
8s	8	40637	16s	16	45942
7d	9	41852	15d	17	45987
8p	9	41863	17s	17	46047
5f	8	42220 ⁽⁺¹⁾	16d	18	46079
9s	9	42719	18s	18	46132
8d	10	43347	17d	19	46156
9p	10	43390	19s	19	46200
6f	9	43584 ⁽⁺¹⁾	18d	20	46220
10s	10	43881	20s	20	46256
9d	11	44243	19d	21	46272
10p	11	44288	21s	21	46302
7f	10	44406 ⁽⁺¹⁾	20d	22	46316
11s	11	44596	22s	22	46342
10d	12	44822	Limit		46670
11p	12	44862	5s5p ²		45946
8f	11	44939 ⁽⁺¹⁾			
12s	12	45067			
11d	13	45217			
9f	12	45303 ⁽⁺¹⁾			
13s	13	45394			

TABLE V. Excitation energies E_{nl} (above the ground state $5p_{1/2}$) for the excited states of the tin ion, corresponding to the spectrum Sn II. The l pattern is $gdpsf$. The states $5s5p^2$ and $5s5p6s$ (in the last two rows) correspond to excitations of the closed $5s$ shell, i.e., of $5s^2$. We note that no $(k+\lambda)$ exceptions occur in all of the 25 states listed, i.e., we have $N_E=0$ and perfect k ordering for this spectrum.

nl	$k=n+l$	$E_{nl}(\text{cm}^{-1})$	nl	k	$E_{nl}(\text{cm}^{-1})$
$5p$	6	2 834	$7g$	11	109 000
$6s$	6	56 886	$9d$	11	109 018
$5d$	7	71 791	$11s$	11	110 695
$6p$	7	72 083	$8g$	12	111 118
$7s$	7	86 280	$10d$	12	111 136
$4f$	7	89 289	$9g$	13	112 570
$6d$	8	90 310	$11d$	13	112 598
$7p$	8	92 145	Limit		118 017
$8s$	8	98 402	$5s5p^2$		61 038
$5f$	8	99 661	$5s5p6s$		112 292
$7d$	9	100 317			
$8p$	9	101 323			
$9s$	9	104 680			
$6f$	9	105 367			
$6g$	10	105 735			
$8d$	10	105 751			
$9p$	10	106 368			
$10s$	10	108 354			

values of Z , Z_{\min} , and Z_{\max} , for which a given pattern is found. For the six cases in which the l pattern changes with increasing k , we have indicated the region of k (or the particular k values) for which the given pattern applies. Thus we have listed $42 + 6 = 48$ entries corresponding to all possible

patterns for the 42 spectra included in the present analysis. The spectra which are underlined correspond to those of Table IX pertaining to the group IIA and IIB elements (and isoelectronic ions). For these cases, there are two n_0s electrons in the ground state, but the excitations considered,

TABLE VI. Excitation energies E_{nl} (above the ground state $6p_{1/2}$) for the excited states of the thallium atom, corresponding to the spectrum Tl I. The l pattern is $pdsf$.

nl	$k=n+l$	$E_{nl}(\text{cm}^{-1})$	nl	k	$E_{nl}(\text{cm}^{-1})$
$6p$	7	5 195	$11p$	12	46 896
$7s$	7	26 478	$10d$	12	46 955
$7p$	8	34 827	$8f$	11	47 005 ⁽⁺¹⁾
$6d$	8	36 167	$12s$	12	47 179
$8s$	8	38 746	$12p$	13	47 466
$8p$	9	41 617	$11d$	13	47 502
$7d$	9	42 034	$13s$	13	47 655
$5f$	8	42 318 ⁽⁺¹⁾	$13p$	14	47 848
$9s$	9	43 166	$12d$	14	47 876
$9p$	10	44 502	$14s$	14	47 983
$8d$	10	44 685	Limit		49 264
$6f$	9	44 824 ⁽⁺¹⁾			
$10s$	10	45 297			
$10p$	11	46 009			
$9d$	11	46 106			
$7f$	10	46 185 ⁽⁺¹⁾			
$11s$	11	46 457			

TABLE VII. Excitation energies (above the ground state $6p_{1/2}$) for the excited states of the lead ion, corresponding to the spectrum Pb II. The l pattern is $dp\text{sf}g$. We note that no $(k+\lambda)$ exceptions occur in all of the 50 states listed. Thus we have $N_E=0$ and perfect k ordering for this spectrum, in the same manner as for Sn* (Table V).

nl	$k=n+l$	$E_{nl}(\text{cm}^{-1})$	nl	k	$E_{nl}(\text{cm}^{-1})$
6p	7	9 387	11d	13	114 491
7s	7	59 448	12p	13	114 685
6d	8	69 274	13s	13	115 496
7p	8	76 334	10f	13	115 655
8s	8	89 180	9g	13	115 797
5f	8	92 520	12d	14	115 901
7d	9	94 896	13p	14	116 037
8p	9	95 851	14s	14	116 615
9s	9	101 346	11f	14	116 729
6f	9	102 874	10g	14	116 833
5g	9	103 559	13d	15	116 912
8d	10	103 872	14p	15	116 958
9p	10	104 821	12f	15	117 521
10s	10	107 930	11g	15	117 600
7f	10	108 533	14d	16	117 660
6g	10	108 968	13f	16	118 121
9d	11	109 304	12g	16	118 183
10p	11	109 734	15d	17	118 230
11s	11	111 574	14f	17	118 588
8f	11	111 942	13g	17	118 637
7g	11	112 230	16d	18	118 675
10d	12	112 444	14g	18	118 996
11p	12	112 726	17d	19	119 027
12s	12	113 912	15g	19	119 286
9f	12	114 147	Limit		121 243
8g	12	114 346	6s6p ²		83 123

TABLE VIII. List of spectra of group IB elements (noble metals) and their isoelectronic ions, having a single n_0s electron outside a closed nd shell (configuration nd^{10}). Among the levels (whose total number is N_L), we have included only those whose configuration is $nd^{10}n'l'$, i.e., where the nd shell remains closed, thus excluding levels of the type $nd^9n_1l_1n_2l_2$ which correspond to a two-electron excitation. As indicated, for Cu I, two different l patterns occur, for $k=5$ to 8, and $k \geq 9$, respectively. In the last row of the table, the totals "Total^{(1)s}" of the N_L and N_E values are listed, together with the corresponding ratio $\Sigma N_E/\Sigma N_L=0.052$. In Total^{(1)s}, the superscript (1) indicates that there is a single valence electron in the ground state, and the superscript s indicates that it is an s electron.

Spectrum	N_L	N_E	N_E/N_L	l pattern
Cu I	22	0	0	$\left\{ \begin{array}{l} pd\text{fs for } k=5 \text{ to } 8 \\ dp\text{fs for } k \geq 9 \end{array} \right.$
Zn II	24	3	0.125	$gfdps$
Ga III	7	1	0.143	$fdps$
Ag I	23	3	0.130	$pdgsf$
Cd II	41	0	0	$gdpsf$
In III	13	2	0.154	$gdpsf$
Au I	19	1	0.053	$pd\text{sf}$
Hg II	35	0	0	$hdpsfg$
Tl III	8	0	0	$dg\text{pfs}$
Total ^{(1)s}	192	10	0.052	

namely n_0s, nl correspond to single-electron excitations.

It is of interest that among the $4! = 24$ possible permutations of the l states $s, p, d,$ and $f,$ only seven are found among the physically realized patterns, all of which end in s or $f,$ i.e., either ks or kf is the highest energy state. For the five patterns which end with $s,$ namely $fdps, dpfs, fpds, pdfs,$ and $dfps,$ we note that they correspond to all but one of the six possible permutations of the l quantum numbers $p, d,$ and $f.$ The missing pattern is $pfds.$

We note that four patterns account for 42 of the spectral entries, namely $fdps, dpsf, dpfs,$ and $pdsf.$ The first pattern considered, namely $fdps,$ is also the sequence in which the atomic ground levels are successively filled up, namely, the se-

quence of decreasing l values, as described by Madelung's rule B (see Refs. 1 and 2). Thus the ten excited state spectra listed for $fdps$ in Table XIV can be regarded as prototypes of the sequence of the filling of ground-state levels, as Z is increased in building up the Periodic Table. From Table XIV, we note that the sequence $fdps$ occurs only in the region of light and medium-light atoms, namely, from $Z_{\min} = 11$ to $Z_{\max} = 33.$ This behavior is in marked contrast to the Z regions for the remaining six patterns, for which Z_{\min} is much larger, namely, $Z_{\min} \geq 29$ (except for the two examples of $fpds$ which occur for KI and CaI). In particular, the sequence $dpsf$ occurs only from $Z_{\min} = 48$ to $Z_{\max} = 88.$ The l pattern $dpfs$ can be derived from the previously mentioned sequence $fdps,$ by simply shifting the f level from the position of lowest en-

TABLE IX. Spectra of group IIA (alkaline earths) and IIB elements and their isoelectronic ions, having a closed n_0s shell in the ground state (configuration n_0s^2), with excited states n_0s, nl as indicated. Although these systems have two external n_0s electrons in the ground state, their configuration in the excited state is $n_0s, nl,$ i.e., a pseudo-one-electron excitation from the ground state. As indicated in the last column, there are two different l patterns for each of the three alkaline-earth atoms: Ca, Ba, and Ra. The last five rows of the table summarize the statistics for N_L and N_E concerning the k ordering for the combined 1155 levels investigated in the present work and in Ref. 1. Thus Total^{(2)s} (two s electrons in ground-state external configuration) is the total for the levels included in the present table (Table IX), while Total^{(1)p} and Total^{(1)s} pertain to Tables I and VIII, respectively, and finally Total (Ref. 1) pertains to the alkalimetal atoms and the alkaline-earth ions considered in Ref. 1. For easier identification, we have also listed in the last column the groups of the periodic table to which the neutral atoms belong, as well as the table concerned. Finally, the last row gives the grand total for all of the one-external-electron cases considered in Ref. 1 and in the present work. The total ΣN_L is 1155, and the total number of $(k + \lambda)$ exceptions ΣN_E is 120, giving an overall ratio of 0.104. Representative cases of the spectra of Table IX are listed in Tables X–XIII.

Spectrum	Excited state	N_L	N_E	N_E/N_L	l pattern
Mg I	3snl	35	9	0.257	<i>fdps</i>
Ca I	4snl	42	0	0	} <i>fpds</i> for $k=5$ and $k \geq 11$ } <i>fdps</i> for $k=6$ to $k=10$
Sr I	5snl	36	7	0.194	
Ba I	6snl	26	6	0.231	<i>dpsf</i> (gen.); <i>pdsf</i> for $k=9$ and 10
Ra I	7snl	8	1	0.125	<i>dpsf</i> ($k=8$); <i>pdsf</i> ($k=9$)
Zn I	4snl	24	0	0	<i>pdfs</i>
Ga II	4snl	14	2	0.143	<i>dfps</i>
Cd I	5snl	31	2	0.065	<i>pdsf</i>
In II	5snl	59	6	0.102	<i>hgdpsf</i>
Sn III	5snl	11	1	0.091	<i>gdpsf</i>
Hg I	6snl	69	10	0.145	<i>pdsf</i>
Tl II	6snl	22	0	0	<i>dpsfg</i>
Pb III	6snl	19	1	0.053	<i>hdpsfg</i>
Total ^{(2)s}		396	45	0.114	IIA, IIB (Table IX)
Total ^{(1)p}		264	26	0.098	IIIA (Table I)
Total ^{(1)s}		192	10	0.052	IB (Table VIII)
Total (Ref. 1)		303	39	0.129	IA (Ref. 1)
Grand total		1155	120	0.104	IA, IB, IIA, IIB, IIIA

TABLE X. Excitation energies E_{nl} (above the ground state $4s^2$) for the excited states $4snl$ of the calcium atom, Ca, corresponding to the spectrum Ca I. The l pattern is pds for $k=5$, $fdps$ for $k=6$ to 10, and $fpds$ for $k \geq 11$. The states $3d4p$, $4p^2$, $3d5s$, and $3d^2$ (in the last four rows) correspond to a double excitation of the closed $4s$ shell, i.e., of $4s^2$. We note that no $(k+\lambda)$ exceptions occur in all of the 42 states listed, i.e., we have $N_E=0$ and perfect k ordering, in the same manner as for Sn^* (Table V) and Pb^* (Table VII).

nl	$k=n+l$	$E_{nl}(\text{cm}^{-1})$	nl	$k=n+l$	$E_{nl}(\text{cm}^{-1})$
4s	4	0	9f	12	47 922
4p	5	17 360	11p	12	47 999
3d	5	20 730	10d	12	48 037
5s	5	31 984	12s	12	48 110
4d	6	37 640	10f	13	48 187
5p	6	37 844	12p	13	48 223
6s	6	40 802	11d	13	48 259
4f	7	42 214	13s	13	48 320
5d	7	42 789	11f	14	48 383
6p	7	42 876	13p	14	48 416
7s	7	44 055	12d	14	48 435
5f	8	44 774	14s	14	48 485
6d	8	45 036	12f	15	48 531
7p	8	45 076	13d	15	48 571
8s	8	45 776	13f	16	48 647
6f	9	46 169	14d	16	48 677
7d	9	46 306	Limit		49 305
8p	9	46 480	3d4p		37 552
9s	9	46 770	4p ²		39 391
7f	10	47 008	3d5s		47 469
8d	10	47 042	3d ²		48 551
9p	10	47 184			
10s	10	47 396			
8f	11	47 551			
10p	11	47 661			
9d	11	47 761			
11s	11	47 815			

ergy state at the beginning of the sequence to the position of highest energy state at the end of the l pattern.

A further observation can be made concerning the results of Table XIV. We have arranged the spectra in the order of increasing Z values, regardless of the state of ionization, as indicated by the Roman numeral following the symbol for each element. We now note that, regardless of the ionization state, and regardless of the one-electron ground state which is being excited (ns or np), there are definite clusterings of spectra belonging to approximately the same value of Z . These clusterings also exist regardless of whether the ground state has one ns or two ns electrons (i.e., the underlined spectra). As an example, for the first pattern, namely, $fdps$, there is a cluster: NaI , $\underline{\text{MgI}}$, MgII , AlI , SiII with Z values in the region from $Z=11$ to $Z=14$. There is a second cluster for

CaI and CaII , with $Z=20$, and a third cluster including ZnII , GaIII , and AsIII extending from $Z=30$ to $Z=33$.

Similar observations can be made about the second pattern $dpsf$, with a first cluster including CdII , InI , $\underline{\text{InII}}$, and SnII ($Z=48$ to $Z=50$), and a second cluster including HgII , $\underline{\text{TlII}}$, and PbII ($Z=80$ to $Z=82$). Similar results are found for the remaining five patterns in Table XIV.

Of course, we realize that our choice of single-electron excitations has restricted us to certain regions of the Periodic Table, namely, those near the Z values for the alkali-metal atoms (group IA) and those near the Z values for the noble-metal atoms (group IB), plus a few units of Z to include the isoelectronic ions. Nevertheless, the fact that five spectra with $Z=11$ to $Z=14$ (NaI , $\underline{\text{MgI}}$, MgII , AlI , and SiII) have the same l pattern ($fdps$) is probably not coincidental, especially when we consider that

TABLE XI. Excitation energies E_{nl} (above the ground state $5s^2$) for the excited states $5snl$ of the strontium atom, Sr, corresponding to the spectrum Sr 1. The l pattern is $pdsf$.

nl	$k=n+l$	$E_{nl}(\text{cm}^{-1})$	nl	$k=n+l$	$E_{nl}(\text{cm}^{-1})$
5s	5	0	9d	11	43 803
5p	6	16 451	11p	12	43 938 ⁽⁻¹⁾
4d	6	18 728	11s	11	44 057
6s	6	29 427	8f	11	44 177
6p	7	33 968	10d	12	44 292
5d	7	34 954	12p	13	44 366 ⁽⁻¹⁾
7s	7	37 680	12s	12	44 457
4f	7	38 950	9f	12	44 548
7p	8	39 308	11d	13	44 622
6d	8	39 685	13p	14	44 675 ⁽⁻¹⁾
8s	8	40 834	10f	13	44 812
8p	9	41 172 ⁽⁻¹⁾	12d	14	44 863
5f	8	41 404	14p	15	44 904 ⁽⁻¹⁾
7d	9	41 861	11f	14	45 008
9p	10	42 462 ⁽⁻¹⁾	13d	15	45 044
9s	9	42 487	12f	15	45 157
6f	9	42 793	Limit		45 926
8d	10	43 059	4d5p		35 516
10p	11	43 328 ⁽⁻¹⁾	5p ²		36 116
10s	10	43 449	4d ²		44 663
7f	10	43 632			

NaI and MgII have a $3s$ ground state, while MgI has a $3s^2$ ground state, and AlI and SiII contain an external $3p$ electron in their ground states. Similar "coincidences" can be easily deduced from Table XIV. In this connection, it may also be significant that out of 24 possible l sequences, only seven are realized at all in the spectra of Table XIV.

III. IMPLICATIONS OF THE PRESENT RESULTS

A. Phase transition from k ordering to hydrogenic ordering

The rearrangement of the excited-state nl levels in going from Mg^+ which has good k ordering to the spectrum of the isoelectronic ion Al^{2+} which is completely hydrogenic has been extensively dis-

TABLE XII. Excitation energies E_{nl} (above the ground state $4s^2$) for the excited states $4snl$ of the zinc atom, Zn, corresponding to the spectrum Zn I. The l pattern is $pdfs$. We note that no $(k+\lambda)$ exceptions occur in all of the 24 states listed, i.e., we have $N_E=0$ and perfect k ordering, in the same manner as for Sn^+ (Table V), Pb^+ (Table VII), and Ca (Table X).

nl	k	$E_{nl}(\text{cm}^{-1})$	nl	k	$E_{nl}(\text{cm}^{-1})$
4s	4	0	8p	9	72 533
4p	5	36 208	7d	9	72 593
5s	5	54 201	9s	9	73 004
5p	6	62 022	9p	10	73 412
4d	6	62 695	8d	10	73 471
6s	6	65 584	10s	10	73 699
6p	7	68 220	10p	11	74 012
5d	7	68 520	9d	11	74 017
4f	7	68 834	11s	11	74 169
7s	7	69 811	10d	12	74 388
7p	8	71 045	12s	12	74 496
6d	8	71 172	Limit		75 767
5f	8	71 323			
8s	8	71 856			

TABLE XIII. Excitation energies E_{nl} (above the ground state $5s^2$) for the excited states $5snl$ of the indium ion, In^* , corresponding to the spectrum In II . The l pattern is $hgdpfs$.

nl	$k=n+l$	$E_{nl}(\text{cm}^{-1})$	nl	k	$E_{nl}(\text{cm}^{-1})$
5s	5	0	9g	13	146 747
5p	6	49 213	9h	14	146 767 ⁽⁻¹⁾
6s	6	94 696	11d	13	146 831
5d	7	105 131	13s	13	147 642
6p	7	108 552	10f	13	147 686
7s	7	121 921	10g	14	147 784
4f	7	123 660	10h	15	147 799 ⁽⁻¹⁾
6d	8	125 259	12d	14	147 846
7p	8	127 238	14s	14	148 445
8s	8	130 938	11f	14	148 474
5f	8	133 954	11g	15	148 551
5g	9	134 509	11h	16	148 562 ⁽⁻¹⁾
7d	9	134 911	13d	15	148 598
8p	9	135 984	15s	15	149 053
9s	9	139 195	12f	15	149 072
6f	9	139 557	12g	16	149 134
6g	10	139 919	12h	17	149 143 ⁽⁻¹⁾
8d	10	140 171	14d	16	149 171
9p	10	140 800	16s	16	149 524
10s	10	142 741	13g	17	149 588
7f	10	142 936	13h	18	149 595 ⁽⁻¹⁾
7g	11	143 181	15d	17	149 617
9d	11	143 348	17s	17	149 897
10p	11	143 733	14g	18	149 948
11s	11	145 009	16d	18	149 971
8f	11	145 123	18s	18	150 193
8g	12	145 297	17d	19	150 257
8h	13	145 324 ⁽⁻¹⁾	19s	19	150 438
10d	12	145 413	Limit		152 195
11p	12	145 658			
12s	12	146 549			
9f	12	146 618			

TABLE XIV. Summary table giving the list of l patterns which have been encountered in the present work and in Ref. 1. The appropriate spectra for each pattern (together with the k regions, if necessary) are listed in the second column of the table. The last three columns list the frequency N_p of each pattern, and the minimum and maximum values of Z (Z_{\min} and Z_{\max}) of the spectra for which the pattern occurs. The spectra which are underlined correspond to cases for which the ground state has the external configuration $(n_0s)^2$, so that the excited states have the configuration n_0s, nl , corresponding to Table IX.

l pattern	Spectra	N_p	Z_{\min}	Z_{\max}
$fdps$	Na I, <u>Mg I</u> , Mg II, Al I, Si II, <u>Ca I</u> ($k=6-10$), Ca II, Zn II, Ga III, As III	10	11	33
$dpsf$	Cd II, In I ($k \geq 9$), <u>In II</u> , Sn II, <u>Ba I</u> (generally), Hg II, <u>Tl II</u> , Pb II, <u>Ra I</u> ($k=8$), Ra II ($k=8, 9$)	10	48	88
$dpfs$	Cu I ($k \geq 9$), Sr II, In III, <u>Sn III</u> , Sb III, Ba II, Tl III, <u>Pb III</u> , Bi III, Ra II ($k=10$)	10	29	88
$pdsf$	Ga I, Rb I, <u>Sr I</u> , Ag I, <u>Cd I</u> , In I ($k=6-8$), Cs I, <u>Ba I</u> ($k=9, 10$), Au I, <u>Hg I</u> , Tl I, <u>Ra I</u> ($k=9$)	12	31	88
$fpds$	K I, <u>Ca I</u> ($k=5$ and $k \geq 11$)	2	19	20
$pdfs$	Cu I ($k=5-8$), <u>Zn I</u>	2	29	30
$dfps$	<u>Ga II</u> , Ge II	2	31	32

cussed in Ref. 1 (see Tables XI and XVII and the discussion at the end of Sec. III of Ref. 1). Both ions have 11 electrons and their nuclear charges Z differ by only one unit. The heavier isoelectronic ions (Si^{3+} , P^{4+} , S^{5+} , Cl^{6+} , Ar^{7+} , etc.) also exhibit pure hydrogenic ordering. It should be added that the spectrum of the neutral Na atom, for which $Z = 11$, is k ordered, in the same manner as Mg^+ . The abrupt change in going from Mg^+ to Al^{2+} made us think of a phase transition between k ordering and hydrogenic ordering, at the time we wrote the first paper. Since that time, we have investigated additional examples of the "phase transition" between k ordering and hydrogenic ordering, as the degree of ionization $Z - N$ (or ionicity) is increased. Here N is the number of electrons in the atom or ion considered. In the following, we will refer to hydrogenic ordering by the abbreviation "H ordering." As an additional example of the transition to H ordering, we may refer to the excited-state spectrum of GeIII, which is isoelectronic with ZnI and GaII (see Table IX of the pres-

ent paper). An inspection of the appropriate table in Moore's compilation⁷ (Vol. II) shows that the spectrum of GeIII is almost purely hydrogenic, and the same is the case for the heavier isoelectronic ions AsIV and SeV. These results are in contrast to those for the neutral ZnI spectrum and the (singly ionized) GaII spectrum, which are purely k ordered (see Table IX).

The rearrangement of the levels in going from Mg^+ to Al^{2+} is graphically shown in Fig. 1. For each ion, we have plotted the values of $\log_{10}(E_L - E_{nl})$, where E_L is the ionization limit, namely, $121\,267\text{ cm}^{-1}$ for Mg^+ and $229\,454\text{ cm}^{-1}$ for Al^{2+} , and E_{nl} is the value of the energy (above the ground state 3s) for all of the observed levels. These logarithms have been plotted on two separate abscissas, and we have joined the identical levels in the two spectra by straight (nearly vertical) lines. A crossing of two lines indicates a particular rearrangement necessary to attain H ordering (Al^{2+}) starting from a situation of k ordering (Mg^+). The approximate regions of constant k have been

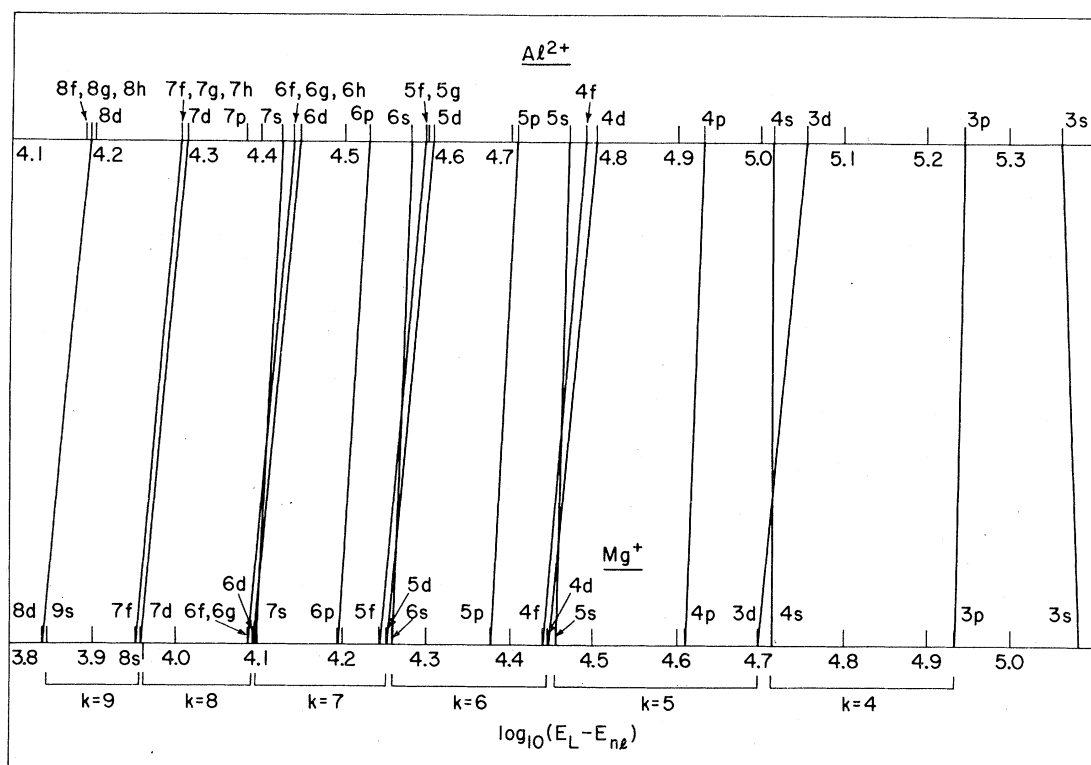


FIG. 1. Energies of the excited-state levels of Mg^+ (lower abscissa) and Al^{2+} (upper abscissa) on a logarithmic scale, on which are plotted the values of $\log_{10}(E_L - E_{nl})$, where E_L is the series limit, $E_L = 121\,267\text{ cm}^{-1}$ for Mg^+ and $E_L = 229\,454\text{ cm}^{-1}$ for Al^{2+} . Levels with the same nl values in the two spectra are connected by (nearly vertical) lines. The frequent crossing of these lines indicates the rearrangement in the spectrum in going from Mg^+ to Al^{2+} , i.e., from k ordering to hydrogenic (H) ordering. These spectra are also listed in Tables XI and XVII of Ref. 1. At the bottom of the lower abscissa, we have shown the successive k regions or bands, from $k = 4$ to $k = 9$.

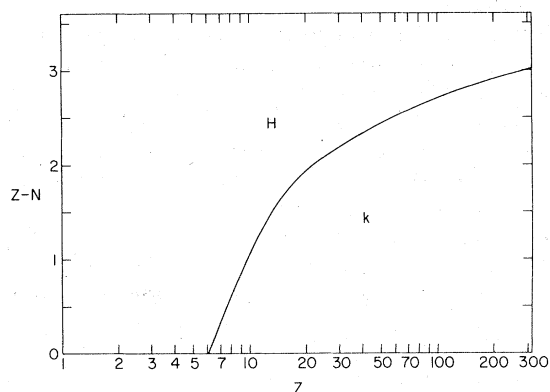


FIG. 2. Regions of validity of k ordering and hydrogenic (H) ordering of the excited-state levels of neutral atoms and ions with small degree of ionization $Z-N$ (Z is the atomic number, N is the number of electrons). The curve separating the two regions is plotted as a graph of $Z-N$ vs Z . If the transition from k ordering to H ordering can actually be described as a phase transition, then Fig. 2 is the appropriate phase diagram.

marked below the Mg^+ abscissa axis. It is seen that the spacing between contiguous k regions is much smaller than the width of each k region. This is a general feature of the k regions for all of the spectra which have been investigated (see Tables II-VII and X-XIII; also Tables II-VI and XI-XV of Ref. 1). In fact, if we consider that the number of levels with constant k is $\frac{1}{2}k$ for k =even, and $\frac{1}{2}(k+1)$ for k =odd, and that the k regions have a tendency to become narrower with increasing k , as shown in Fig. 1, we can conclude that the average spacing between adjacent levels with constant k decreases faster than $1/k$, and perhaps something like $1/k^2$. Thus the high k regions can be referred to as k bands. According to this view, the "exceptions" of the type $k+\lambda$, with $\lambda=\pm 1$, refer to cases where successive k regions or k bands overlap somewhat.

In Ref. 1, we have extensively discussed the fact that the spectrum for the lithium atom Li ($Z=3$) is purely hydrogenic, and the same is also true for the excited states $1snl$ of He ($Z=2$), $2snl$ of Be ($Z=4$), and $2s^2nl$ of B ($Z=5$). The first alkali-metal atom for which k ordering takes place is sodium Na ($Z=11$). Possible explanations involving the presence of a filled $2p$ shell in Na were proposed in Ref. 1. We will consider these explanations further in the following discussion.

For the present, we note that in a plot of ionicity $Z-N$ vs atomic number Z , we can draw an approximate curve which separates the regions of k and H ordering. This has been done in Fig. 2. The separation curve was plotted, starting from $Z-N=0$ at $Z=6$ to $Z-N=1.5$ for $Z=12$ (midway between Mg^+ with $Z-N=1$ and Al^{2+} with $Z-N=2$). The

curve was then continued to pass through the point $Z-N=2.5$ at $Z=57$, to take into account the fact that for La^{2+} ($Z=57$), which is isoelectronic with Ba^+ , there is still almost complete k ordering, as discussed at the end of Sec. III of Ref. 1. We thus obtain the curve shown in Fig. 2, which extrapolates to an ionicity $Z-N=3$ for a hypothetical ion with $Z=300$. If the extensive rearrangement from k ordering to H ordering (see Fig. 1) can actually be considered as a phase transition, then Fig. 2 represents the appropriate phase diagram.

We note that Fig. 2 pertains to the k -vs-H ordering of the *excited* states of atoms and ions as a function of the ionicity $Z-N$. A similar study for the *ground* states of ions with variable ionicity has been carried out by Goudsmit and Richards,⁸ as was already discussed in Ref. 1.

B. Core-polarization effects

As we have discussed in Sec. IV of Ref. 1, the ultimate explanation of the extensive k ordering for neutral or near-neutral atomic systems will probably involve a core polarization effect of the same type as is involved in the quadrupole antishielding factors R and γ_∞ .^{3,5,9} In addition, it has been shown¹⁰ that the inverted fine structure of the excited nd states of the alkali-metal atoms can also be attributed to exchange effects with the core electron perturbations $np \rightarrow p$ and $nd \rightarrow d$ produced by the fine-structure Hamiltonian. The best evidence for core polarization effects as the source of the k -ordering phenomena lies in the presence of the effect for Na and the heavier alkalis, all of which possess closed np (and nd) shells, and its absence for the case of Li, which has no p electrons in the core. This difference has also been noted¹⁰ for the case of the inverted fine structure, which is absent for lithium.

As added evidence in favor of core polarization effects, we may note the results of Table XIV of the present paper, which show that in many cases, atoms and ions with different ground states (n_0s , n_0s^2 , or n_0p) but nearly the same values of Z exhibit identical l patterns. This indicates that as far as the excited states are concerned, the ground state of the valence electron is of relatively little importance, but what is important is the number and the character (np, nd) of the closed shells of the core, which are identical for the neighboring values of Z involved in cases where the l patterns are identical.

It may also be remarked that in view of the great importance of core polarization effects for both the quadrupole moment hyperfine structure (antishielding factors),^{3,5,9} and for the fine structure,¹⁰ it would be surprising if core polarization effects did

not also play a significant role for the so-called gross structure of the spectrum, which determines the relative position of different nl levels for single-electron excitations of the atom or ion.

However, in addition to the possible relevance of core polarization effects, we should emphasize the suggestion made in Ref. 1 that the ultimate explanation of both the k ordering and the constant l patterns may well involve group-theoretical considerations. A discussion of these considerations has been given in Ref. 1. We have noted in particular the explanation of the orthogonality property of Pasternack and Sternheimer¹¹ in terms of the noncompact groups $O(4, 2)$ and $O(2, 1) \times O(3)$ by Armstrong.¹² In this connection, we note that an extensive discussion of the group-theoretical properties of the hydrogen atom has been given by Bander and Itzykson¹³ for the nonrelativistic case, and by Barut and Bornzin¹⁴ for the relativistic case. However, as we have emphasized in Ref. 1, the k ordering and the correlated l patterns are properties of medium and large Z atoms which are neutral or nearly neutral ($Z - N \lesssim 2$). Thus the basic group, if it exists, must pertain to the Hamiltonian with the complete potential function:

$$V = - \sum_i^N \frac{Ze^2}{r_i} + \sum_{i>j}^N \frac{e^2}{r_{ij}}, \quad (8)$$

including the important second term on the right-hand side which describes the electrostatic repulsion between different electrons. Thus the V of Eq. (8) is a very different potential function than that considered in Refs. 12–14 for hydrogenlike systems.

The fact that the k ordering holds for both the nonrelativistic (αZ small) and the relativistic ($\alpha Z \sim 1$) cases has been pointed out in Sec. IV of Ref. 1. This result has been strongly confirmed in the present investigation. As an example, probably the most convincing example of k ordering is the case of PbII, i.e., the spectrum of the Pb^+ ion (Table VII), for which $\alpha Z = 0.60$. Moreover, referring to Table XIV, we note that for 13 cases (out of a total of 48), i.e., for all cases with Z from 79 to 88, we have $\alpha Z \geq 0.58$. Therefore, we conclude that if the explanation of k ordering can be given in terms of a Hamiltonian involving the potential function V of Eq. (8), then the Dirac formulation of the Hamiltonian must be employed. Of course, these results are also in concordance with the fact that Madelung's rules A and B for the ground states continue to hold at least up to $Z = 120$, as has been previously discussed.¹

C. Quantum numbers

In considering the tables of averaged energy levels of Ref. 1 (Tables II–V and XI–XV) and those of

the present paper (Tables II–VII and X–XIII), it becomes apparent that the primary quantum numbers in the k -ordering region (or phase) are k and l , rather than n and l as is the case for the H-ordering region (or phase). In this connection we note that we have:

$$n = k - l, \quad (9)$$

in view of Eq. (1). When we compare Eq. (9) with Eq. (2) for q , and realize the significance of q as a "radial node quantum number," then it becomes suggestive that n itself (or $n - 1$) may be a radial node quantum number in some higher hyperspace, in which k plays the same role as n in the ordinary three-dimensional space. Possibly the appropriate k hyperspace has four dimensions, as would be suggested by the groups $O(4)$ and $O(4, 2)$ which have been used in group-theoretical descriptions of the hydrogen atom. Then in the k hyperspace, the principal quantum number n , or possibly $n - 1$, may represent the number of "radial nodes" of the appropriate total wave function.

IV. SUMMARY

Following the discovery of k ordering and l patterns in the alkali-metal atom and alkaline-earth ion spectra, as discussed in Ref. 1, we have made a systematic study of other "one-electron" spectra of various atoms and ions in the extensive and valuable tables of Moore.⁷ We believe that we have found essentially all of these spectra, and have reported on them in the present paper. We have included three types of spectra: (i) those of group IIIA elements, with a single p electron outside closed shells in the ground state; (ii) those of Group IB elements, with a single s electron outside a filled nd shell (configuration nd^{10}); (iii) those of group IIA and IIB elements, with the external configuration $(n_0s)^2$ which is excited to the pseudo-one-electron levels n_0s, nl . For all three categories, we have included not only the neutral atoms, but also their isoelectronic ions of low ionicity $Z - N$, where the k ordering is expected to prevail.

Following this program, we have investigated a total of 852 atomic or ionic levels, in addition to the 303 levels discussed in Ref. 1, giving a total of 1155 levels. The result of this investigation is an overwhelming confirmation of the existence of k ordering and the associated l patterns, which are therefore fundamental features of the excited level spectra of neutral atoms (with $Z \geq 10$), and of their isoelectronic ions having low ionicity ($Z - N \lesssim 2$). The groups of levels having the same value of the quantum number k [Eq. (1)] can be called k bands (see Fig. 1), and there is little or no overlapping of different k bands in all of the spectra which have

been investigated. We note that the present paper reports on the analysis of 33 spectra, which together with the nine spectra of Ref. 1, gives a total of 42 spectra. The "exceptions" of the type $(k + \lambda)$ (with $\lambda = \pm 1$ usually) correspond to a partial overlapping of neighboring k bands. The total number of $(k + \lambda)$ "exceptions" is only $\sum N_E = 120$, out of a total number of levels $\sum N_L = 1155$, a fraction of only $\sim 10\%$.

It is significant that there are many spectra with $N_E = 0$; in fact, we have $N_E = 0$ in a total of 50 levels for the case of PbII (Pb⁺). Moreover, for 36 out of 42 spectra, the l pattern is completely independent of k (up to $k = 50$ for the case of Rb, as discussed in Ref. 1). The statistics of the frequency N_P of different l patterns, as given in Table XIV, shows that only four different patterns (namely, *fdps*, *dpsf*, *dpfs*, and *pdsf*) account for 42 out of the total of 48 patterns encountered in the analysis of the spectra.

In Sec. III, we have discussed the possibility that the region in which k ordering prevails and the region of hydrogenic ordering (H ordering) form two different phases, and the appropriate phase diagram of ionicity ($Z - N$) vs atomic number Z has been shown in Fig. 2. The possibility of a phase transition between k and H ordering was suggested to the present author by the abruptness of the transition from k to H ordering in going from Mg⁺ to the isoelectronic ion Al²⁺, for which Z changes by only one unit. The extensive rearrangement of the levels in going from Mg⁺ to Al²⁺ is illustrated in Fig. 1.

In connection with the possibility of a phase transition between the k -ordered state and the H ordered state, we note that the number of "objects" in our system, i.e., the number of energy levels E_{nl} , becomes doubly infinite as $n \rightarrow \infty$. The reason is that, if we consider a large n , to be denoted by n_{\max} , the number of nl states $N(nl)$ with $n \leq n_{\max}$ is given by the area under the 45° line in a graph of l vs n . This area is given by $\frac{1}{2} n_{\max}^2$ for the n values up to $n = n_{\max}$, i.e., one-half the area of a square whose side is n_{\max} . Hence the number of "objects" which are to be ordered becomes infinite like n_{\max}^2 as $n_{\max} \rightarrow \infty$, and is in principle larger than the number of atoms ($\sim 10^{23}$) which participate in a phase transition from body-centered cubic to face-centered cubic (close packed) in a finite solid as a

result of an increase of the pressure.

Concerning the possible phase transition from k ordering to H ordering in the excited level spectrum of ions as the ionicity is increased for a fixed Z (Fig. 2), we may note a possible though remote analogy to the critical angular momentum¹⁵ (J_{cr}), which constitutes the boundary of the "variable-moment-of-inertia"¹⁶ (VMI) phase of nuclear structure.

In summary, we can state that there is overwhelming evidence from the tabulated spectra of Moore for the k ordering of the excited atomic levels, with the associated l patterns (provided that $Z \geq 10$), both for the neutral atoms and for their isoelectronic ions of low ionicity $Z - N \lesssim 2$. In the present study together with Ref. 1, we have included essentially all of the available spectra with one electron outside of closed shells plus the pseudo-one-electron levels with the configuration $n_0 s, nl$ in the excited states of the alkaline-earth atoms. The present results confirm the relevance of the quantum number $k \equiv n + l$, which was already demonstrated in Ref. 1. We have also shown that the region of k ordering and the region of hydrogenic (H) ordering may be thought of as two distinct phases, and the associated phase diagram is shown in Fig. 2.

Concerning a possible explanation of the k -ordering phenomenon, we have proposed (in Ref. 1) the possibility of the action of core-polarization effects, of the type encountered in the study of the quadrupole antishielding factors^{3,5,9} γ_∞ and R . This possibility is strengthened by the evidence presented in Table XIV, according to which the presence of a particular l pattern (e.g., *fdps*) depends mainly on the atomic number Z , i.e., on the number and type of closed shells of the core, and is essentially independent of the state of ionization or the nature of the ground state of the valence-electron configuration ($n_0 s$, $n_0 s^2$, or $n_0 p$).

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