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Ordering of the excited-state atomic energy levels and fine-structure inversion in atomic and ionic spectra

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The k-ordering properties of the spectra of atoms and ions consisting of a single valence electron outside a core of closed shells ($k = n + l$) have been introduced and discussed extensively in three previous papers, together with the constant l sequences within each group of levels having the same value of k (k bands). Here we have extended the discussion of the k ordering by a closer consideration of the three spectra: Ga I, Rb I, and Sr I. Thus it has been found that 119 additional atomic enegy levels exhibit perfect k ordering, and the resulting total number of levels included among the 42 spectra considered becomes 1274. A correlation has been shown to exist between the occurrence of inverted fine structure and the limiting angular momentum l_1 for k ordering, and the limiting ionicity δ_1. We have discussed the probable existence of a basic symmetry characterized by the quantum number k, which is partially broken by the "l-dependent interaction", giving rise to a multiplet of levels with different l values, such that $l \lesssim l_1$, and $n = k - l$ (semi-fine-structure). The overwhelming evidence (1274 levels) in favor of perfect k ordering for $l \lesssim l_1$ and $\delta \lesssim \delta_1$ can probably be used in future analyses of atomic and ionic spectra, in order to assist in the assignment of n and/or l values to the observed energy levels E_{nl}.

I. INTRODUCTION

In three previous papers,[1-3] we have introduced the concept of the quantum number

$$k = n + l \tag{1}$$

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^+),[1] and, in addition, states with one electron outside closed shells in the spectra of the Group IB, IIA, IIB, and IIIA elements of the Periodic Table, and their isoelectronic ions.[2] In Ref. 1, we have considered a total of 303 excited states, while in Ref. 2, we have analyzed a total of 852 additional energy levels, giving a total of 1155 levels, which provide overwhelming evidence for the existence of a phenomenon which we have called "k ordering," namely, the grouping together of levels having the same value of k and having nearly the same energy (term value in the spectrum). Thus the excited states of each spectrum can be divided into successive k groups, and within each k group (or "k band"), the levels increase (slightly) in energy according to a fixed sequence of l values, which we have called the "l pattern." Except in a few cases, the l pattern does not change with increasing k, and, for instance, the l pattern is *pdsf* for the excited states of rubidium from $k=6$ to $k=50$, i.e., over a range of 45 k values.

The k ordering and the l sequences of the levels have been exhibited specifically in nine j-averaged spectra in Ref. 1 and in ten j- averaged spectra in Ref. 2. By j-averaged spectra, we mean that we have averaged the energy values E_{nlj} listed in the tables of Moore[4] using the weighting factors $(2j+1)$ for the two levels with $j=l+\frac{1}{2}$ and $j=l-\frac{1}{2}$, so as to average over the effects of the fine structure. Altogether, a total of 42 spectra have been analyzed in this fashion, and the l patterns of these spectra have been tabulated in Table XIV of Ref. 2.

In the present paper, we will address ourselves mainly to several additional features concerning the k-ordering properties of the spectra described in Refs. 1–3. There are a number of apparent exceptions to the k-ordering, which have been called "$k+\lambda$ exceptions." By $k+\lambda$ exception is meant the occurrence of a level with value k_0 in the k band with k value $k_0+\lambda$. As an example, in the spectrum of Rb (rubidium) (see Table IV of Ref. 1), the $6h$ level with $k_0 = 6+5 = 11$ occurs at a value $E_{6h} = 30\,644$ cm^{-1}, i.e., in the region of the $k=10$ band which extends from $E_{6g} = 30\,637$ cm^{-1} to $E_{7f} = 31\,442$ cm^{-1}. We have $k = k_0 - 1$, so that $\lambda = -1$ in the above notation, and the level is accordingly identified with a superscript (-1) in Table IV of Ref. 1. Actually the particular type of $k+\lambda$ exception associated with E_{6h} of Rb was identified in the discussion of Ref. 3 as being due to the angular momentum $l=5$ of $6h$ being larger than the limiting angular momentum $l_1 = 4$ of the Rb spectrum, for which the "phase transition" from k ordering to hydrogenic ordering sets in. For hydrogenic ordering the levels are ordered according to the value of the principal quantum number n, with a slight increase of the energy value E_{nl} as l is increased. Indeed, Table IV of Ref. 1 shows that $E_{6h} = 30\,644$ cm^{-1} lies only 7 cm^{-1}

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above $E_{6g} = 30\,637$ cm^{-1}, an energy difference of only $7/8.07 = 0.867$ meV.

Thus we have shown in Ref. 3 that out of a total of 71 apparent $k+\lambda$ exceptions included in the tables of Ref. 1 ($\Sigma N_E = 39$, see Table XVI of Ref. 1) and in the tables of Ref. 2 ($\Sigma N_E = 32$), there appear to be only 12 "true" $k+\lambda$ exceptions, which are not associated with l being larger than the limiting angular momentum l_1 (see the discussion on p. 1757 and Fig. 1 of Ref. 3).

It has been recently pointed out to the author by Edlén[5] and zu Putlitz[6] that the values of n in some of the spectra may have been misidentified in the references available when the tables of Moore[4] were published (1949–1958), and that when the revised and correct values of n are used, the corresponding $k+\lambda$ exceptions disappear, at least in the majority of the cases. This was especially pointed out by Edlén who referred the author to the more recent paper of Johansson and Litzén[7] on the Ga I spectrum and to that of Garton and Codling[8] on the Sr I spectrum.

The purpose of Sec. II is to reexamine the $k+\lambda$ exceptions in the 19 spectra of Refs. 1 and 2, in the light of the suggestion described above.

In Sec. III, we will discuss in detail a correlation which we have observed between the occurrence of the inverted fine structure ($\Delta\nu < 0$), which was calculated in previous papers,[9-13] and the limiting angular momentum l_1 for k ordering as well as the limiting ionicity δ_1 ($\delta = Z - N$), which also separates the k-ordering phase from the hydrogenic-ordering phase. Here Z is the atomic number, and N is the number of electrons in the atom or ion considered.

In Sec. IV, we give a discussion of the probable theoretical explanation of the k ordering. The discovery of the k ordering in the excited-state spectra of pseudo-one-electron atoms and ions has led us to identify a new level structure in these spectra, which we have called the "semi-fine-structure," corresponding to the multiplet splitting of a hypothetical primitive k level into the observed levels having the same value of k and the various l values with $l \leqslant l_1$. Finally, in Sec. V we give a brief summary of the results of the present paper.

II. REEXAMINATION OF THE APPARENT $k+\lambda$ EXCEPTIONS

We will first discuss the case of the Ga I spectrum. There are several errors in the *nf* levels reported in the tables of Moore,[4] as is shown by the work of Johansson and Litzén[7] (see Table 3 of Ref. 7). The resulting corrected Ga I spectrum is shown in Table I. It can be seen that the corrected spectrum exhibits perfect k ordering with the l pattern being *pdfs*.

TABLE I. Revised spectrum of the neutral gallium atom, Ga I, as obtained from the tables of Moore (Ref. 4), combined with the results of Johansson and Litzen (Ref. 7) for the *nf* levels and the series limit. The l pattern is *pdfs*. The resulting k ordering is perfect ($N_E = 0$).

nl	k	E_{nl} (cm^{-1})	nl	k	E_{nl} (cm^{-1})
4*p*	5	551	7*d*	9	45 074
5*s*	5	24 789	6*f*	9	45 313
5*p*	6	33 118	9*s*	9	45 537
4*d*	6	34 786	8*d*	10	45 971
6*s*	6	37 585	7*f*	10	46 131
6*p*	7	40 404	10*s*	10	46 274
5*d*	7	40 808	9*d*	11	46 549
4*f*	7	41 454	8*f*	11	46 661
7*s*	7	42 158	11*s*	11	46 758
7*p*	8	43 455	10*d*	12	46 942
6*d*	8	43 579	9*f*	12	47 022
5*f*	8	43 955	12*s*	12	47 093
8*s*	8	44 332			
			Limit		48 388
			$4s4p^2$		49 213

Next we discuss the case of the Sr I spectrum, as shown in Table XI of Ref. 2. From the work of Garton and Codling[8] (Table I of Ref. 8), it appears that the level at 41 172 cm^{-1} in Moore's tables[4] has been misidentified as 8*p*, and that the actual 8*p* level is located at 42 462 cm^{-1}, i.e., at the position listed as 9*p* in Table XI of Ref. 2, which is based on Moore's tables. In the present discussion, we will simply omit the unit cm^{-1} for the sake of brevity. With $E_{8p} = 42\,462$, the apparent $k+\lambda$ exception at this energy is removed, and we obtain a perfectly k-ordered group $k = 9$, containing the levels 7*d*, 8*p*, 9*s*, 6*f* in the l sequence *dpsf*. In a similar manner, the determinations of Garton and Codling give $43\,328 = E_{9p}$ (instead of E_{10p} in Ref. 2), $43\,937 = E_{10p}$, $44\,366 = E_{11p}$, $44\,676 = E_{12p}$, $44\,904 = E_{13p}$, thus removing all of the apparent $k+\lambda$ exceptions in Table XI of Ref. 2. The resulting k ordering of the 36 levels of the Sr I spectrum is perfect, and the l sequence is *pdsf* for $k = 6$, 7, and 8, and *dpsf* for $k \geqslant 9$. The transition from the l pattern *pdsf* to *dpsf* between $k = 8$ and $k = 9$ occurs because $E_{6d} = 39\,685$ lies *above* $E_{7p} = 39\,308$, whereas $E_{7d} = 41\,861$ lies *below* $E_{8p} = 42\,462$. The resulting corrected spectrum of Sr I is shown in Table II.

We will now discuss the spectrum of the neutral cesium atom, Cs, i.e., the spectrum Cs I given in Table V of Ref. 1. We have nine $k+\lambda$ exceptions involving the *nf* levels for $n = 4$–12. As we have

TABLE II. Revised spectrum of the strontium atom Sr, i.e., the spectrum Sr I, as obtained from the tables of Moore (Ref. 4), combined with the results of Garton and Codling (Ref. 8) for the levels $5snp$ and the series limit. The l pattern is $pdsf$ for $k = 6$, 7, and 8, and $dpsf$ for $k \geq 9$. Only the excitation energies E_{nl} of the excited states $5snl$ are listed in the table. The resulting k ordering is perfect ($N_E = 0$). We have also included six additional levels for which k = 16, 17, and 18, so that the total number of levels above the ground state becomes $N_L = 42$.

nl	k	E_{nl} (cm^{-1})	nl	k	E_{nl} (cm^{-1})
$5s$	5	0	$7d$	9	41 861
$5p$	6	16 451	$8p$	9	42 462
$4d$	6	18 728	$9s$	9	42 487
$6s$	6	29 427	$6f$	9	42 793
$6p$	7	33 968	$8d$	10	43 059
$5d$	7	34 954	$9p$	10	43 328
$7s$	7	37 680	$10s$	10	43 449
$4f$	7	38 950	$7f$	10	43 632
$7p$	8	39 308	$9d$	11	43 803
$6d$	8	39 685	$10p$	11	43 937
$8s$	8	40 834	$11s$	11	44 057
$5f$	8	41 404	$8f$	11	44 177
$10d$	12	44 292	$13d$	15	45 044
$11p$	12	44 366	$14p$	15	45 075
$12s$	12	44 457	$12f$	15	45 157
$9f$	12	44 548	$15p$	16	45 208
$11d$	13	44 622	$13f$	16	45 275
$12p$	13	44 676	$15d$	17	45 287
$10f$	13	44 812	$16p$	17	45 312
$12d$	14	44 863	$16d$	18	45 373
$13p$	14	44 904	$17p$	18	45 395
$11f$	14	45 008			
			Limit		45 932

discussed in Ref. 3 (Sec. II, p. 1753, where ng should be replaced by nf in line 16 from the bottom), the situation for Cs is somewhat confused, because of the large number of apparent $k+\lambda$ exceptions. For this reason we have calculated the quantum defects δ_{nl} of all of the f levels, δ_{nf}. If we denote the series limit by $L = 31\,407$ cm^{-1}, δ_{nl} is given by

$$\delta_{nl} = n - \left(\frac{R_\infty}{L - E_{nl}}\right)^{1/2} = n - n^*_{nl}\,, \qquad (2)$$

where n^*_{nl} is the effective n for the level nl, R_∞ = Rydberg unit = 109 737 cm^{-1}, and E_{nl} is the energy of the level nl as measured from the ground state, taken as zero, i.e., the value listed in Table V of Ref. 1. We note that the $4f$ level in Table V should be 24 472 (instead of 24 772). For $4f-12f$, we thus obtain $\delta_{4f} = 0.022$, $\delta_{5f} = 0.026$, $\delta_{6f} = 0.028$, $\delta_{7f} = 0.030$, $\delta_{8f-12f} = 0.031$.

Returning now to the nine $k+\lambda$ exceptions for nf in Table V of Ref. 1, we believe that these $k+\lambda$ exceptions are connected with the proximity of $l = 3$ to the limiting angular momentum l_1 as defined in Ref. 3 (Sec. II). The reason for this belief is the proximity of E_{5f} to E_{5g}, and the proximity of E_{6f} to E_{6g} and E_{6h}, indicating that the hydrogenic part of the spectrum starts at $l_1 = 3$ for the case of Cs. Thus we would conclude that $l_1 = 3$ for Cs, instead of the range $l_1 = 4-5$ suggested in Ref. 3 (p. 1753, and Table I).

We now wish to make some comments on the spectrum of the neutral rubidium atom, i.e., the spectrum Rb I, as shown in Table IV of Ref. 1. In order to keep this table down to a reasonable size, we have listed only a fraction (<30%) of the levels in Moore's tables[4] which exhibit k ordering. Thus only 45 levels were included in Table IV of Ref. 1, whereas the total number of levels involved is $N_L = 158$. The 113 levels which were omitted for the sake of brevity belong to three classes.

(i) The 34 levels extending from $14p$, $13d$ ($k = 15$) to $30p$, $29d$ ($k = 31$). In this region of k, only the p and d levels are given in Ref. 4, but they exhibit perfect k ordering, i.e., each doublet of k levels $k = k_0$ occurs above the doublet $k = k_0 - 1$ and below the doublet $k = k_0 + 1$, and the sequence for a given k is always pd, which is of course a subsequence of the l pattern $pdsf$, which has been established for $k \leq 11$ and $k = 32-50$ in Table IV of Ref. 1.

(ii) For the region which extends from $k = 33$ to $k = 50$, all four levels (p, d, s, f) have been observed for each value of k. The k ordering is perfect for these $16 \times 4 = 64$ levels.

(iii) In the region from $k = 51$ to $k = 56$, Moore's tables[4] list the following 15 levels, which also exhibit perfect k ordering. In the order of increasing energy E_{nl}, we have $50p$, $49d$, $51s$ ($k = 51$); $51p$, $50d$, $52s$ ($k = 52$); $52p$, $51d$, $53s$ ($k = 53$); $53p$, $52d$ ($k = 54$); $54p$, $53d$ ($k = 55$); and $55p$, $54d$ ($k = 56$). Above $54d$, only the np levels are listed, as obtained by Kratz.[14]

In summary, we thus have $34 + 64 + 15 = 113$ levels not listed in Table IV of Ref. 1. Together with the 45 levels listed in this table, this gives a total of $N_L = 158$ levels, with only one apparent $k+\lambda$ exception, namely, the $6h$ level at $E_{6h} = 30\,644$ cm^{-1}. However, as has been discussed in Ref. 3 (see p. 1753), this level is a clear example of $l > l_1$, i.e., the breakdown of k ordering on account of l being too large ($l = 5$). Thus the $6h$ level is very close to the $6g$ level at $E_{6g} = 30\,637$ cm^{-1}, and we can assume that the hydrogenic ordering prevails for $l > l_1$ where $l_1 = 4$ for rubidium.

The spectrum of Rb I with 158 levels is by far the most extensive which we have investigated, and it exhibits perfect k ordering for all levels with $l \leq 4$ ($l_1 = 4$). Thus the total number of levels among the alkali-metal atoms (Table VI of Ref. 1) becomes $171+113=284$, and similarly the total number of levels in the nine spectra of Ref. 1 (see Table XVI of Ref. 1) becomes

$$N_L(\text{Ref. 1})=284+132=416\,. \tag{3}$$

Concerning the number of levels in the ten spectra of Ref. 2, as discussed above, in Table II of the present paper, pertaining to Sr I, we have been able to include six additional levels (with $k=16, 17, 18$), so that the total number of levels pertaining to Ref. 2 becomes $852+6=858$ (see Table IX of Ref. 2), and the grand total for the 19 spectra of both Refs. 1 and 2 becomes $858+416=1274$ (instead of 1155, as reported in Ref. 2). With the removal of the seven apparent $k+\lambda$ exceptions involving the np states of Sr I, and the revision of the Ga I spectrum (Tables I and II of the present paper), the number of apparent $k+\lambda$ exceptions is decreased by 11, and more importantly, the remaining $k+\lambda$ exceptions in the spectra of Refs. 1 and 2 involve only states of high angular momentum (f, g, h). These exceptions can therefore be ascribed to l being larger than l_1 (limiting angular momentum), or possibly in some cases to misidentifications of spectral levels of the same type as those which were corrected in Refs. 7 and 8, leading to the perfect k ordering in the revised spectra of Ga I (Table I) and Sr I (Table II).

There are, however, five remaining $k+\lambda$ exceptions in the spectra of Ba^+ and Ra^+ (Tables XIV and XV of Ref. 1), of which one involves the $9p$ level of Ra^+ and the other four involve nd levels ($6d$ of Ba^+; and $7d, 8d, 9d$ of Ra^+). These apparent exceptions involve states of low angular momentum ($l=1$ or 2). Concerning the spectrum of Ba^+, we have calculated the quantum defects δ_{nl} for all of the nd levels using Eq. (2), and no irregularity was detected for δ_{6d} in comparison with neighboring values of δ_{nd}. Thus $\delta_{5d}=2.586$, $\delta_{6d}=2.438$, $\delta_{7d}=2.410$, $\delta_{8d}=2.398$, $\delta_{9d}=2.390$, $\delta_{10d}=2.386$, $\delta_{11d}=2.384$, and $\delta_{12d}=2.382$. However, it is possible that the $k+\lambda$ exception for the $6d$ level is connected with the change of the l pattern from $dpsf$ for $k=7$ to $dpfs$ for $k\geqslant 8$.

Concerning the spectrum of Ra^+, there is a similar change of the l pattern from $dpsf$ for $k=8$ and 9 to $dpfs$ for $k=10$, which may be responsible for some of the anomalies. The δ_{nl} values of the d levels [Eq. (2)] do not show any irregularity. Thus we obtain $\delta_{6d}=3.474$, $\delta_{7d}=3.342$, $\delta_{8d}=3.310$, and $\delta_{9d}=3.298$. The data given by Moore[4] are based on an early analysis of the Ra^+ spectrum by Rasmussen,[15] and it is possible that more recent data exist, which might change the situation with respect to the apparent $k+\lambda$ exceptions.

III. FINE-STRUCTURE INVERSION IN ATOMIC AND IONIC SPECTRA

In this section, we wish to discuss an approximate correlation which we have noticed between the angular momentum l_{inv} of the states of the alkali-metal atoms and ions for which the fine structure is inverted and the limiting angular momentum l_1 for k ordering, as discussed above and in Ref. 3. Furthermore, we will discuss an additional correlation between the presence or absence of fine-structure inversion and the limiting ionicity δ_1 for k ordering, as discussed in Refs. 1 and 2.

Concerning the experimental material, we can refer to the original tables of Moore[4] and to the recent papers of Farley and Gupta,[16] Gallagher, Cooke, Edelstein, and Hill,[17] and Persson and Pira,[18] who also give extensive references to previous experimental work on this subject. Among the calculations of this effect, we may note the early work of Phillips[19] in 1933, and the recent calculations of Refs. 9–13. We also note the experimental work of Liao *et al.*,[20] Fabre, Gross, and Haroche[21] and the investigations of Gallagher, Hill, and Edelstein.[22]

From the preceding and other investigations, the following picture emerges. For Na, the nd states are inverted, but the nf states are noninverted, with a fine-structure splitting $\Delta\nu$ which is within a few percent of the hydrogenic value.[23] The deviation of the fine-structure splitting $\Delta\nu_{nf}$ from the hydrogenic value has been calculated in the paper of Sternheimer, Rodgers, and Das,[12] and the calculations are in essential agreement with the experimental values of Gallagher *et al.*[17] (deviations ~5% for $11f-17f$). In Ref. 23, we have given a complete list of references to the investigations on $\Delta\nu$ of Na nd, nf, ng, and nh. Not only the nf states, but also the ng and nh states are not inverted, as shown by Gallagher *et al.*[23] Since only the nd states are inverted, we find $l_{\text{inv}}=2$ for Na, which is identical with the value of l_1 for Na, as discussed on p. 1753 of Ref. 3. In this connection, we note that for Li, the fine structure of d states is normal, i.e., essentially hydrogenic, and simultaneously, and most probably not by accident, the k ordering does not occur (see Table VIII of Ref. 1).

Turning now to the higher members of the Na isoelectronic sequence, we have the following results. For Mg II, $3d$-$8d$, $\Delta\nu_{nd}$ is negative (inverted); for $4f$-$6f$, $\Delta\nu_{nf}$ is positive, as obtained from the paper of Risberg.[24] For Al III, $3d$-$6d$, $\Delta\nu_{nd}<0$ (from Isberg[25]). For Si IV, $3d$-$4d$, $\Delta\nu_{nd}<0$ (from Toresson[26]). However, $\Delta\nu_{nd}$ for Si IV becomes positive for[26] $n\geqslant 5$. Similarly, for P V, according to Magnusson and Zetterberg,[27] $\Delta\nu_{nd}$ is positive for all n. The same result holds for the isoelectronic K IX and Ca X, according to the paper of Edlén and Bodén[28]; thus all $\Delta\nu_{nd} > 0$ for these ions. However, $\Delta\nu_{6f}$ is negative (inverted)[28] for the $6f$ state of Ca X.

We will now discuss the K isoelectronic sequence. For K I, the *nd* states are inverted, but for the isoelectronic Ca II, the *nd* level fine structure is large and positive, i.e., noninverted, as already shown by the tables of Moore.[4] Similarly, for Sc III and Ti IV, the data of Moore[4] show that the *nd* fine-structure intervals $\Delta\nu_{nd}$ are positive in all cases. These earlier data are supplemented by the following more recent references. For K I, it was shown by Risberg[29] that $\Delta\nu_{nd} < 0$ for $3d$-$11d$, and by Harper and Levenson[30] that $\Delta\nu_{nd} < 0$ for $8d$-$19d$. In addition, the group of Gallagher[31] at Stanford Research Institute found that $\Delta\nu_{nd} < 0$ in the region of $15d$-$20d$. Thus $l_{\rm inv} = 2$ for K, the same as for Na. For the $4f$ state, Johansson[32] found that $\Delta\nu_{4f}$ is positive, noninverted, i.e., also the same as for Na. According to Litzén,[32] the $5g$ fine structure is unresolved.

For Ca II, Sc III, and Ti IV, the results of Edlén and Risberg[33] (Ca II), Van Deurzen *et al.* and Holmstrom[34] (Sc III), and Swensson and Edlén[35] (Ti IV) confirm the corresponding data of Moore, namely, that no fine-structure intervals (*nd* or *nf*) are negative. For V V Van Deurzen *et al.*[36] found that $\Delta\nu_{4f} < 0$, but Ekberg[37] obtained $\Delta\nu_{nf} > 0$ for $5f$-$9f$. Finally, for Cr VI, Ekberg[38] found no negative fine-structure intervals. Thus in the K I sequence, the negative fine-structure intervals seem to be restricted almost exclusively to K *nd*. We will discuss below the probable correlation of negative fine structure with the region of *k* ordering, where the ionicity lies below the limiting ionicity δ_1 (see Fig. 2 of Ref. 2).

We will now discuss briefly the Rb I isoelectronic sequence. The tables of Moore[4] show that the $4d$ interval is negative, but the higher *nd* intervals $\Delta\nu_{nd}$ are positive, i.e., noninverted. We should also mention the important paper of Farley and Gupta, which has already been referred to above.[16] The results of this paper show that the $6f$ and $7f$ fine structures are clearly inverted, and the values of the intervals are $\Delta\nu_{6f} = -0.0162$ cm^{-1} and $\Delta\nu_{7f} = -0.0116$ cm^{-1}. The existing data for the Na sequence *nd* states are usefully summarized in Fig. 6 of Ref. 16. We note that according to Litzén,[32] the $5g$ fine structure of Rb is unresolved.

For the case of the isoelectronic Sr II spectrum (Sr^+ ion), the extensive measurements of Persson and Pira[18] which have been referred to above show that the intervals $\Delta\nu_{nf}$ are negative for the states $4f$-$8f$, in complete similarity to the results for Rb I. However, we may note that the negative values of $\Delta\nu$ for Sr II are considerably larger than those for the Rb I states: As an example, Persson and Pira[18] obtained $\Delta\nu_{6f}(\mathrm{Sr}^+) = -0.569 \pm 0.005$ cm^{-1}, which exceeds the value of $\Delta\nu_{6f}(\mathrm{Rb}) = -0.0162$ cm^{-1} by a factor of 35.1. A similar factor is found for $7f$, namely, $0.368/0.0116 = 31.7$. This comparison shows clearly that it is considerably easier to measure the fine-structure intervals for singly (or possibly doubly) ionized states, as compared to the measurements for the neutral atoms.

For Y III (Y^{2+}), $\Delta\nu_{nf}$ passes through zero between $n = 4$ and $n = 5$ (i.e., $\Delta\nu_{4f} < 0$, $\Delta\nu_{nf} > 0$ for $n \geqslant 5$), as found by Epstein and Reader.[39] For Zr IV (Zr^{3+}), $\Delta\nu_{nf}$ is positive for all n values, according to measurements of Kiess.[40] Similarly, for Mo VI (Mo^{5+}), Romanov and Striganov[41] obtained no negative *nf* fine-structure intervals. We also note that the authors of Refs. 39–41 were not able to resolve the fine structure of *ng* states in the spectra of Y III, Zr IV, and Mo VI, respectively.

As pointed out by Persson and Pira,[18] the behavior of the $\Delta\nu_{nf}$ interval for the Rb I isoelectronic sequence is very similar to that of the $\Delta\nu_{nd}$ interval for the Na I sequence. In both cases, the fine-structure splitting ($\Delta\nu_{nd}$ for the Na sequence, $\Delta\nu_{nf}$ for the Rb sequence) is negative for a large number of states of the neutral atom and the few-times ionized ions, but becomes positive when the ionicity becomes larger than a certain critical value. We now note that this value of the ionicity δ is approximately equal to the limiting ionicity δ_1 for *k* ordering (see Fig. 2 of Ref. 2). Thus the region of inverted fine structure coincides approximately with the region of *k* ordering, when the ionicity δ is plotted against the atomic number Z. Here, of course, $\delta = Z - N$, where N is the number of electrons in the atom or ion. If we define $\delta_{\rm inv}$ as the ionicity of a state with inverted fine structure, we can write the following relations:

$$\delta_{\rm inv} \lesssim \delta_{\rm inv,max} , \tag{4}$$

$$\delta_{\rm inv,max} \simeq \delta_1 . \tag{4a}$$

To be more specific, for the Na I isoelectronic sequence, we find $\delta_{\rm inv,max} = 2$, since $\Delta\nu_{nd}$ is negative only for the 3^2D and 4^2D states of Si IV (Si^{3+}), so that the vast majority of the n^2D states of Si IV have $\Delta\nu_{nd} > 0$. The value $\delta_{\rm inv,max} = 2$ can be compared with the limiting ionicity for *k* ordering in the Na-Mg region, which is $\delta_1 = 1.5$, to take into account the "phase transition" which occurs in going from Mg^+ to Al^{2+} (see Fig. 1 of Ref. 2).

Similarly for the Rb I isoelectronic sequence, for Y III (Y^{2+}), $\Delta\nu_{nf}$ passes through zero between[39] $n = 4$ and $n = 5$, and for Zr IV (Zr^{3+}), $\Delta\nu_{nf}$ is positive for all n values.[40] According to our criterion for δ_{inv}, we may write $\delta_{\text{inv}}=2$ for the *nf* states of the Rb I sequence. On the other hand, the limiting ionicity for *k* ordering at $Z=37$ is also $\delta_1 \simeq 2$ (see Fig. 2 of Ref. 2), and therefore Eq. (4a) is satisfied in this case.

Next we wish to discuss the correlation between the angular momentum l_{inv} of the states of the atoms and ions of the Na, K, and Rb isoelectronic sequences and the limiting angular momentum l_1 for *k* ordering as discussed in Sec. II and in Ref. 3. Thus $l_{\text{inv}}=2$ for the Na I sequence, which is identical with the value of l_1 for Na, as discussed on p. 1753 of Ref. 3. For the K I sequence, the *nd* states are inverted, so that $l_{\text{inv}}=2$, the same as for Na. Except for the result of Van Deurzen *et al.*[36] who found that $\Delta\nu_{4f}<0$ for V V, the *nf* fine-structures intervals $\Delta\nu_{nf}$ are positive in the K I sequence, in particular K 4*f* (Johansson[32]), and V V 5*f*-9*f* (Ekberg[37]). The K I spectrum exhibits *k* ordering up to and including the *nf* states (see Table III of Ref. 1), so that a tentative value of l_1 is 3, one unit larger than l_{inv}: $l_1=l_{\text{inv}}+1$. Nevertheless l_{inv} is clearly comparable to l_1 for the K I sequence.

Considering now the Rb I sequence, for Rb I, the only *d* state which is inverted is 4*d* ($\Delta\nu_{4d}=-0.44$ cm^{-1}).[20] However, the *nf* states are clearly inverted, as is shown by the results of the tables of Moore[4] (4*f*, 5*f*, 6*f*, 7*f* inverted) and the more recent results of Farley and Gupta[16] (6*f*, 7*f*). Moreover, as discussed above, the results of Persson and Pira[18] demonstrate that the states of 4*f*-8*f* of Sr II have inverted fine structure, and the experiment of Epstein and Reader[39] shows that $\Delta\nu_{4f}<0$ for Y III. Thus $l_{\text{inv}}=3$ for the Rb I sequence, and the value of l_1 as deduced from the spectrum of Rb (Table IV of Ref. 1) is $l_1=4$. Again the value of l_{inv} is comparable to, but slightly smaller than l_1. However, the important point is that in going from K to Rb, both l_1 and l_{inv} increase by approximately one unit.

In view of the preceding results, we can write the approximate relation:

$$l_{\text{inv}} \simeq l_1 . \tag{5}$$

To be more precise, the states with inverted fine structure occur in a narrow band slightly below or actually including the phase boundary l_1 vs Z for the occurrence of *k* ordering (Fig. 2 of Ref. 2). Incidentally, the reasons why the *np* levels of the alkali-metal atoms do not show any tendency towards fine-structure inversion have been elucidated in an extensive calculation carried out by Sternheimer, Rodgers, Lee, and Das.[11]

We will now discuss the Cs I isoelectronic sequence. The tables of Moore[4] list seven inverted *nf* levels of Cs I (4*f*-10*f*), and the more recent experimental data of Eriksson and Wenåker[42] give more accurate values for nine inverted *nf* levels (4*f*-12*f*). The aforementioned paper of Litzén[32] reports that the 5*g* fine structure of Cs I is unresolved. An additional paper of Popescu *et al.*[43] confirms that the *nd* levels 5*d*-34*d* have $\Delta\nu_{nd}$ positive. Thus we have $l_{\text{inv}}=3$ for the Cs I spectrum. On the other hand, the revised value of l_1 as obtained in Sec. II of the present paper [discussion following Eq. (2)] is $l_1=3$. For the Ba II spectrum, the levels 4*f*-8*f* are well resolved and noninverted.[4] For the isoelectronic ion La^{2+} (La III spectrum), two additional references give the following results: The paper of Sugar and Kaufman[44] gives the results that $\Delta\nu_{nd}>0$ for 5*d*-8*d*, $\Delta\nu_{nf}>0$ for 4*f*-8*f*, and $\Delta\nu_{ng}$ for 5*g*, 6*g*, 7*g* is unresolved. The fact that $\Delta\nu_{nf}$ changes sign in going from Cs to Ba$^+$ and La^{2+} can be correlated with the higher ionicity. Thus we have $\delta_{\text{inv,max}}\cong 2$, in good agreement with the value of δ_1 suggested in Ref. 2, namely, $\delta_1 \cong 2.5$ for La^{2+}, since the spectrum of La^{2+} still exhibits almost perfect *k* ordering. The second reference, published by Odabasi,[45] gives confirming results for La^{3+}, namely, $\Delta\nu_{9d}>0$ and $\Delta\nu_{ng}>0$ for 5*g*-8*g*.

Summarizing this discussion of the Cs I sequence, we can state that the two relations of Eqs. (4a) and (5) are well satisfied for this sequence.

We will now discuss the sequences pertaining to the noble metals Cu, Ag, and Au, i.e., the Group IB elements and their isoelectronic ions. As in Ref. 2, we consider only those levels with the configuration $nd^{10}\,n'l$, i.e., having a single electron ($n'l$) outside the closed *nd* shell ($n=3$ for Cu, $n=4$ for Ag, $n=5$ for Au). For the Cu I spectrum itself (Ref. 4, Vol. II, p. 112), the fine-structure intervals are positive for $n'd$, but vary erratically for the $n'p$ and $n'f$ states. As an example, $\Delta\nu(3d^{10}5p)=-0.31$ cm^{-1}, $\Delta\nu(3d^{10}6p)=-243.7$ cm^{-1}, $\Delta\nu(3d^{10}7p)=+529.4$ cm^{-1}. Therefore, no conclusions can be drawn from this spectrum, except for the strong possibility of series perturbations which completely obscure the sign and magnitude of the actual unperturbed fine-structure splittings.

For the isoelectronic spectrum Zn II, the levels 4*f*, 5*f*, 7*f*, 8*f*, and 5*g* are inverted according to the tables of Moore.[4] However, the magnitudes of $\Delta\nu_{nf}$ vary erratically, and moreover, $\Delta\nu_{6f}=+35.4$ cm^{-1} is anomalous and positive. The signs of these intervals have been generally confirmed by the works of Crooker and Dick[46] and of Martin and Kaufman.[47] For Ga III, the 4*d*, 4*f*, and 5*d* levels are noninverted.[4,48]

For the Ag I sequence, Ref. 4 lists six inverted fine-structure levels, namely, 5*f*, 6*f*, 7*f*, and 10*f* of Cd II, and 4*f*, 5*g* of Sn IV. However, especially for the case of Cd II, the fine-structure intervals $\Delta\nu_{nf}$ vary so erratically with n, both as regards to sign and magnitude, that one suspects the presence of strong series perturbations, similar to those which have been hypothesized for the Cu I spectrum. Thus no definite conclusions can be drawn from the Ag I sequence.

For the Au I sequence, eight levels with $\Delta\nu_{nl} < 0$ are listed in Ref. 4, namely, $5f$ of Au I, $5f, 6f, 7f, 8f, 10f$ of Hg II, $5f$ of Tl III, and $5g$ of Pb IV. The evidence for inverted fine structure is rather convincing for the nf levels of Hg II, since the $\Delta\nu_{nf}$ values vary smoothly with n from $5f$ to $8f$ ($\Delta\nu_{5f} = -257$, $\Delta\nu_{6f} = -83$, $\Delta\nu_{7f} = -19$, $\Delta\nu_{8f} = -3.4\ \text{cm}^{-1}$). For the spectra of Tl III and Pb IV, the work of Gutmann and Crooker[49] gives a conflicting result for $5f$ ($\Delta\nu_{5f} > 0$), but it agrees with the general trend for the other nf and ng levels, namely, $\Delta\nu_{6f}, \Delta\nu_{7f} < 0$, $\Delta\nu_{5g} < 0$ for Tl III, and $\Delta\nu_{5f-7f} < 0$, $\Delta\nu_{5g} < 0$ for Pb IV. Altogether, it can probably be concluded from these data for the Au I isoelectronic sequence that in this region of the Periodic Table ($Z \sim 80$), the nf levels and the $5g$ level are generally inverted, so that l_{inv} is in the range from 3 to 4. The corresponding values of l_1 are in the range of 4 to 5 (see Table I of Ref. 3, p. 1754), so that again Eq. (5) of the present paper is approximately satisfied.

Finally, we will discuss briefly the isoelectronic sequences of the Group IIIA elements, namely, Al, Ga, In, and Tl. In this case, we consider only states with the outermost configuration $(ns)^2 n'l$, so that we again have a single electron $(n'l)$ outside closed shells. (We have $n = 3$ for Al, $n = 4$ for Ga, $n = 5$ for In, $n = 6$ for Tl.) For the Al I sequence, there is no recorded case of inverted fine structure in the tables of Moore.[4] The more recent references indicate a confusing picture. Thus for Al I, Ericksson and Isberg[50] obtain $\Delta\nu_{3d-10d} > 0$, $\Delta\nu_{4f,5f} > 0$, and $\Delta\nu_{6f-8f}$ unresolved. On the other hand, for Si II, Shenstone[51] finds $\Delta\nu_{3p-9p} > 0$, $\Delta\nu_{3d-7d} > 0$, but $\Delta\nu_{4f-8f} < 0$. The situation is even more confusing for the spectrum of P III, where Magnusson and Zetterberg[52] obtain an erratic behavior of $\Delta\nu_{np}$ (with $\Delta\nu_{6p} < 0$) and of $\Delta\nu_{nd}$, where $\Delta\nu_{3d}$ and $\Delta\nu_{6d}$ are positive, but $\Delta\nu_{4d-5d}$ are negative. Similarly, $\Delta\nu_{4f} > 0$, whereas $\Delta\nu_{5f} < 0$. This situation clearly indicates the presence of strong series perturbations, which completely mask the "true" sign and magnitude of the unperturbed splittings.

For the Ga I sequence, the situation is a little more clear-cut. Thus, although for Ga I itself, there are no fine-structure inversions according to both Ref. 4 (Moore) and Ref. 7 (Johansson and Litzén), for the case of Ge II, the levels $4f$-$7f$ are inverted according to Moore,[4] and the more recent investigation of Shenstone[53] essentially confirms this result, namely the fine-structure intervals $\Delta\nu_{4f-9f}$ are negative (inverted), whereas all other fine-structure splittings ($4p$-$11p$, $4d$-$10d$, and $5g$-$7g$) are positive. Thus $l_{\text{inv}} = 3$ for Ge II ($Z = 32$), which is slightly smaller than, but comparable to, the corresponding value of $l_1 = 4$ (see Table I of Ref. 3). Thus we have obtained an additional confirmation of the approximate relation $l_{\text{inv}} \simeq l_1$ of Eq. (5). We also note that the tables of Moore list the $4f$ levels of As III and Se IV as being inverted, in agreement with the results for Ge II.

We now consider the In I sequence. For the case In I, according to the measurements of Johnsson and Litzén,[7] there are no negative $\Delta\nu$'s, and the intervals $\Delta\nu_{4f-8f}$ are unresolved. However, for Sn II $4f$ and $5f$, and for Sb III $4f$, the tables of Moore list negative $\Delta\nu_{nf}$ intervals, so that it appears that there is a tendency towards inversion of the nf levels in the In I sequence, and we have $l_{\text{inv}} = 3$, thus confirming Eq. (5) for this sequence.

The Tl I sequence has by far the largest number of inverted fine structure levels in the tables of Ref. 4. Thus, although for Tl I itself, the nf levels are unresolved, for the isoelectronic Pb II spectrum, we have no less than ten inverted levels, namely, $6d$ (which may be anomalous), and all of the nf levels from $5f$ to $13f$. In addition, the measurements of Wood *et al.*[54] indicate that the ng levels from $5g$ to $10g$ have the inverted fine structure. Thus even if we exclude $6d$, we have a total of $9 + 6 = 15$ inverted fine-structure levels for the spectrum of Pb II. In addition, according to Ref. 4, Bi III has six inverted fine-structure levels, namely, $5f$, $6f$, and $5g$, $6g$, $7g$, $8g$. Thus both for Pb II ($Z = 82$) and Bi III ($Z = 83$), both nf and ng levels are inverted, and correspondingly l_{inv} has both the values $l_{\text{inv}} = 3$ and $l_{\text{inv}} = 4$. The corresponding value of l_1 is ~5 (see Table I of Ref. 3), so that Eq. (5) is confirmed again.

We can see in these results for $Z \sim 80$ a continuation of the trend observed above in going from K ($Z = 19$) to Rb ($Z = 37$), namely, that in going from $Z \sim 40$ to $Z \sim 80$, both l_{inv} and l_1 increase by approximately one unit. We also note that in view of all of the experimental evidence, for $Z \gtrsim 35$, a more accurate equation for heavy atoms than Eq. (5) is the following approximate relation:

$$l_{\text{inv}} \simeq l_1 - 1 \quad (Z \gtrsim 35). \tag{5a}$$

Thus, especially for heavy atoms, the l_{inv} for which the inverted fine structure occurs lies well inside the region of k ordering in the phase diagram of l vs Z. This result is similar to that observed above for the ionicity values δ_{inv} for which the inverted fine structure occurs [Eqs. (4) and (4a)], with the important difference that *all* of the atomic or ionic species with $\delta \lesssim \delta_1$ in the phase diagram of δ vs Z are expected to exhibit inverted fine structure, whereas only one or at most two l values will be involved, if we consider the phase diagram of l vs Z, and the affected l values will lie close to but somewhat below the phase boundary given by the limiting angular momentum l_1 [see Eqs. (5) and (5a)].

It is apparent from the preceding discussion that the phenomenon of inverted fine structure is directly connected with the existence of the phase diagrams for k ordering. A possible explanation of these correlations is that a necessary condition for the existence of k ordering is an adequate amount of penetration of the valence orbital inside the core, which can occur only if l is sufficiently small, i.e., $l \lesssim l_1$. This point has been extensively discussed in Ref. 3 (pp. 1755, 1756). Such a penetration ensures an adequate overlap of the valence wave function $v(nl)$ with the core wave functions $u_0(n_c l_c)$ and their perturbations $u_1(n_c l_c \rightarrow l_c')$, and such an overlap is believed to be responsible for the k ordering via exchange-core polarization effects, similar to those which lead to both the inverted fine structure[9-12] and the quadrupole antishielding effects first introduced by the author.[55,56] What is of crucial importance in making this correlation is the observation[1-3,9-12] that all three effects (k ordering, inverted fine structure, and quadrupole antishielding) depend directly on the presence of closed np (and nd) shells in the core of the atom or ion considered.

Before leaving this discussion of the conditions for inverted fine structure, we wish to emphasize that the phenomenon of inverted fine structure is a quite widespread effect, which is obviously directly related to the k ordering. Among the three groups investigated here (Groups IA, IB, and IIIA), the isoelectronic sequences pertaining to the Group IA elements (alkali-metal atoms) provide the largest number of examples of inverted fine structure, namely, $N_{\mathrm{IA}} = 61$, which are distributed as follows: Na I sequence, 25 cases; K I sequence, 18 cases; Rb I sequence, 9 cases; and Cs I sequence, 9 cases.

For the Group IB elements (noble metals) and their isoelectronic ions, no conclusions can be drawn for the Cu I and Ag I sequences, on account of the erratic behavior of the fine-structure intervals, which is probably caused by series perturbations, as discussed above. However, for the Au I sequence, we find 13 cases with $\Delta\nu_{nf} < 0$ or $\Delta\nu_{ng} < 0$, which are probably genuine cases of inverted fine structure, so that we obtain $N_{\mathrm{IB}} = 13$.

Finally, for the Group IIIA elements (Al, Ga, In, Tl) and their isoelectronic ions, we have a total of 32 cases of inverted fine structure, after the apparently spurious cases in the Al I sequence (i.e., for Si II and P III) and in In II are discounted. These 32 cases are distributed as follows: Ga I sequence, 8 levels (pertaining to Ge II, As III, and Se IV); In I sequence, 3 levels (pertaining to Sn II and Sb III); Tl I, 21 levels (pertaining to Pb II and Bi III). Thus we obtain $N_{\mathrm{IIIA}} = 32$, and the total number of genuine inverted fine structure levels (not affected by series perturbations) becomes

$$N_{\mathrm{inv}} = N_{\mathrm{IA}} + N_{\mathrm{IB}} + N_{\mathrm{IIIA}} = 61 + 13 + 32 = 106 \text{ levels}. \tag{6}$$

In connection with Eqs. (4) and (5), and the similarity of the behavior of l_1 vs Z and δ_1 vs Z (see Fig. 2 of Ref. 2 and Fig. 1 of Ref. 3), we have attempted to represent the curves of l_1 vs Z and δ_1 vs Z by simple expressions of the form

$$l_1 = a_l (Z-6)^{b_l}, \tag{7}$$

$$\delta_1 = a_\delta (Z-6)^{b_\delta}, \tag{8}$$

where a_l, b_l, a_δ, and b_δ are appropriate constants determined from the condition that Eqs. (7) and (8) fit the values of Refs. 1 and 2 for two values of Z, in addition to the zero at $Z=6$, which is ensured by the form of Eqs. (7) and (8).

Considering first the curve of l_1 vs Z (Ref. 3), we have obtained a_l and b_l from the requirement that $l_1 = 2$ at $Z = 11$ (Na) and $l_1 = 5$ at $Z = 55$ (Cs). We thus obtain $a_l = 1.048$ and $b_l = 0.4015$, which gives

$$l_1 = 1.048(Z-6)^{0.4015} \quad (6 < Z \lesssim 100). \tag{9}$$

Equation (9) gives $l_1 = 2.935$ at $Z = 19$, i.e., for potassium, where l_1 is actually ≈ 3. Furthermore, Eq. (9) yields $l_1 = 4.161$ at $Z = 37$, i.e., for rubidium, where l_1 is actually ≈ 4. For $Z = 88$ (Ra), Eq. (9) gives $l_1 = 6.15$, whereas the actual value of l_1 is in the range of 5–6 (see Table I of Ref. 3). Thus we conclude that Eq. (9) is approximately valid for $6 < Z \lesssim 100$, as indicated.

We now turn to Eq. (8) for δ_1. As discussed in Ref. 2, the curve of Fig. 2 of that paper (p. 471) was obtained by assuming a limiting ionicity δ_1 $(= Z - N)$ of 1.5 for $Z = 12$ and 2.5 for $Z = 57$, corresponding to Mg^+ and La^{2+}, respectively. By fitting Eq. (8) to these values of δ_1, we obtain $a_\delta = 0.9781$ and $b_\delta = 0.2386$, which gives the approximate relation

$$\delta_1 = 0.9781(Z-6)^{0.2386} \quad (6 < Z \lesssim 100). \tag{10}$$

Equation (10) yields $\delta_1 = 2.799$ for Ra ($Z = 88$) and $\delta_1 = 3.796$ for a hypothetical ion with $Z = 300$. The latter value somewhat exceeds the extrapolated value $\delta \cong 3$ for $Z = 300$ in Fig. 1 of Ref. 2 and for this reason, we have indicated an effective limit $Z \lesssim 100$ for the validity of Eq. (10) above.

As we have extensively discussed in Refs. 1–3 and 12, there is good evidence that the three phenomena of the k ordering of the atomic spectra (gross structure), the inverted fine structure, and the quadrupole antishielding factors[55,56] γ_∞ and R (hyperfine structure) are related to the same basic cause, namely, core-polarization effects. It therefore seems of interest also to try to represent the ionic antishielding factor γ_∞ by an expression of the type of Eqs. (7) and (8), namely,

$$\gamma_\infty = a_\gamma (Z-6)^{b_\gamma} . \qquad (11)$$

A summary table of the values of γ_∞ obtained by the author[57] is given in Table VI of Ref. 57 (see p. 148). In order to obtain the values of the parameters a_γ and b_γ, we have fitted Eq. (11) to the values $\gamma_\infty = -4.56$ for Na^+ ($Z=11$) and $\gamma_\infty = -102.5$ for Cs^+ ($Z=55$). We thus obtain $a_\gamma = -0.5079$ and $b_\gamma = 1.3637$, which gives the approximate relation

$$\gamma_\infty = -0.5079(Z-6)^{1.3637} \quad (6 \leqslant Z \leqslant 55) . \qquad (12)$$

Equation (12) gives good agreement with our calculated values of γ_∞ for singly ionized alkali-metal atoms throughout the range from $Z=11$ to $Z=55$. Thus for K^+ ($Z=19$), Eq. (12) gives $\gamma_\infty = -16.8$, as compared to the calculated value[57] -17.32. Similarly for Rb^+ ($Z=37$), Eq. (12) yields $\gamma_\infty = -54.9$, which is in fairly good agreement with the calculated value[57] -47.2.

It should be emphasized that Eq. (12) applies only to the alkali-metal ions (singly ionized), both because of the strong dependence of γ_∞ on the ionicity and because the alkali-metal ions have the following essential feature in common, namely, the existence of an outermost filled np shell. Thus for the isoelectronic ions F^-, Na^+, and Al^{3+}, $|\gamma_\infty|$ decreases rapidly from 22.53 for F^- to 4.56 for Na^+ and to 2.36 for Al^{3+}. Similar relationships for other pairs of isoelectronic ions can be readily seen in Table VI of Ref. 57, e.g., $\gamma_\infty(Br^-) = -123.0$, as compared to $\gamma_\infty(Rb^+) = -47.2$.

The second point which we have emphasized above relates to the relatively small values of $|\gamma_\infty|$ when the outermost filled shell is a d shell, in particular for Cu^+ (filled $3d$ shell) and Ag^+ (filled $4d$ shell). Thus[57] $\gamma_\infty(Cu^+) = -15.0$, whereas Eq. (12) would give -36.5 for $Z=29$; similarly,[57] we have $\gamma_\infty(Ag^+) = -34.9$, whereas from Eq. (12), we would calculate a value of -80.4. In spite of these shortcomings, if we restrict ourselves to the alkali-metal ions, namely, Na^+, K^+, Rb^+, and Cs^+, Eq. (12) gives a good representation of the behavior of γ_∞ vs Z, and this reinforces our previous conclusions[1-3,12] as to the basic similarity of the three effects represented by the quantities l_1, δ_1, and γ_∞.

IV. *k*-SYMMETRY BREAKING IN ATOMIC SPECTRA

In Ref. 3, we have briefly discussed the possibility that the arrangement of atomic levels in nonoverlapping k bands, and the l-dependent splittings within each k band may be the result of a symmetry-breaking mechanism, similar to the SU(3) scheme of Gell-Mann and Ne'eman[58] for the mass spectrum of the elementary particles and their excited states (see Ref. 3, p. 1756). Thus we assume that there are primitive (unobserved) levels having only the quantum number k, and we refer to this structure of levels as the k gross structure. The primitive k levels are split into several levels with different l values, and with $n=k-l$ in each case. This structure which is caused by an l-dependent interaction, will be called the semi-fine-structure of the atomic levels. An example of the primitive $k=9$ and $k=10$ levels and the associated semi-fine-structure is shown in Fig. 1 for the case of the rubidium atom Rb (see Table IV of Ref. 1 for the j-averaged energy values E_{nl} of the individual nl levels). The energy values of the primitive (unobserved) k levels are obtained by taking the average (centroid) of the E_{nl} values for the s, p, d, f, g levels in each k band (see Table VII of Ref. 1). Thus for $k=9$, we find

$$E(k=9) = \tfrac{1}{5}(29,298 + 29,848 + 30,281 + 30,499 + 30,628) = 30\,111 \text{ cm}^{-1} , \qquad (13)$$

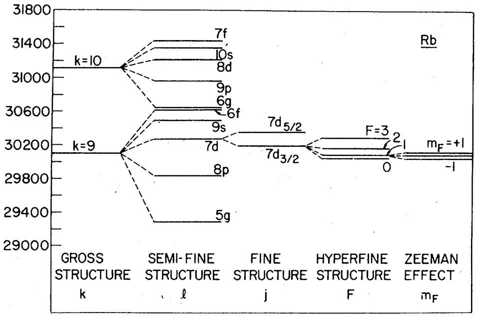

FIG. 1. Levels with $k=9$ and $k=10$ of the spectrum of neutral rubidium Rb. The primitive $k=9$ and $k=10$ levels which are unobserved were obtained by taking an average of the observed $k=9$ and $k=10$ levels, respectively [see Eq. (13)]. These observed levels constitute the semi-fine-structure. The energy scale E_{nl} is shown on the left-hand ordinate. This scale does not apply to the fine structure of $7d$, the hyperfine structure of the $7d_{3/2}$ level for Rb^{87} ($I=3/2$), and the Zeeman splitting of the $F=1$ level, which are shown schematically enlarged in the right-hand part of the figure. The hierarchy of spectral structures is described in the bottom part of the figure, together with the specific quantum numbers (k, l, j, F, m_F) which characterize each structure.

and similarly, $E(k=10)=31\,126\ \text{cm}^{-1}$. [The precise form of the averaging in obtaining $E(k)$ does not matter much; thus we could have taken the midpoint between the $6f$ and $5g$ levels for $k=9$, which would give $29\,963\ \text{cm}^{-1}$, i.e., only $148\ \text{cm}^{-1}$ below the value of Eq. (13).]

In Fig. 1, we note that the two k bands do not overlap, but the distance between $E_{6f}=30\,628\ \text{cm}^{-1}$ (top of $k=9$ band) and $E_{6g}=30\ 637\ \text{cm}^{-1}$ (bottom of $k=10$ band) is only $9\ \text{cm}^{-1}$. This small separation of neighboring k bands has been discussed extensively in Ref. 3 (see p. 1757–1759, and Table II). Besides the gross structure (quantum number k) and the semi-fine-structure (l), we have shown schematically and on a progressively enlarged scale, the fine structure of the $7d$ state ($7d_{3/2}$ and $7d_{5/2}$), the hyperfine structure of $7d_{3/2}$ for the case of ^{87}Rb with nuclear spin $\text{I}=\frac{3}{2}$, and finally the Zeeman effect of the $F=1$ hyperfine level. The quantum numbers appropriate to each level structure are shown at the bottom of Fig. 1, i.e., k, l, j, F, and m_F.

Thus there exists a hierarchy of five level structures for the rubidium atom (and, of course, also for other pseudo-one-electron atoms with $Z \geqslant 11$, as explained in Refs. 1–3). If we consider now again the k gross structure and the l-dependent semi-fine-structure, we wish to point out an important analogy to the SU(3) scheme[58] of the strongly interacting particles. In the latter case, for both the mesons and the baryons, the primitive J^P level is also unobserved, and is split into a number of observed particle levels having different strangeness S and isotopic spin I. Thus, as mentioned in Ref. 3, k is the analogue of J^P (spin-parity), and l is the analog of the doublet (S, I) in the particle case. The lack of overlap of neighboring k bands, i.e., what we have called the perfect (or near-perfect) k ordering is similar to the approximate nonoverlap of different J^P multiplets, e.g., π, K, η, η' ($J^P=0^-$) and $\rho, \omega, K^*, \varphi$ ($J^P=1^-$) for the low-lying meson states.

In view of these similarities, we believe that a symmetry breaking, similar to that for the hadronic particle spectrum, operates also in the present case. However, the relevant group for the pseudo-one-electron atomic and ionic spectra may well be different from the SU(3) group for the strong interactions (hadrons). It would indeed be interesting if the same type of physics would apply in both situations, since the average level spacing for the hadronic case, e.g., for the baryon octet (N, Λ, Σ, Ξ) is $\frac{1}{3}(1320-939)=127$ MeV, as compared to the following average spacing $\langle\Delta\rangle$ for the $k=9$ group of levels for Rb:

$$\langle\Delta\rangle_{k=9}=\frac{E_{6f}-E_{5g}}{4}=\frac{30\,628-29\,298}{4}=332.5\,\text{cm}^{-1}. \qquad (14)$$

Here we have divided by 4, since there are four successive intervals involving the five levels shown in Fig. 1. Now $332.5\ \text{cm}^{-1}=332.5/8.07=41.2$ meV, and the ratio of the level spacings in the two cases is

$$\frac{\langle\Delta\rangle_{\text{baryon}}}{\langle\Delta\rangle_{k=9}}=\frac{127\times10^{6}}{41.2\times10^{-3}}=3.08\times10^{9}. \qquad (15)$$

A few general comments can be made concerning the hierarchy of spectral structures shown in Fig. 1. Thus in going from a semi-fine level nl (or kl) to the fine structure, we can use the Dirac equation which automatically accounts for the spin of the electron, and therefore leads us from the orbital angular momentum l to the total angular momentum j. Similarly, the introduction of the nuclear spin I and the associated properties of the nuclear moments μ and Q lead us to an explanation of the hyperfine structure. Finally the introduction of an external magnetic field $\vec{\text{H}}$ gives rise to the Zeeman splitting.

In the preceding context, it is not clear what is the nature of the l-dependent interaction which leads to the breaking of the primitive (global) k symmetry and to the precise sequence of levels with different l values (and $n=k-l$), which constitutes the l patterns which have been extensively discussed in Refs. 1 and 2. Whatever the nature of the l-dependent interaction, it must explain the following three features: (a) In general, the l pattern does not change with increasing k, e.g., for Rb, it is $\{l_i\}=gpdsf$ from $k=6$ to $k\sim55$, i.e., from the lowest-lying levels up to highly excited levels very close to the ionization limit. (b) The k bands are separated from each other, i.e., sets of levels with neighboring k values do not overlap in general, provided that $l<l_1$ and the ionicity $\delta<\delta_1$. This is what is meant by "perfect k ordering" (see, e.g., Tables I and II of the present paper). (c) k is a "good quantum number" for the total energy E_{nl} throughout the region of Z from $Z=11$ (Na) (nonrelativistic region) up to $Z\sim120$ (relativistic region). As discussed in Refs. 2 and 3, the presence of a particular l pattern (e.g., *fdps*, *dpsf*, *pdsf*, *dpfs*) depends mainly on the atomic number Z, i.e., on the number and type of closed shells of the core, in particular the np and nd shells which appear to be mainly responsible for the k ordering, as well as the inverted fine structure and the large quadrupole antishielding factors γ_∞ of ions.

V. SUMMARY AND DISCUSSION

In the present paper, we have investigated certain aspects of the k ordering of atomic energy levels and the inverted fine structure, which had not been discussed in our previous papers on these subjects (Refs. 1–3 and 9–12). More specifically, the discussion of Secs. II and IV can be considered as a direct continuation of the previous discussion in our earlier three papers[1-3] on k ordering. In this connection, the author apologizes for the rather frequent cross references to the papers of Refs. 1–3. However, in order to avoid needless duplication of the tables of Refs. 1–3 (altogether 33 tables) and of the three pertinent figures, it seemed desirable to write up this paper as was done here including the cross references. For those readers who are interested in the k-ordering properties of atomic and ionic spectra, and their associated l patterns, the three aforementioned papers should be studied in sequence. As concerns the inverted fine structure which is discussed in Sec. III, a preliminary study of the paper of Ref. 12 may be helpful, especially the discussion of pp. 509–510.

In Sec. II of the present paper, we have discussed in detail the revised spectra of Ga I and Sr I, as obtained from the more recent determinations of Johansson and Litzén[7] and of Garton and Codling,[8] respectively. The revised spectra are given in Tables I and II, respectively, and exhibit perfect k ordering (number of $k+\lambda$ exceptions $N_E = 0$). Thus a total of $4+7=11$ apparent $k+\lambda$ exceptions as obtained from the tables of Moore[4] are removed (see Ref. 2, Tables I and IX).

At the end of Sec. II, we have reexamined the excited-state spectrum of Rb I, as given in the tables of Moore.[4] Thus in Table IV of Ref. 1, we had omitted a large number of levels for the sake of brevity. Instead of the 45 levels included in the table of Ref. 1, there is actually a total of 158 levels in Moore's tables, which exhibit k ordering (from $k=6$ to $k=56$). The additional 113 levels are described in Sec. II. If we would include these 113 levels in Table IV of Ref. 1, we would obtain a total of $171+113=284$ levels for the alkali-metal atoms Na, K, Rb, and Cs, and therefore a grand total of $284+132=416$ levels for the nine spectra of Ref. 1 (alkali-metal atoms and alkaline-earth ions). (See Tables VI and XVI of Ref. 1.)

Concerning the ten spectra of Ref, 2, we have been able to include six additional levels in the revised spectrum of Sr I (Table II of present paper). These levels have k values $k=16$, 17, and 18. Thus the total number of levels pertaining to the 33 spectra of Ref. 2 becomes $N_L = 858$, and the grand total for the 42 spectra of both Refs. 1 and 2 is $\sum N_L = 858 + 416 = 1274$ (instead of 1155 as reported in Ref. 2).

The 19 spectra which have been explicitly tabulated in Refs. 1 and 2 include 416 levels for Ref. 1 (if we include the 113 additional levels for Rb) and 368 levels for Ref. 2 (including the additional six levels for Sr I), thus giving a total

$$\sum N_L = 416 + 368 = 784 \text{ levels}. \qquad (16)$$

Among these 784 levels, we have found only five $k+\lambda$ exceptions connected with np and nd levels ($6d$ of Ba$^+$; $7d$, $8d$, $9d$, and $9p$ of Ra$^+$). These exceptions cannot be associated with l being larger than the limiting angular momentum l_1 for k ordering. They represent less than 1% of the total $\sum N_L$ of Eq. (16), and, as discussed in Sec. II, these apparent $k+\lambda$ exceptions may be removed by a reanalysis of the spectra of Ba II and Ra II. The data given in Moore's tables[4] for these spectra are mainly based on the early work of Rasmussen[15,59] for Ba II (Ref. 59) and Ra II (Ref. 15). The preceding comments and the overwhelming evidence in favor of the k ordering and l sequence suggests that the k ordering can be used as a tool in the future analyses of one-electron spectra, in order to assign the correct value of n and/or l for certain excited-state energy levels, where there is a reasonable doubt about the present assignments.

In Sec. III, we have discussed in detail the occurrence of the inverted fine structure in the spectra of atoms and ions with one electron outside closed shells. Thus we have found that the l value for which the inversion occurs, denoted by l_{inv}, is comparable to l_1, the limiting angular momentum for k ordering (Ref. 3). In some cases, l_{inv} is somewhat smaller than l_1, but in general the approximate relations of Eqs. (5) and (5a) hold, namely, $l_{\text{inv}} \sim l_1$. In addition, if we consider ions, the fine-structure inversion occurs only in the region of ionicity $\delta \lesssim \delta_1$, i.e., in the region of k ordering where the ionicity $\delta = Z - N$ does not exceed the limiting ionicity for k ordering (see Fig. 2 of Ref. 2). At present, we have no detailed explanation of these correlations, expressed by Eqs. (4), (4a), (5), and (5a). However, it is believed that both correlations involve the overlap of the valence-electron wave function with the core-electron wave functions $u_0(nl)$ and their perturbations $u_1(nl \rightarrow l)$, as we have discussed in Ref. 3 (see pp. 1755 and 1756).

Finally, in Sec. IV we have discussed the strong possibility that the prevailing existence of nonoverlapping k bands consisting of levels having the same k value but different l values arises from a symmetry-breaking process which leads to the splitting of a primitive k level (gross structure) into a multiplet of l levels having the same value of k, which we have called the semi-fine-structure. This symmetry breaking for atomic spectra would be in a general sense similar to the SU(3) symmetry breaking of the mass spectrum of the elementary particles, as introduced by Gell-Mann and Ne'eman.[58] However, it should be noted that the underlying group for the atomic case may be different from SU(3). An example of this proposed symmetry breaking is shown in Fig. 1 for the energy levels with $k=9$ and $k=10$ in the spectrum of the rubidium atom Rb I.

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[1] R. M. Sternheimer, Phys. Rev. A 15, 1817 (1977).

[2] R. M. Sternheimer, Phys. Rev. A 16, 459 (1977).

[3] R. M. Sternheimer, Phys. Rev. A 16, 1752 (1977).

[4] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U. S.) Circ. No. 467 (U. S. GPO, Washington, D. C., 1949–1958), Vols. I–III.

[5] B. Edlén (private communication).

[6] G. zu Putlitz (private communication).

[7] I. Johansson and U. Litzén, Ark. Fys. 34, 573 (1967).

[8] W. R. S. Garton and K. Codling, J. Phys. B 1, 106 (1968).

[9] H. M. Foley and R. M. Sternheimer, Phys. Lett. A 55, 276 (1975).

[10] T. Lee, J. E. Rodgers, T. P. Das, and R. M. Sternheimer, Phys. Rev. A 14, 51 (1976).

[11] R. M. Sternheimer, J. E. Rodgers, T. Lee, and T. P. Das, Phys. Rev. A 14, 1595 (1976).

[12] R. M. Sternheimer, J. E. Rodgers, and T. P. Das, Phys. Rev. A 17, 505 (1978).

[13] L. Holmgren, I. Lindgren, J. Morrison, and A.-M. Mårtensson, Z. Phys. A 276, 179 (1976); I. Lindgren, J. Lindgren, and A.-M. Mårtensson, Phys. Rev. A 15, 2123 (1977); E. Luc-Koenig, Phys. Rev. A 13, 2114 (1976).

[14] H. R. Kratz, Phys. Rev. 75, 1844 (1949).

[15] E. Rasmussen, Z. Phys. 86, 24 (1933); 87, 615 (1934).

[16] J. Farley and R. Gupta, Phys. Rev. A 15, 1952 (1977).

[17] T. F. Gallagher, W. E. Cooke, S. A. Edelstein, and R. M. Hill, Phys. Rev. A 16, 273 (1977).

[18] W. Persson and K. Pira, Phys. Lett. A 66, 22 (1978).

[19] M. Phillips, Phys. Rev. 44, 644 (1933); 45, 428 (1934). See also D. R. Beck and H. Odabasi, Ann. Phys. (N. Y.) 67, 274 (1971).

[20] K. H. Liao, L. K. Lam, R. Gupta, and W. Happer, Phys. Rev. Lett. 32, 1340 (1974).

[21] C. M. Fabre, M. Gross, and S. Haroche, Opt. Commun. 13, 393 (1975).

[22] T. F. Gallagher, R. M. Hill, and S. A. Edelstein, Phys. Rev. A 13, 1448 (1976).

[23] P. Risberg, Ark. Fys. 10, 583 (1956); C. M. Fabre *et al.*, Opt. Commun. 13, 393 (1975); P. F. Liao and J. E. Björkholm, Phys. Rev. Lett. 36, 1543 (1976); T. F. Gallagher *et al.*, Phys. Rev. A 13, 1448 (1976); 14, 744 (1976); 16, 273 (1977).

[24] P. Risberg, Ark. Fys. 9, 483 (1955).

[25] B. Isberg, Ark. Fys. 35, 551 (1968).

[26] Y. G. Toresson, Ark. Fys. 17, 179 (1960).

[27] C. E. Magnusson and P. O. Zetterberg, Phys. Scr. 10, 177 (1974).

[28] B. Edlén and E. Bodén, Phys. Scr. 14, 31 (1976).

[29] P. Risberg, Ark. Fys. 10, 583 (1956).

[30] C. D. Harper and M. D. Levenson, Phys. Lett. A 56, 361 (1976).

[31] T. F. Gallagher (private communication).

[32] I. Johansson, Ark. Fys. 20, 135 (1961); U. Litzén, Phys. Scr. 1, 253 (1970).

[33] B. Edlén and P. Risberg, Ark. Fys. 10, 553 (1956).

[34] C. H. Van Deurzen *et al.*, J. Opt. Soc. Am. 63, 158 (1973); J. E. Holmstrom, Phys. Scr. 5, 249 (1972).

[35] J. W. Swensson and B. Edlén, Phys. Scr. 9, 335 (1974).

[36] C. H. Van Deurzen *et al.*, J. Opt. Soc. Am. 64, 498 (1974).

[37] J. O. Ekberg, Phys. Scr. 9, 96 (1974).

[38] J. O. Ekberg, Phys. Scr. 8, 35 (1973).

[39] G. L. Epstein and J. Reader, J. Opt. Soc. Am. 65, 310 (1975).

[40] C. C. Kiess, J. Res. Natl. Bur. Stand. 56, 167 (1956).

[41] N. P. Romanov and A. R. Striganov, Opt. Spectrosc. 27, 8 (1969).

[42] K. B. S. Eriksson and I. Wenåker, Phys. Scr. 1, 21 (1970).

[43] D. Popescu *et al.*, Phys. Rev. A 8, 1666 (1973).

[44] J. Sugar and V. Kaufman, J. Opt. Soc. Am. 55, 1283 (1965).

[45] H. Odabasi, J. Opt. Soc. Am. 57, 1459 (1967).

[46] A. M. Crooker and K. A. Dick, Can. J. Phys. 46, 1241 (1968).

[47] W. C. Martin and V. Kaufman, J. Res. Natl. Bur. Stand. Sec. A 74, 11 (1970).

[48] Y. N. Joshi *et al.*, Spectrochim. Acta 28, 149 (1973).

[49] F. Gutmann and A. M. Crooker, Can. J. Phys. 51, 1823 (1973).

[50] K. B. S. Eriksson and H. B. S. Isberg, Ark. Fys. 23, 527 (1963).

[51] A. G. Shenstone, Proc. R. Soc. London Ser. A 261, 153 (1961).

[52] C. E. Magnusson and P. O. Zetterberg, Phys. Scr. 15, 237 (1977).

[53] A. G. Shenstone, Proc. R. Soc. London Ser. A 276, 293 (1963).

[54] D. R. Wood *et al.*, J. Opt. Soc. Am. 64, 1159 (1974).

[55] R. M. Sternheimer, Phys. Rev. 80, 102 (1950); 84, 244 (1951); 95, 736 (1954); 105, 158 (1957); 146, 140 (1966); 164, 10 (1967); Phys. Rev. A 6, 1702 (1972).

[56] H. M. Foley, R. M. Sternheimer, and D. Tycko, Phys. Rev. 93, 734 (1954); R. M. Sternheimer and H. M. Foley, Phys. Rev. 102, 731 (1956); R. M. Sternheimer, Phys. Rev. 130, 1423 (1963); 132, 1637 (1963); 159, 266 (1967).

[57] R. M. Sternheimer, Phys. Rev. 146, 140 (1966).

[58] M. Gell-Mann, Phys. Rev. 125, 1067 (1962); Y. Ne'eman, Nucl. Phys. 26, 222 (1961).

[59] E. Rasmussen, Z. Phys. 83, 404 (1933).