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

R. M. Sternheimer

*Brookhaven National Laboratory, Upton, New York 11973*

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In two previous papers, the quantum number $k \equiv n + l$ was considered as an energy-ordering quantum number for the excited states of 42 atoms and ions, which can be regarded as being composed of a single excited valence electron outside closed shells. It was shown that the energy levels of the valence electron are energy ordered according to the (increasing) values of $k$, and moreover within each $k$ group or $k$ band, there is a definite and generally constant sequence of $l$ values for each atom or ion, as the electronic energy is increased within the $k$ band; this sequence has been called the "$l$ pattern." Altogether 42 spectra involving 1155 levels were included in the previous investigation. Of these 1155 levels, 120 show a small deviation from $k$ ordering, and these have been called "$k + \lambda$ exceptions." In the present work, a thorough analysis of these $k + \lambda$ exceptions has been made, and it has been found that in the vast majority of the cases, the $k + \lambda$ exceptions arise from the fact that the angular momentum $l$ is too large, and is close to or larger than the limiting angular momentum $l_l$ for which a "phase transition" occurs from $k$ ordering to hydrogenic (H) ordering, which is similar to the phase transition which arises when the ionicity $\delta \equiv Z - N$ ($N$ being the number of electrons) is too large, and exceeds the "limiting ionicity" $\delta_l$. A diagram showing the regions of validity of $k$ and H ordering as a function of the angular momentum $l$ and the atomic number $Z$, i.e., the curve of $l_l$ vs $Z$, has been obtained. A tentative explanation of the phase diagrams of $\delta$ vs $Z$ and $l$ vs $Z$ is discussed, i.e., the reason why too large a value of $\delta$ or $l$ will destroy the $k$ ordering phase of the spectrum.

## I. INTRODUCTION

In two previous papers,[1,2] we have introduced the concept of the quantum number

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

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 the spectrum can be divided into successive $k$ groups, and within each $k$ group, 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 50, i.e., over a range of forty-five $k$ 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[3] 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. Actually, for six of these 42 spectra, the $l$ pattern changes somewhat with increasing $k$, and therefore the $l$ patterns for 48 cases are listed in the table. In those cases, where the $l$ pattern changes with increasing $k$, the pertinent region of $k$ values is listed for each pattern. As an example, for the spectrum of Ra II ($Ra^+$), the $l$ pattern is *dpsf* for the groups $k = 8$ and 9, and it is *dpfs* for the group $k = 10$.

It is apparent from the preceding discussion that for a spectrum where the $k$ ordering prevails, the basic quantum numbers are $k$ and $l$, and the derived quantum number $n$ is given by:

$$n = k - l. \tag{2}$$

It was found in Ref. 1, that for the isoelectronic spectra for systems with 11 electrons ($N = 11$), the spectra of Na and $Mg^+$ exhibit good $k$ ordering, whereas the spectra of $Al^{2+}$, $Si^{3+}$, $P^{4+}$, etc. are hydrogenic, i.e., their energy levels are grouped according to the value of the principal quantum number $n$, with a slight increase in the energy as $l$ is increased from $l = 0$ to the maximum value $l_{max} = n - 1$. Here $N$ is the number of electrons in the atom or ion considered. Thus $Z-N$ is the degree of ionization or ionicity. As $Z-N$ is increased from $Z-N=1$ to $Z-N=2$ for $Z=11$, there is essentially a phase transition from $k$ ordering to hydrogenic ordering, which will be denoted by H ordering. The phase diagram representing the regions of validity of $k$ and H ordering is shown in Fig. 2 of Ref. 2.

It should be pointed out that the present paper constitutes the sequel to the papers of Refs. 1 and 2, and for those readers who are interested in the $k$-ordering properties of atomic and ionic spectra, and their associated $l$ patterns, the two aforementioned papers should be studied in sequence. In order to avoid needless duplication of the tables of Refs. 1 and 2 (altogether 31), and of the two figures of Ref. 2, we have not included these in the present paper. The author hopes that the frequent cross references to the results of Refs. 1 and 2 will not cause an undue inconvenience to the reader.

Section II contains a determination of the curve of the limiting angular momentum $l_1$ vs $Z$. In Sec. III, we will present a general discussion of the results of the present paper and of Refs. 1 and 2. We will give a partial explanation of the phase transitions which occur as $l$ or $Z-N$ is increased beyond the critical value on the corresponding phase boundary. For simplicity, we denote the ionicity $Z-N$ by $\delta$, and the values on the phase boundary of Fig. 2 of Ref. 2 will be denoted by $\delta_1$, in complete analogy to $l_1$ for the angular momentum. In Sec. III, we will also give a possible explanation of the $k$ ordering and the splitting of the different $l$ levels contained within each $k$ group, involving an analogy to the SU(3) symmetry scheme for the strongly interacting particles.

## II. LIMITING ANGULAR MOMENTUM $l_1$ FOR $k$ ORDERING

The idea of a limiting angular momentum $l_1$ occurred to the present author in connection with an examination of the so-called $k+\lambda$ exceptions in the spectra of Refs. 1 and 2. It may be recalled that a $k+\lambda$ exception corresponds to a level with a value $k_0$ which lies in the region occupied mostly by levels in the group whose $k=k_0+\lambda$, where $\lambda$ is generally $+1$ or $-1$.

Referring to Table II of Ref. 1, which pertains to the spectrum of Na, it was noticed that the $k+\lambda$ exceptions generally consist of the $nf$ levels, for which $\lambda=-1$. We now note that the $4f$ level at $E_{4f}=34\,589$ cm$^{-1}$ has the value $\lambda=-1$ because it lies near the $4d$ level at $E_{4d}=34\,549$ cm$^{-1}$, i.e., only 40 cm$^{-1}$ above the $4d$ level. A similar comment can be made concerning the $5f$ level with $E_{5f}=37\,058$ cm$^{-1}$ and $\lambda=-1$, which lies only 22 cm$^{-1}$ above the $5d$ level having $E_{5d}=37\,037$ cm$^{-1}$. In addition the $5g$ level with $E_{5g}=37\,060$ cm$^{-1}$ and $\lambda=-2$ lies very close to $5f$. This sequence: $5d, 5f, 5g$ is exactly what is expected for a hydrogenically ordered spectrum. The $6h$ level with $E_{6h}=38\,403$ cm$^{-1}$ and $\lambda=-3$ is also an indication of hydrogenic ordering, since it lies only 3 cm$^{-1}$ above the $6f$ level, at $E_{6f}=38\,400$ cm$^{-1}$. (The $6g$ level for Na is not included in the tables of Moore,[3] but it undoubtedly lies between $6f$ and $6h$.)

Thus for the case of Na, we conclude that the limiting angular momentum $l_1$ equals 2, since beginning with the $f$ levels ($l=3$) we have hydrogenic ordering. Proceeding now to the spectrum of potassium, as given in Table III of Ref. 1, we note that the $nf$ levels are at a considerable distance from the $nd$ levels, thus showing that $k$ ordering is still obeyed for $l=3$. However, for the $5g$, $6g$, and $6h$ levels, we have $k+\lambda$ exceptions, with $\lambda=-1$ for $5g$ and $6g$ and $\lambda=-2$ for $6h$. The $5g$ level with $E_{5g}=30\,620$ cm$^{-1}$ lies only 14 cm$^{-1}$ above the $5f$ level for which $E_{5f}=30\,606$ cm$^{-1}$. The $6f$, $6g$, and $6h$ levels lie very close together at energies of 31 953, 31 961, and 31 961 cm$^{-1}$, respectively. Thus we conclude that the limiting angular momentum $l_1$ for K is $l_1=3$, an increase of one unit above $l_1=2$ for Na, as described above.

For the case of rubidium, as shown in Table IV of Ref. 1, we note that the $5g$ and $6g$ levels still obey $k$ ordering, although just barely, since $E_{5g}-E_{5f}=29\,298-29\,278=20$ cm$^{-1}$ only, and $E_{6g}-E_{6f}=30\,637-30\,628=9$ cm$^{-1}$ only. On the other hand, the $6h$ level at 30 644 cm$^{-1}$ constitutes a $k+\lambda$ exception with $\lambda=-1$, being very close to the $6g$ level at 30 637 cm$^{-1}$. Although this is the only $k+\lambda$ exception in the spectrum, we conclude that $l_1=4$ for Rb, another increase of one unit in $l_1$ as compared to $l_1$ for the previous alkali (K).

For the case of cesium, as shown in Table V of Ref. 1, the situation is somewhat confused, since the $ng$ levels have a *positive* $\lambda$, namely $\lambda=+1$. On the other hand, the $5f$ level ($E_{5f}=26\,971$ cm$^{-1}$) is not close to the $5d$ level, but it is close to the $5g$ level ($E_{5g}=27\,010$ cm$^{-1}$). A similar result is observed for the $6f-6g$ energy difference, which is quite small, since $E_{6g}-E_{6f}=28\,347-28\,330=17$ cm$^{-1}$. Moreover the $6h-6g$ energy difference is still smaller, namely $E_{6h}-E_{6g}=28\,356-28\,347$ $=9$ cm$^{-1}$. These results indicate that $l_1$ is in the range from $l_1=4$ to $l_1=5$.

A similar analysis can be carried out for the alkaline-earth ionic spectra listed in Tables XI–XV of Ref. 1. The results are $l_1=2$ for Mg$^+$, $l_1=3$ for Ca$^+$, $l_1\geq 5$ for Sr$^+$, $l_1\geq 5$ for Ba$^+$, and $l_1=5$ or 6 for Ra$^+$. The reason for assigning the value $l_1$ $\geq 5$ for both Sr$^+$ and Ba$^+$ is that the $ng$ levels are still very well $k$ ordered, so that $l_1$ must be at least 5, and may well be 6 or higher. In this connection, we note that for Sr$^+$, the 6$g$ and 10$s$ levels are close together, both having $k = 10$ ($E_{6g} = 79\,984$ and $E_{10s} = 80\,702$ cm$^{-1}$). In order to appreciate the radical departure from hydrogenic ordering which is involved in this contiguity of 6$g$ and 10$s$, we note that for a hydrogenic ordering situation, the following levels would be located between 6$g$ and 10$s$: 6$h$, all 7$l$ levels, all 8$l$ levels, and all 9$l$ levels, giving a total of $1 + 7 + 8 + 9 = 25$ levels.

For the case of Ra$^+$ (Table XV of Ref. 1), the $k+\lambda$ exceptions for the $nd$ and 9$p$ levels do not seem to be connected with the transition to hydrogenic ordering, since for example $E_{8d} - E_{8p} = 61\,878 - 51\,797 = 10\,081$ cm$^{-1}$ is very large, and similarly for $E_{9p} - E_{9s} = 63\,191 - 59\,165 = 4\,026$ cm$^{-1}$. The 5$g$ level is listed below 6$f$, and similarly for 6$g$ and 10$s$. We thus conclude that $l_1 > 4$, and $l_1$ may well be as large as 5, 6, or still larger.

The same technique can be used to determine $l_1$ for the spectra of Ref. 2 (Tables II–VII and X–XIII). The resulting values of $l_1$ (or limits on them) have been listed in Table I of the present paper for the 19 spectra of Refs. 1 and 2. We note that for the case of Sn$^+$ (Table V of Ref. 2), we have listed $l_1 \geq 5$, since the $g$ states are still well $k$ ordered. For Tl (spectrum Tl I, Table VI of Ref. 2), it is possible that the $nf$ states (with $\lambda = +1$) lie close to the $ng$ states, in which case $l_1 = 4$, but $l_1$ might also be larger. Finally, for the Pb$^+$ spectrum (spectrum Pb II, Table VII of Ref. 2), we have perfect $k$ ordering up to and including the $g$ states, so that we must have $l_1 \geq 5$.

For Ca I (Table X of Ref. 2), we have perfect $k$ ordering up to and including the $f$ states, but no $g$ states have been observed, so that we must have $l_1 \geq 4$. For Sr I (Table XI of Ref. 2), the $np$ states have $\lambda = -1$, and this $k+\lambda$ exception is most probably not connected with the limiting angular momentum $l_1$. Since no $g$ states have been observed, we conclude that $l_1 \geq 4$. A similar situation exists for the spectrum of Zn I (Table XII of Ref. 2), where we have perfect $k$ ordering, but the $g$ states have not been observed. Thus, we conclude $l_1 \geq 4$. Finally, for In$^+$ (spectrum In II, see Table XIII of Ref. 2), the 8$g$ and 8$h$ states are quite close together ($145\,324 - 145\,297 = 27$ cm$^{-1}$) and similarly for 9$g$ and 9$h$, 10$g$ and 10$h$, 11$g$ and 11$h$, 12$g$ and 12$h$, and 13$g$ and 13$h$. Moreover the $nh$ states have $\lambda = -1$. Thus we conclude that $l_1 = 4$ for the In$^+$ ion.

In order to obtain a composite picture of the dependence of $l_1$ on $Z$, we have drawn an approximate curve (in Fig. 1) through the following values: $l_1 = 0$ at $Z = 6$, $l_1 = 2$ at $Z = 11$, $l_1 = 3$ at $Z = 19$, $l_1 = 4$ at $Z = 30$, $l_1 = 5$ at $Z = 50$, and $l_1 = 6$ at $Z = 88$. Figure 1 can be regarded as the phase diagram for the $k$ and H ordering regions as a function of $l$ vs $Z$. The curve of $l_1$ vs $Z$ extrapolates to $l_1 \cong 8$ for a hypothetical atom or ion having $Z = 300$.

Upon comparing the present Fig. 1 with Fig. 2

TABLE I. Limiting angular momentum $l_1$ (as discussed in Sec. II) for the 19 spectra tabulated in Refs. 1 and 2. $l_1$ separates the regions of validity of $k$ ordering ($l < l_1$) and hydrogenic ordering ($l > l_1$).

| Atom or Ion | $Z$ | $l_1$ |
|---|---|---|
| Na | 11 | 2 |
| Mg$^+$ | 12 | 2 |
| K | 19 | 3 |
| Ca | 20 | $\geq 4$ |
| Ca$^+$ | 20 | 3 |
| Zn | 30 | $\geq 4$ |
| Ga | 31 | $\geq 4$ |
| Ge$^+$ | 32 | 4 |
| Rb | 37 | 4 |
| Sr | 38 | $\geq 4$ |
| Sr$^+$ | 38 | $\geq 5$ |
| In | 49 | $\geq 4$ |
| In$^+$ | 49 | 4 |
| Sn$^+$ | 50 | $\geq 5$ |
| Cs | 55 | 4,5 |
| Ba$^+$ | 56 | $\geq 5$ |
| Tl | 81 | $\geq 4$ |
| Pb$^+$ | 82 | $\geq 5$ |
| Ra$^+$ | 88 | 5,6 |

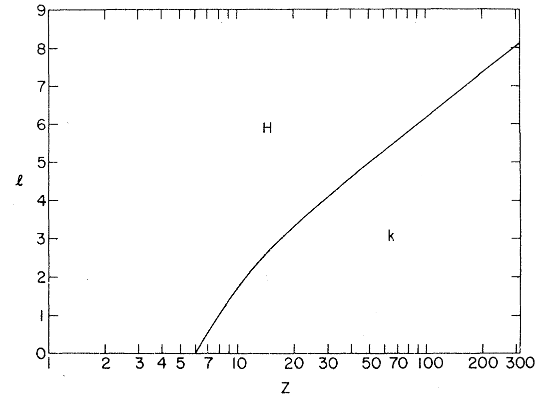

FIG. 1. Diagram showing the regions of validity of $k$ ordering and hydrogenic H ordering of the excited-state levels of neutral atoms and ions with small degree of ionization ($Z-N \gtrsim 2$). The curve separating the two regions is plotted as a graph of the limiting angular momentum $l_1$ vs $Z$. If the transition from $k$ ordering to H ordering as $l$ is increased can actually be described as a phase transition, then Fig. 1 is the appropriate phase diagram in the $l$ vs $Z$ plane, in the same manner as Fig. 2 of Ref. 2 pertaining to the limiting ionicity $Z-N$ as a function of $Z$.

of Ref. 2 for the limiting ionicity $\delta_1$ vs $Z$, ($\delta \cong Z - N$), we note many similarities, although the curve of $l_1$ vs $Z$ extrapolates to a higher $l_1$ at $Z = 300$ than the corresponding value of $\delta_1 = 3$. In accordance with this observation, it may be noted that the curve of $Z - N$ vs $Z$ tends to bend over more appreciably than the curve of $l_1$ vs $Z$, which becomes asymptotic to a straight line, when plotted as a function of $\log_{10} Z$.

In Sec. III, we will discuss a possible explanation of both the phase diagrams for $\delta_1$ vs $Z$ (Fig. 2 of Ref. 2) and for $l_1$ vs $Z$ (Fig. 1).

We also note that for the case of sodium, the approximate degeneracy of the states 15*d*, 15*f*, 15*g*, and 15*h* has been noted by Gallagher, Hill, and Edelstein,[4] whereas the 15*s* and 15*p* energy levels are depressed by comparison (larger quantum defects). Thus, the relevant energy differences are as follows[4]: $E_{15f} - E_{15d} = 25\,632$ MHz $= 0.854$ cm$^{-1}$; $E_{15g} - E_{15f} = 2297$ MHz $= 0.077$ cm$^{-1}$, $E_{15h} - E_{15g} = 527$ MHz $= 0.018$ cm$^{-1}$. On the other hand, we find from the tables of Moore[3]: $E_{15d} - E_{15p} = 40\,958 - 40\,901 = 57$ cm$^{-1}$. These results confirm our assignment of $l_1 = 2$ for the limiting angular momentum of the sodium atom. It may also be remarked that an expression for the quantum defect $\delta_l$ of hydrogenic levels ($l > 2$) of sodium has been obtained by Freeman and Kleppner.[5]

## III. DISCUSSION

In the present section, we wish to discuss several aspects of the *k* ordering, in particular as concerns the phase transitions to hydrogenic H ordering, when either the ionicity $\delta \equiv Z - N$ exceeds the value of $\delta_1$ (Fig. 2 of Ref. 2) or the angular momentum $l$ exceeds the limiting value $l_1$ (Fig. 1 of this paper).

(i) In Refs. 1 and 2, we have extensively discussed the strong possibility that the *k* ordering arises as a result of core-polarization effects of the same type as are involved in the quadrupole antishielding factors[6,7] $R$ and $\gamma_\infty$ for the quadrupole hyperfine structure, and in the inverted fine structure for the *nd* states of the alkali-metal atoms.[8,9] In the latter case, only exchange-core-polarization effects contribute, whereas for the quadrupole antishielding factors[6] $R$ both the direct and the exchange interaction with the perturbed wave functions of the core electrons enter into the final results. One of the strongest pieces of evidence in favor of the core-polarization explanation of *k* ordering is that the effect occurs only for $Z \gtrsim 11$ (Na, Mg$^+$), where there is already a closed *p* shell in the core. On the other hand, it does not exist for lighter atoms, in particular, Li($Z = 3$), Be($Z = 4$), and B($Z = 5$), which have no *p* shells in the core. This is strongly reminiscent of the situation for the quadrupole antishielding factor[7] $\gamma_\infty$, which does not become large until Na$^+$($Z = 11$), because of the presence of the closed 2*p* shell for Na and the resulting possibility of $2p \to p$ excitations of the core by the nuclear quadrupole moment $Q$. The same situation holds for the inverted fine structure of *d* states which is found for Na, K, and Rb, but not for Li. Again a $2p \to p$ excitation of the 2*p* electrons by the fine-structure Hamiltonian has been invoked[8] to explain and calculate this effect for the case of Na. A similar calculation for Rb involves mostly the $4p \to p$ excitation of the 4*p* closed shell.[8]

Now, if the exchange-core polarization leads in some way also to the observed *k* ordering, then what is involved is the overlap of the valence electron wave function $v_0(nl)$ with the core wave functions $u_0(n_c l_c)$. Since $v_0(nl)$ ($= r$ times the actual wave function) behaves near $r = 0$ as $ar^{l+1}$, it can be easily seen that if $l$ is too large the valence wave function $ar^{l+1}$ is essentially zero in the region of the atomic core, and therefore no effective overlap with the core wave functions $u_0(n_c l_c)$ can occur. This property would seem to explain the existence of the limiting angular momentum $l_1$, such that for $l > l_1$, the exchange-core polarization is negligible and the *k* ordering disappears as a result, to be replaced by hydrogenic ordering, as is observed in Fig. 1.

We believe that we can also explain the slow increase of $l_1$ with increasing $Z$ in the following fashion. The radial part of the Hamiltonian $H_l$ for the state $nl$ can be written as follows for a neutral atom:

$$H_l = \frac{l(l+1)}{r^2} - \frac{2(Z-1)\chi(r)}{r} - \frac{2}{r}, \tag{3}$$

where $\chi(r)$ is the Thomas-Fermi function,[10] with the properties $\chi(0) = 1$, and $\chi(\infty) \to 0$. The Hamiltonian $H_l$ of Eq. (3) is expressed in Rydberg units, which accounts for the factors of 2 in the second and third terms on the right-hand side. Now the centrifugal term $l(l+1)/r^2$ leads to the behavior of $v_0(nl)$ near $r = 0$:

$$v_0(nl) = ar^{l+1} + \cdots . \tag{4}$$

On the other hand, the negative Coulomb terms, which reduce to $-2Z/r$ near the nucleus, tend to counteract the effect of the centrifugal term, since they have opposite sign (Coulomb attraction to the nucleus). Therefore, with increasing $Z$, we may expect that the coefficient $a$ will increase somewhat, and therefore for a given $l$ value, at a given radius $r$, $v_0(nl)$ will increase, thus increasing the overlap with the core wave functions. Hence the atom (or ion) will exhibit *k* ordering in a larger region of $l$ values as $Z$ is increased, and thus the limiting angular momentum $l_1$ increases with increasing $Z$, as is shown in Fig. 1, which is based on the observed spectra (Sec. II).

Concerning the dependence of $k$ ordering on the ionicity $Z - N = \delta$, as shown in Fig. 2 of Ref. 2, we have the following tentative explanation. Let us first rewrite Eq. (3) for the case where $\delta > 0$. Since the potential seen by the valence electron at large $r$ is $-2(1+\delta)/r = -2(1+Z-N)/r$, we must modify the second term on the right-hand side of Eq. (3), so as to make the potential go over into $-2Z/r$ at small radii $r$. We thus obtain:

$$H_l = \frac{l(l+1)}{r^2} - \frac{2(Z-\delta-1)\chi(r)}{r} - \frac{2(1+\delta)}{r}. \qquad (5)$$

It can be easily verified from Eq. (5) that the potential near the nucleus ($\chi \to 1$) becomes $-2Z/r$, which is, of course, the correct value independently of the degree of ionization. On the other hand, for large $r$ ($\chi \to 0$), the potential becomes $-2(1+\delta)/r = -2(1+Z-N)/r$, which is also correct.

We now note that by far the major part of the valence electron density lies in the region outside the core, and in that region the potential is hydrogenic, namely $-2(1+\delta)/r$, i.e., the potential of a point charge whose magnitude is $(1+\delta)e = (1+Z-N)e$. We believe that there is a delicate balance between the $k$-ordering properties caused by the exchange-core polarization, and therefore by the magnitude of the valence wave function inside the core, and on the other hand, the large region of $r$ where the potential is essentially hydrogenic. If $\delta$ is made too large, the hydrogenic potential tends to predominate at a smaller radius over the nuclear potential, which is essentially $-2Z\chi(r)/r$. Thus as $\delta$ is increased, the region of $r$ where the potential is hydrogenic tends to predominate over the region of the core, where the exchange-polarization phenomena can occur, which would lead to $k$ ordering. This mechanism would explain the existence of a limiting ionicity $\delta_1$, such that when $\delta > \delta_1$, the ordering of the levels becomes hydrogenic. The increase of $\delta_1$ with increasing $Z$ (Fig. 2 of Ref. 2) can also be understood in terms of the competition between the core region with potential $-2Z\chi/r$, and the hydrogenic region with potential $-2(1+\delta)/r$. It can be concluded from this discussion that the effect of a large ionicity is similar to the effect of a large angular momentum $l$. Both effects can destroy the $k$-ordering phase, for reasons which are essentially related, as described above. This would explain the basic similarity of the two phase diagrams in the plane of $\delta$ vs $Z$ and the plane of $l$ vs $Z$.

(ii) Concerning the $k$ ordering, it should be emphasized that $k$ is a good quantum number for the total energy of the atom throughout the energy region of the excited states from the ground state up to the ionization limit (see the tables in Refs. 1 and 2). In this connection, we note that for the case of rubidium, the evidence for $k$ ordering[3] extends beyond $k = 50$ (where we have the last observed $f$ state, namely $47f$), and up to $k = 56$, where we have the two states $55p$ and $54d$. These states lie only 40 $\text{cm}^{-1}$ below the ionization limit. We also note that the fine structure of the Rb $nd$ levels up to $n = 55$ has been recently investigated by Harvey, Bolton, and Stoicheff.[11]

The fact that $k$ is a good quantum number both in the nonrelativistic region (small $Z$, $\alpha Z \ll 1$) and in the relativistic region (large $Z$, $\alpha Z \sim 1$) has been previously emphasized in Refs. 1 and 2. Because of the validity of $k$ throughout the energy region of the excited states, and for both $\alpha Z \ll 1$ and $\alpha Z \sim 1$, we believe that $k$ is a fundamental quantum number for all one-electron states of atoms and ions, with the only restriction that $Z \gtrsim 11$, so that there is at least one filled $p$ shell of the atomic core. As long as the ionicity $\delta$ and the angular momentum $l$ are not too large, so that we are in the $k$ ordering phase of the appropriate phase diagrams (Fig. 2 of Ref. 2, and Fig. 1 of this paper), we believe that $k$ is more fundamental than the principal quantum number $n$, and will probably emerge from a future theory along with $l$ to characterize the state of the atom or ion with one electron outside of closed shells.

(iii) We now wish to make some remarks about the $k$ bands and $l$ patterns which have been discussed extensively in Refs. 1 and 2. The structure of the spectrum in terms of $k$ bands (for low values of $l$, $l < l_1$) can be called the $k$-ordering gross structure. The different $l$ levels within a given $k$ band [with their characteristic $(l_1 l_2 l_3 l_4)$ pattern, as given in Table XIV of Ref. 2] can then be called the semifine structure of the spectrum. As has been discussed extensively in Refs. 1 and 2, we have envisaged the possibility that the $k$ ordering and the associated constant $l$ patterns will ultimately be explained by group-theoretical considerations. In this connection, we note the strong similarity to the phenomenon of symmetry breaking, which has been previously encountered in the broken-symmetry SU(3) scheme of Gell-Mann and Ne'eman[12] for the mass spectrum of the elementary particles and their excited states. Thus, although the situation is very different, quantitatively speaking, in terms of the energies or masses involved, we may have a basic group-theoretical symmetry for which the appropriate quantum number is $k$, and the basic (primitive) $k$ symmetry is broken by the $l$-dependent interaction, which gives rise to the well-documented $l$ sequences and splittings, which have been described extensively in Refs. 1 and 2.

Upon using this description of the $k$ bands and the $l$ sequences, we conclude that the quantum number $k$ is the analogue of the angular momentum $J$ and parity $P$, i.e., of $J^P$ for the strong interactions, whereas the angular momentum $l$ of the atomic problem which gives rise to the symmetry breaking would be the analogue of the strangeness $S$ and the isotopic spin $I$ quantum numbers of the elementary particles and their excited states.

We should note another quantitative difference between the two situations. Whereas only relatively few multiplets $J^P$ have been discovered for the spectrum of the elementary particles, the number of $k$ bands which have been observed is much larger, e.g., about 50 bands for the spectrum of the rubidium atom.

(iv) In view of the discussion of Sec. II concerning the limiting angular momentum $l_1$, and the fact that $l_1$ is generally $\geq 3$ ($f$ state) in the physically interesting range of medium and high $Z$ values, the following explanation of the $k+\lambda$ "exceptions" for $nf$, $ng$, and $nh$ states presents itself naturally, namely that these exceptions to the $k$ ordering for high angular-momentum states are due to the phase transition from $k$ to hydrogenic ordering, which is implied by the discussion of Sec. II and the resulting phase diagram of Fig. 1 of this paper.

Thus, the only "true" $k+\lambda$ exceptions, i.e., those which cannot be explained in terms of the limiting angular momentum $l_1$, are those involving $p$ and $d$ states. These few true $k+\lambda$ exceptions are probably due to some sort of series perturbations for the corresponding $p$ and $d$ states. Now we will show that the number of true $k+\lambda$ exceptions is astonishingly small. For this purpose, we will consider the 19 spectra which have been tabulated in Refs. 1 and 2.

Upon considering first the nine spectra of Ref. 1, the only true $k+\lambda$ exceptions occur for Ba$^+$ ($6d$; see Table XIV) and Ra$^+$ ($7d$, $8d$, $9d$, and $9p$; see Table XV), giving us a total of 5 true exceptions among a total of 303 levels, i.e., a ratio of only $5/303=0.017$. Thus out of the total ratio $\Sigma N_E/\Sigma N_L=0.129$ (see Table XVI of Ref. 1), the major part, namely 0.112, is due to the $k\rightarrow$H phase transition at the limiting angular momentum $l_1$.

We consider now the ten spectra of Ref. 2. First of all, for the six spectra of Tables II–VII, i.e., for the spectra of Ga, Ge$^+$, In, Sn$^+$, Tl, and Pb$^+$, there are no true $k+\lambda$ exceptions. Instead, among the 19 exceptions, 17 involve $nf$ states and 2 involve $ng$ states (for Ge$^+$ $6g$ and $7g$; see Table III), all of which lie close to $l=l_1$. Finally, we consider the four spectra of Tables X–XIII, namely those of Ca, Sr, Zn, and In$^+$. For the spectra of Ca and Zn, we have no $k+\lambda$ exceptions, i.e., $N_E=0$. For the spectrum of Sr (see Table XI), we have seven exceptions involving the $np$ states ($8p$–$14p$). These exceptions are true $k+\lambda$ exceptions and are the result of the tendency of the $np$ states to lie very close to the $ns$ states having the same $n$ value (e.g., $E_{9p}=42\,462$ cm$^{-1}$, $E_{9s}=42\,487$ cm$^{-1}$). On the other hand, for the spectrum of In$^+$ (see Table XIII), we have $N_E=6$, with all six exceptions involving the $nh$ states ($8h$–$13h$) which are very close to the corresponding $ng$ levels (e.g., $E_{10g}=147\,784$ cm$^{-1}$, $E_{10h}=147\,799$ cm$^{-1}$). These six exceptions are clearly cases of the transition from $k$ ordering to H ordering, because $l=5$ for the $h$ states is larger than the limiting angular momentum $l_1=4$.

Thus we have a total of $5+7=12$ true $k+\lambda$ exceptions in the tables of Refs. 1 and 2. For comparison, the total number of levels considered in the ten tables of Ref. 2 is $\Sigma N_L=362$, so that the total $\Sigma N_L$ for all 19 spectra is $303+362=665$, giving us a ratio of $\Sigma N_E\,(\text{true})/\Sigma N_L=12/665=0.0180$. This fraction can be compared to the overall ratio of 0.120 (see Table IX of Ref. 2), so that of this ratio of 0.120, an amount $0.120-0.018=0.102$ represents "apparent" $k+\lambda$ "exceptions," which are connected with $l$ being larger than $l_1$, and therefore in the H ordering region of Fig. 1.

In summary, when allowance is made for the existence of the limiting angular momentum $l_1$ (see Sec. II and Fig. 1), the $k$ ordering of the excited atomic levels is seen to be even more accurately fulfilled than had been previously believed (in Refs. 1 and 2), with the number of true $k+\lambda$ exceptions amounting to less than 2% of the levels which have been investigated, i.e., $\lesssim 20$ levels as compared to a total of 1155 levels included in the 42 spectra of Table XIV of Ref. 2.

(v) In connection with the separation of $k$-band levels with consecutive values of $k$, which has been mentioned above, it is of interest to make a quantitative analysis of this phenomenon. For this purpose, we consider four representative spectra, two from Ref. 1, namely Rb (Table IV) and Sr$^+$ (Table XIII), and two from Ref. 2, namely Pb$^+$ (Table VII) and In$^+$ (Table XIII). We define the width $W_k$ of the $k$ band as

$$W_k=E_{k,\max}-E_{k,\min}\,, \tag{6}$$

where $E_{k,\max}$ and $E_{k,\min}$ are the maximum and minimum values of the energy $E_{kl}$ within this $k$ band. We also define the separation $S_{k,k+1}$ between the bands $k$ and $k+1$ as

$$S_{k,\,k+1} \equiv E_{k+1,\,\mathrm{min}} - E_{k,\,\mathrm{max}}. \tag{7}$$

As an example, for the case of Rb (Table IV of Ref. 1), we have

$$W_6 = 20\,134 - 12\,737 = 7391 \text{ cm}^{-1}, \tag{8}$$

$$S_{6,\,7} = 23\,767 - 20\,134 = 3633 \text{ cm}^{-1}. \tag{9}$$

TABLE II. $k$-band widths $W_k$ and separations $S_{k,k+1}$ between successive $k$ bands (in units cm$^{-1}$) for the four spectra of Rb, Sr$^+$, In$^+$, and Pb$^+$, as obtained from the appropriate tables in Refs. 1 and 2. $W_k$ and $S_{k,k+1}$ are defined by Eqs. (6) and (7) of the text. The last four rows of the table give the values of $\langle R_k\rangle$, $k_{\max}$, $\langle\delta_k\rangle$, and the ratio $\langle R_k\rangle/\langle\delta_k\rangle$, where $R_k$ is defined by Eq. (10), and $\delta_k$ is the ratio $\Delta_{l_1l_2}(k)/W_k$ of the spacing $\Delta_{l_1l_2}(k)$ between consecutive $l$ levels within a given $k$ band to the width $W_k$ of the band.

| Energy | Rb | Sr$^+$ | In$^+$ | Pb$^+$ |
|---|---|---|---|---|
| $W_6$ | 7 397 | 33 013 | 45 483 | ··· |
| $S_{6,7}$ | 3 633 | 5 601 | 10 435 | ··· |
| $W_7$ | 3 025 | 11 626 | 18 529 | 50 061 |
| $S_{7,8}$ | 1 066 | 2 583 | 1 599 | 9 826 |
| $W_8$ | 1 420 | 5 690 | 8 695 | 23 246 |
| $S_{8,9}$ | 20 | 1 397 | 555 | 2 376 |
| $W_9$ | 1 330 | 3 224 | 5 048 | 8 663 |
| $S_{9,10}$ | 9 | 839 | 362 | 313 |
| $W_{10}$ | 805 | 2 005 | 3 017 | 5 096 |
| $S_{10,11}$ | 217 | 544 | 245 | 336 |
| $W_{11}$ | 310 | 1 330 | 1 942 | 2 926 |
| $S_{11,12}$ | 148 | 376 | 174 | 214 |
| $W_{12}$ | 178 | 928 | 1 321 | 1 902 |
| $S_{12,13}$ | 141 | 265 | 129 | 145 |
| $W_{13}$ | 79 | 674 | 939 | 1 306 |
| $S_{13,14}$ | 152 | 197 | 98 | 104 |
| $W_{14}$ | 58 | 314 | 690 | 932 |
| $S_{14,15}$ |  | 339 | 77 | 79 |
| $W_{15}$ |  | 215 | 521 | 688 |
| $S_{15,16}$ |  |  | 62 | 60 |
| $W_{16}$ |  |  | 390 | 523 |
| $S_{16,17}$ |  |  | 64 | 47 |
| $W_{17}$ |  |  | 309 | 407 |
| $S_{17,18}$ |  |  | 51 | 38 |
| $W_{18}$ |  |  | 245 | 321 |
| $S_{18,19}$ |  |  | 64 | 31 |
| $W_{19}$ |  |  | 181 | 259 |
| $\langle R_k\rangle$ | 0.269 | 0.254 | 0.115 | 0.089 |
| $k_{\max}$ | 11 | 13 | 17 | 15 |
| $\langle\delta_k\rangle$ | 0.300 | 0.276 | 0.286 | 0.291 |
| $\langle R_k\rangle/\langle\delta_k\rangle$ | 0.897 | 0.920 | 0.402 | 0.306 |

It is apparent from a casual inspection of the tables of Refs. 1 and 2 that the separations $S_{k,k+1}$ are in general much smaller than the corresponding widths $W_k$ for the same value of $k$. This trend is shown clearly in Table II, in which we have listed the consecutive widths $W_k$ and separations $S_{k,k+1}$ for the four above-mentioned spectra, namely, Rb, Sr$^+$, In$^+$, and Pb$^+$. We note that some separations are unusually small, in particular for Rb, we have $S_{8,9} = 20$ cm$^{-1}$, as compared to $W_8 = 1420$ cm$^{-1}$, and $S_{9,10} = 9$ cm$^{-1}$, as compared to $W_9 = 1330$ cm$^{-1}$. It is therefore of interest to calculate the ratios $R_k$, defined as

$$R_k = S_{k,\,k+1}/W_k\ , \tag{10}$$

and then to calculate the average $\langle R_k\rangle$ for the spectrum, where $\langle R_k\rangle$ is given by

$$\langle R_k\rangle = \frac{1}{n_k}\sum_{k_{\min}}^{k_{\max}} R_k. \tag{11}$$

Here $k_{\min}$ is the minimum value of $k$ occurring in the spectrum, i.e., $k_{\min} = 6$ for Rb, Sr$^+$, and In$^+$, and $k_{\min} = 7$ for Pb$^+$. For $k_{\max}$, we choose the largest value of $k$ for which the band contains at least four levels, the reason being that when only two or three levels are included (as obtained from the tables of Moore[3]), it follows that at least two and possibly three levels with low $l$ ($l \le l_1$) have not been observed, so that the band is artificially narrow. On the other hand, with four or five levels observed in the $k$ band, it is likely that most (if not all) of the levels with $l \le l_1$ have been included, so that the width $W_k$ obtained from Eq. (6) has a realistic value. The values of $k_{\max}$ thus obtained are: 11 for Rb, 13 for Sr$^+$, 17 for In$^+$, and 15 for Pb$^+$. In Eq. (11), the number $n_k$ of $k$ bands included is simply given by

$$n_k = k_{\max} - k_{\min} + 1. \tag{12}$$

The resulting values of $\langle R_k\rangle$ (together with the values of $k_{\max}$) are listed at the bottom of Table II. It is seen that $\langle R_k\rangle$ is of the order of $\frac{1}{4}$ for Rb and Sr$^+$, and is even smaller ($\sim\frac{1}{10}$) for In$^+$ and Pb$^+$.

The smallness of $\langle R_k\rangle$ led us to the idea that the separations $S_{k,k+1}$, besides being smaller than $W_k$, may also be smaller than the average spacing of the $l$ levels (semi-fine structure) within each $k$ band. In order to obtain the mean spacing of the $l$ levels and compare it with $W_k$, we performed the following simple calculation. For each of the four spectra, we have calculated the average number of levels per $k$ band by taking the total number of levels and dividing by the number $n_k$ of $k$ bands. As an example, for Rb, we have 3 levels for $k = 6$, 4 levels each for $k = 7$ and 8, and 5 levels each for $k = 9$, 10, and 11, giving a total of 26 levels. On the other hand, from Eq. (12), we find $n_k = 11 - 6 + 1 = 6$. Thus the average number of levels $\langle\nu_k\rangle$ per $k$ band is $26/6 = 4.33$. We note that for an integral number of levels $\nu_k$ in a given $k$ band, the average spacing $\langle\Delta_{l_1l_2}(k)\rangle$ will be $W_k/(\nu_k - 1)$, since we have $\nu_k - 1$ intervals for $\nu_k$ levels. We note that $\Delta_{l_1l_2}(k)$ has been defined in Eq. (11) of Ref. 1, i.e.,

$$\Delta_{l_1l_2}(k) \equiv E(k, l_1) - E(k, l_2). \tag{13}$$

Therefore, the ratio $\langle\Delta_{l_1 l_2}(k)\rangle/W_k$ is simply $1/(\langle\nu_k\rangle - 1)$, which is $1/3.33 = 0.300$ for the case of Rb discussed above. This ratio will be denoted by $\langle\delta_k\rangle$. We note that $\langle\nu_k\rangle$ is approximately the same for the four spectra considered. Specifically, $\langle\nu_k\rangle = 4.63$ for $\mathrm{Sr}^+$, $\langle\nu_k\rangle = 4.50$ for $\mathrm{In}^+$, and $\langle\nu_k\rangle = 4.44$ for $\mathrm{Pb}^+$. Thus, we obtain the values of $\langle\delta_k\rangle$:

$$\langle\delta_k\rangle = 1/(\langle\nu_k\rangle - 1), \qquad (14)$$

which are listed at the bottom of Table II. The last row of this table lists the values of the ratio $\langle R_k\rangle/\langle\delta_k\rangle$, showing that for Rb and $\mathrm{Sr}^+$, the separations $S_{k,k+1}$ are of the order of the semifine structure intervals $\Delta_{l_1 l_2}(k)$, whereas for $\mathrm{In}^+$ and $\mathrm{Pb}^+$, the separations $S_{k,k+1}$ are on the average a factor of 2.5 to 3 smaller than the average $\langle\Delta_{l_1 l_2}(k)\rangle$.

The results of Table II illustrate the fact that the separations $S_{k,k+1}$ between consecutive $k$ bands are on the average very small compared to the $k$ band widths $W_k$, and that they tend to be even smaller than the mean spacing between $(k, l)$ levels within a $k$ band, especially for heavy ions such as $\mathrm{In}^+$ and $\mathrm{Pb}^+$.

In summary, the energy region between the ground state and the ionization limit is occupied mostly by the successive $k$ bands, consisting of levels with $l \leq l_1$, with relatively little space between adjacent $k$ bands. It may be hoped that a future theory will explain this feature of the spectrum, in addition to the basic $k$ ordering itself and the associated $l$ patterns.

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