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Ordering of the energy levels of the excited states of the alkali-metal atoms*

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The Madelung rules for the order of the filling of successive electron shells in the ground states of neutral atoms (and hence the properties of the resulting periodic table) suggest that the sum $n + l \equiv k$ is in the nature of an "energy-ordering" quantum number. Thus for neutral atoms, the levels of the outermost electron are filled in the order of increasing k values as the atomic number Z is increased. For a constant k, the shells are filled in the order of increasing n or decreasing l values. The general applicability of these ordering rules suggests that they may also be relevant to the structure of the excited-state energy spectrum of the valence electron of the alkali-metal atoms. With the exception of lithium, it was found that the excited-state levels are energy ordered according to the increasing value of k ("k ordering"). For states with the same value of k, the levels with increasing energy E_{nl} exhibit a sequence of l values (the "l pattern") which is characteristic of the alkali-metal atom considered (Na, K, Rb, and Cs), and is independent of k. Important additional evidence for the k ordering and the constant l patterns has been obtained from the energy spectra of the singly ionized alkaline-earth atoms, i.e., the Mg^+, Ca^+, Sr^+, Ba^+, and Ra^+ ions. Several possible implications of the present results are discussed.

I. INTRODUCTION

It has been known for some time that the order in which the electron shells are successively filled for the case of neutral atoms, as Z is increased, is governed by two general rules which were originally discovered by Madelung.[1] These rules state that:

(A) The electron shells are filled in the order of increasing values of the quantum number sum $n+l$, where n is the principal quantum number and l is the azimuthal quantum number of the shell (nl).

(B) For electron shells with the same value of $n+l$, the shells are filled in the order of increasing n, or decreasing l values.

As an example, for $n+l=7$, the shells are filled in the order $4f(l=3)$, $5d(l=2)$, $6p(l=1)$, and $7s(l=0)$.

Although these rules were discovered by Madelung as early as 1926, according to a statement published by Goudsmit,[2] they were published by Madelung only in 1936, as an Appendix in a textbook.[1] These rules were subsequently rediscovered by several authors.[3-9] The resulting version of the periodic table of the chemical elements has been constructed by several of the authors of Refs. 2–9, and also appears in the textbook of Moeller.[10]

In connection with the renewed interest in the possible existence of superheavy elements ($Z=126$ and other elements in this region of Z), as a result of the experiment of Gentry *et al.*,[11] we have independently rediscovered the rules A and B discussed above, and the resulting version of the periodic table. As already implied by footnote 3, we became subsequently aware of the existence of the earlier work (Refs. 1, 2, 4–9) through the review article of Mann[3] and its reference to the textbook of Moeller.[10] To the above references, we should also add the later papers of Klechkovskii[12] and Goldanskii[13] and the well-known review article of Seaborg.[14] References 12–14 also made use of the $(n+l)$ rule, which was derived directly by Klechkovskii[12] from the properties of the Thomas-Fermi model of the atom.

In rederiving rules A and B, we have noted the fact that the combination $n+l$ which we denote by k:

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

can be regarded as an "energy-ordering quantum number" for the energy of the outermost electron for atoms with $Z \gtrsim 20$, since it is at $Z=19$ that the succession $3p$, $3d$ first breaks down. The succession $3p, 3d$, which would be expected from a hydrogenlike spectrum, is replaced by the succession $3p, 4s$, i.e., the $4s$ shell fills up at $Z=19$ and $Z=20$, thus delaying the occurrence of $3d$ until scandium Sc, with $Z=21$.

The following facts also led us to believe that the quantum number k may be more generally relevant than just to determine the order of the filling up of the shells nl for the ground states of atoms:

(1) At the beginning of the rare-earth (lanthanide) series, there is a serious competition between $5d$ and $4f$. In fact for lanthanum (La, $Z=57$), before the $4f$ shell starts to fill, there is a single $5d$ electron in the ground state, outside the $6s^2$ shell of the barium-like configuration. The near-degeneracy of $5d$ and $4f$ persists throughout the

lanthanide series. We note that both for 5d and 4f, we have $n+l=k=7$.

(2) In 1970, it was noted[15] by the author that for two states in both copper (Cu) and terbium (Tb),[16] namely 3d and 4p of Cu, and 4f and 5d of Tb, the atomic quadrupole shielding (or antishielding) factors[17] R are similarly related, and in fact lead to approximately the same values of the experimentally observed ratio $\rho \equiv (1-R_{n_1 l_1})/(1-R_{n_2 l_2})$ (where $n_1 l_1$ and $n_2 l_2$ are the two sets of nl values involved), namely $\rho \approx 1.4$. Here $n_1 l_1 = 4p$, $n_2 l_2 = 3d$ for Cu, and $n_1 l_1 = 5d$, $n_2 l_2 = 4f$ for Tb. It was noted then[15] that in both cases, $n_2 = n_1 - 1$ and $l_2 = l_1 + 1$. In view of the definition of k [Eq. (1)], we have $k=5$ for both Cu states and $k=7$ for both Tb states.

In connection with Eq. (1), it is natural also to consider the difference of the quantum numbers n and l, and we denote this difference by q. Thus

$$q \equiv n - l\,. \qquad (2)$$

We note that in the above example, both states $n_2 l_2$ have the same q value, namely $q=1$, whereas both states $n_1 l_1$ have $q=3$.

(3) To reinforce the conclusion from point (1), we note that also for the actinides, there is a strong competition between 6d and 5f, for both of which $k=8$. Thus[18] it is believed that one 6d electron exists in the ground-state configuration of actinium Ac ($Z=89$) and two 6d electrons for thorium Th ($Z=90$), before the 5f shell starts to be occupied at protactinium, and even for Pa and also for uranium U ($Z=92$) and neptunium Np ($Z=93$), there is still a single 6d electron along with the configurations $5f^2$, $5f^3$, and $5f^4$, respectively, for these three atoms.

(4) Finally, the near-degeneracy of the levels 5g, 6f, and 7d in the region $Z=120$ to 125, which has been extensively documented by Seaborg,[14] led the present author to consider $n+l=k$ as a "good" quantum number for the energy of the outermost electron of medium and heavy atoms. We note that $k=9$ for the three above-mentioned levels. It should be mentioned that Seaborg's conclusions were based on the extensive calculations of electron configurations in the superactinide series, from $Z=120$ to $Z=131$, carried out by Waber, Cromer, and Liberman.[19] Subsequent self-consistent relativistic calculations using the Dirac-Fock equations by Mann and Waber[20] have confirmed the conclusions of Ref. 19.

II. RELEVANCE OF THE QUANTUM NUMBER $k=n+l$ TO THE ENERGY SPECTRA OF THE ALKALI-METAL ATOMS

Before discussing the relevance of $k=n+l$ to the energy spectra of the excited states of the alkali-metal atoms, we wish to introduce some terminology pertaining to the quantum numbers $k=n+l$ and $q=n-l$ [Eqs. (1) and (2)].

The set of all shells nl with the same value of $k=n+l$ will be called a supershell. As an example, the $k=7$ supershell consists of the shells 4f, 5d, 6p, and 7s. As mentioned above, the quantum number k can be called the "energy-ordering quantum number." (It is also possible to refer to it as the "global quantum number," as will be discussed below in Sec. IV.) The quantum number q can be referred to as the "radial-node quantum number," since $n-l-1=q-1$ is the number of nodes of the (nonrelativistic) radial wave function of the state considered.

In terms of the value of q, Madelung's Rule B can be rephrased as follows: within a given supershell (constant k), the nl shells are filled up in the order of increasing q values. It can be easily seen that for a given k, the possible values of q increase in steps of 2 units. Thus for $k=$ even, we have

$$q=2,4,\ldots,k-2,k\,, \qquad (3)$$

while for $k=$ odd, we have

$$q=1,3,\ldots,k-2,k\,. \qquad (4)$$

The value $q=0$ is excluded, since $q=n-l \geqslant 1$.

In Table I, we have listed the shells $n_i l_i$ in the order prescribed by the two rules A and B given above. The corresponding values of q_i are listed in the third column. The next three columns list the number of elements $N(k)$ in the supershell k, the element (with atomic number Z_a) for which the supershell begins, and the corresponding element (with atomic number Z_b) for which the supershell is completed. By comparing with the usual tabulations of the observed level fillings,[18] it is seen that the observed sequence of electronic levels is exactly that given by Table I, with the few exceptions mentioned in points (1) and (3) above, concerning the 5d electron of La, and the configurations 6d and $6d^2$ for Ac and Th, respectively, which precede the start of the 5f shell, which begins at Pa ($Z=91$).

The number $N(k)$ of elements (Z_i) within a supershell k can be easily obtained from the equation

$$N(k)=\sum_{l=0}^{l_{\max}} 2(2l+1) = 2(l_{\max}+1)^2\,, \qquad (5)$$

which can be rewritten as follows

$$N(k)=k^2/2, \quad (k=\text{even})\,, \qquad (6)$$

$$N(k)=(k+1)^2/2, \quad (k=\text{odd})\,. \qquad (7)$$

TABLE I. The set of shells $\{n_i l_i\}$ involved for each supershell k, the corresponding values of q_i, the number of chemical elements $N(k)$ for a given k, the first element of the supershell series k, with atomic number Z_a, and the last element of the supershell series k, with its atomic number denoted by Z_b. The supershells are filled in the order of increasing k (rule A). Within each supershell, the shells $n_i l_i$ are occupied in the order listed in the table, i.e., in the order of increasing q_i (rule B).

k	$\{n_i l_i\}$	$\{q_i\}$	$N(k)$	Element (Z_a)	Element (Z_b)
1	1s	1	2	H(1)	He(2)
2	2s	2	2	Li(3)	Be(4)
3	2p, 3s	1, 3	8	B(5)	Mg(12)
4	3p, 4s	2, 4	8	Al(13)	Ca(20)
5	3d, 4p, 5s	1, 3, 5	18	Sc(21)	Sr(38)
6	4d, 5p, 6s	2, 4, 6	18	Y(39)	Ba(56)
7	4f, 5d, 6p, 7s	1, 3, 5, 7	32	La(57)	Ra(88)
8	5f, 6d, 7p, 8s	2, 4, 6, 8	32	Ac(89)	Eka Ra(120)
9	5g, 6f, 7d, 8p, 9s	1, 3, 5, 7, 9	50	121	170
10	6g, 7f, 8d, 9p, 10s	2, 4, 6, 8, 10	50	171	220
11	6h, 7g, 8f, 9d, 10p, 11s	1, 3, 5, 7, 9, 11	72	221	292
12	7h, 8g, 9f, 10d, 11p, 12s	2, 4, 6, 8, 10, 12	72	293	364

It is of interest that the end of the supershell $k=9$, with $Z_b=170$, coincides approximately with the Z value (≈ 172) at which there occurs the diving of the 1s energy level into the electron-positron continuum, as calculated by Rafelski, Müller, and Greiner.[21]

Concerning the quantum numbers k and q [Eqs. (1) and (2)], we note that the normalized radial wave function R_{nl} for the hydrogenic atoms also involves the combinations $k=n+l$ and $q=n-l$, since it is given by[22]

$$R_{nl}=-\left[\left(\frac{2Z}{na_H}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2}e^{-\rho/2}\rho^l L_{n+l}^{2l+1}(\rho)\,, \tag{8}$$

with $\rho=(2Z/na_H)r$, and L_{n+l}^{2l+1} is the associated Laguerre polynomial. Thus R_{nl} is proportional to

$$R_{nl}\propto\left(\frac{(q-1)!}{(k!)^3}\right)^{1/2}L_k^{k-q+1}(\rho)e^{-\rho/2}\rho^{(1/2)(k-q)}\,. \tag{9}$$

The preceding considerations pertain to the ground state of the outermost electrons of the various elements of the periodic table, and these ground-state energy levels provide abundant evidence for the relevance of the quantum numbers k and q (or k and l) in determining the order in which the electron shells are successively filled up. In this connection, it occurred to us that there might be similar evidence for the relevance of k and q from a consideration of the excited states of individual atoms. The group of atoms for which it is simplest to isolate a single outermost electron are, of course, the alkali-metal atoms, which possess a single electron outside closed nl shells.

The results of this investigation are presented below, and they provide ample evidence for the ordering of the electron energy levels of the valence electron according to the (increasing) value of k. Within a given set of levels having the same k value, the energy levels increase in general according to a fixed pattern of l values, i.e., a fixed sequence of l levels, which is appropriate for each alkali-metal atom considered.

We will first consider the four alkali-metal atoms: sodium Na ($Z=11$), potassium K ($Z=19$), rubidium Rb ($Z=37$), and cesium Cs ($Z=55$). The case of lithium Li ($Z=3$) will be discussed subsequently. The energy levels of the four atoms Na, K, Rb, and Cs were obtained from the extensive tables of Moore.[23] These tables list the energies E_{nl} of the levels minus the energy of the ground state (3s for Na, 4s for K, 5s for Rb, and 6s for Cs) which is taken as zero. The values of E_{nl} are given in units of cm^{-1}. For most states nl, two values of E_{nlj} are listed, where $j=l+\frac{1}{2}$ or $l-\frac{1}{2}$, where j is the total angular momentum including the spin. In these cases, we have averaged over the energies of the fine-structure doublet states, using the appropriate weight factors $(2j+1)$.

The resulting average energy levels E_{nl} are given in Tables II–V, for Na, K, Rb, and Cs, respectively, where we have also listed the values of k and l for each level. The order in which we have listed these levels is essentially that of increasing E_{nl} values (as is done in Moore's tables), except that for a few cases involving nf, 5g, 6g, and 6h levels, we have grouped these levels together with the levels (s, p, or d) having the same value of k. However, these few exceptions are clearly marked, as follows: as a superscript for the value of E_{nl}, we have listed (λ), where the meaning of λ is that $E_{nl}^{(\lambda)}$ lies in the region where most (if not all) of the levels $k+\lambda$ are located. As an example, for Na 4*f* (Table II), the superscript (−1) of $E_{4f}=34\,589$ cm^{-1} indicates that although we have listed this level with the other $k=7$ levels, its energy value lies in the region occupied by the $k-1=6$ levels, which extends from 34 549 to 36 373 cm^{-1}.

We should note, at once, that aside from the few exceptions described above, the order of increasing energy values E_{nl} is the same as the order of increasing k values for all of the four alkali-metal atoms considered. This result provides additional important evidence for the relevance of the quantum number $k=n+l$ and rule A for the study of atomic structure in both the ground state and the excited states.

Within a given k region, the order of the levels follows also a characteristic pattern of l values, which (with one exception) is the same throughout the spectrum for a given alkali atom. This pattern is expressed most simply by listing the sequence of l values according to which E_{nl} increases for a given k. Thus for Na (Table II), the pattern is $l=3, 2, 1, 0$ or f, d, p, s, i.e., the order of increasing q values which is the same as that exhibited in Table I, corresponding to rule B and the order of filling of shells in the periodic table. This "coincidence" with rule B provides additional evidence for the relevance of rule B to the energy levels of the excited states of Na. The 5*g* and 6*h* states are energy-ordered in the same manner, and this is why we have denoted the pattern as $(h,g)f, d, p, s$ and $(5, 4)3, 2, 1, 0$ in the heading of

TABLE II. Excitation energies E_{nl} (above the ground state) for the excited states of the neutral sodium atom, in units of cm^{-1}, for values of $k=n+l$ from 4 to 17. The order in which the levels are listed is the same as the order of increasing energies E_{nl}, except where the value of E_{nl} is followed by a superscript (λ), meaning that the level nl with the listed value of $k=n+l$ lies in the region occupied by most (or all) of the levels in the group $k+\lambda$ (see Sec. II of text). The convention with respect to the superscript (λ) is the same for similar tables which follow, namely Tables III–V and XI–XV. For the case of Na, the l pattern, i.e., the sequence of l values within a given group of levels having the same k value, is $(h,g)f,d,p,s=(5,4)3,2,1,0$. $[(h,g)=(5,4)$ is in parentheses because there are only two levels involved, namely 5*g* and 6*h*.] The series limit listed at the bottom of the table corresponds to the ionization of the valence electron, i.e., the ground state of the Na$^+$ ion.

nl	E_{nl}	k	l	nl	E_{nl}	k	l
3*p*	16 968	4	1	6*h*	$38\,403^{(-3)}$	11	5
4*s*	25 740	4	0	8*f*	$39\,734^{(-1)}$	11	3
3*d*	29 173	5	2	9*d*	40 091	11	2
4*p*	30 271	5	1	10*p*	40 137	11	1
5*s*	33 201	5	0	11*s*	40 274	11	0
4*d*	34 549	6	2	9*f*	$40\,093^{(-1)}$	12	3
5*p*	35 042	6	1	10*d*	40 349	12	2
6*s*	36 373	6	0	11*p*	40 383	12	1
4*f*	$34\,589^{(-1)}$	7	3	12*s*	40 483	12	0
5*d*	37 037	7	2	10*f*	$40\,351^{(-1)}$	13	3
6*p*	37 297	7	1	11*d*	40 540	13	2
7*s*	38 012	7	0	12*p*	40 566	13	1
5*f*	$37\,058^{(-1)}$	8	3	13*s*	40 645	13	0
6*d*	38 387	8	2	11*f*	$40\,539^{(-1)}$	14	3
7*p*	38 541	8	1	12*d*	40 686	14	2
8*s*	38 968	8	0	13*p*	40 706	14	1
5*g*	$37\,060^{(-2)}$	9	4	14*s*	40 770	14	0
6*f*	$38\,400^{(-1)}$	9	3	13*d*	40 799	15	2
7*d*	39 201	9	2	14*p*	40 814	15	1
8*p*	39 299	9	1	14*d*	40 890	16	2
9*s*	39 575	9	0	15*p*	40 901	16	1
7*f*	$39\,209^{(-1)}$	10	3	15*d*	40 958	17	2
8*d*	39 729	10	2	16*p*	40 971	17	1
9*p*	39 795	10	1				
10*s*	39 983	10	0	Limit	41 450		

Table II.

However, proceeding now to K (Table III), we note that the pattern for this atom is somewhat different, namely $(h,g)f,p,d,s$, i.e., the order of the p and d levels (for the same k) has been interchanged from that for Na. For both Na and K, we should emphasize that the tables of Moore are complete up to at least $k=14$, and for this com-

TABLE III. Excitation energies E_{nl} (in cm^{-1}) for the excited states of the neutral potassium atom, K. The values of $k=n+l$ are listed in the third column of the table. The convention with respect to the superscripts (λ) has been explained in the heading of Table II. The l pattern, as defined in the text and in Table II is $(h,g)f,p,d,s=(5,4)3,1,2,0$, with the exception of the group $k=5$, for which we have the sequence $p,s,d=1,0,2$.

nl	E_{nl}	k	l
4p	13 024	5	1
5s	21 027	5	0
3d	21 535	5	2
5p	24 714	6	1
4d	27 397	6	2
6s	27 451	6	0
4f	28 128	7	3
6p	29 005	7	1
5d	30 185	7	2
7s	30 274	7	0
5f	30 606	8	3
7p	31 073	8	1
6d	31 696	8	2
8s	31 765	8	0
5g	30 620$^{(-1)}$	9	4
6f	31 953	9	3
8p	32 229	9	1
7d	32 598	9	2
9s	32 648	9	0
6g	31 961$^{(-1)}$	10	4
7f	32 765	10	3
9p	32 942	10	1
8d	33 178	10	2
10s	33 214	10	0
6h	31 961$^{(-2)}$	11	5
8f	33 291	11	3
10p	33 411	11	1
9d	33 572	11	2
11s	33 598	11	0
9f	33 652	12	3
11p	33 737	12	1
10d	33 852	12	2
12s	33 870	12	0
12p	33 973	13	1
11d	34 057	13	2
13s	34 069	13	0
Limit	35 010		

TABLE IV. Excitation energies E_{nl} for the excited states of the neutral rubidium atom, Rb. The l pattern is $(h,g)p,d,s,f=(5,4)1,2,0,3$. The remarkable persistence of the l-pattern p,d,s,f is shown by the sequence of energy values E_{nl} for the k groups $k=32$, 33, and 50.

nl	E_{nl}	k	l
5p	12 737	6	1
4d	19 355	6	2
6s	20 134	6	0
6p	23 767	7	1
5d	25 702	7	2
7s	26 311	7	0
4f	26 792	7	3
7p	27 858	8	1
6d	28 689	8	2
8s	29 047	8	0
5f	29 278	8	3
5g	29 298	9	4
8p	29 848	9	1
7d	30 281	9	2
9s	30 499	9	0
6f	30 628	9	3
6g	30 637	10	4
9p	30 966	10	1
8d	31 222	10	2
10s	31 362	10	0
7f	31 442	10	3
6h	30 644$^{(-1)}$	11	5
10p	31 659	11	1
9d	31 832	11	2
11s	31 917	11	0
8f	31 969	11	3
11p	32 117	12	1
10d	32 228	12	2
12s	32 295	12	0
12p	32 436	13	1
11d	32 515	13	2
13p	32 667	14	1
12d	32 725	14	2
31p	33 554.5	32	1
30d	33 557.0	32	2
32s	33 559.2	32	0
29f	33 559.9	32	3
32p	33 563.6	33	1
31d	33 566.0	33	2
33s	33 567.7	33	0
30f	33 568.5	33	3
49p	33 639.9	50	1
48d	33 640.5	50	2
50s	33 641.0	50	0
47f	33 641.3	50	3
Limit	33 691.1		

TABLE V. Excitation energies for the excited states of the neutral cesium atom, Cs. The l pattern is $(h)p, d, s(g)f = (5)1, 2, 0(4)3$, i.e., it is essentially the same as that for Rb, since it contains the sequence $p, d, s, f = 1, 2, 0, 3$.

nl	E_{nl}	k	l
$6p$	11 548	7	1
$5d$	14 558	7	2
$7s$	18 536	7	0
$4f$	$24\,772^{(+1)}$	7	3
$7p$	21 886	8	1
$6d$	22 615	8	2
$8s$	24 317	8	0
$5f$	$26\,971^{(+1)}$	8	3
$8p$	25 764	9	1
$7d$	26 062	9	2
$9s$	26 911	9	0
$5g$	27 010	9	4
$6f$	$28\,330^{(+1)}$	9	3
$9p$	27 667	10	1
$8d$	27 818	10	2
$10s$	28 300	10	0
$6g$	28 347	10	4
$7f$	$29\,148^{(+1)}$	10	3
$6h$	28 356	11	5
$10p$	28 745	11	1
$9d$	28 833	11	2
$11s$	29 130	11	0
$8f$	$29\,679^{(+1)}$	11	3
$11p$	29 415	12	1
$10d$	29 471	12	2
$12s$	29 666	12	0
$9f$	$30\,043^{(+1)}$	12	3
$12p$	29 861	13	1
$11d$	29 899	13	2
$10f$	$30\,302^{(+1)}$	13	3
$13p$	30 172	14	1
$12d$	30 198	14	2
$11f$	$30\,495^{(+1)}$	14	3
$14p$	30 397	15	1
$13d$	30 417	15	2
$12f$	$30\,641^{(+1)}$	15	3
$15p$	30 566	16	1
$14d$	30 681	16	2
$16p$	30 696	17	1
$15d$	30 708	17	2
Limit	31 407		

plete sequence of k values ($k=4$ to $k=14$ for Na), the sequence f, d, p, s is maintained (for each given k) for Na. The sequence f, p, d, s is valid for K in the same region of k values, with one exception, namely that the level $5s$ of K lies below the $3d$ level, although by a relatively small amount: $21\,535 - 21\,027 = 508$ cm^{-1} = 0.063 eV. This anomaly could arise as a result of a small perturbation of either the ns or nd series in this region of n values. We note that the number of "exceptions" N_E of the type $E_{nl}^{(k+\lambda)}$, as described above, is only $N_E = 10$ out of a total number of levels $N_L = 48$ for Na, while for K, we have $N_E = 3$ out of a total $N_L = 38$.

For the cases of Rb and Cs (Tables IV and V), the observed pattern is p, d, s, f, as indicated in the corresponding table headings. For the case of Rb (Table IV), although the ns and nf levels are not listed in Moore's tables for $13 \leq k \leq 31$, they are listed again in the region from $k=32$ to $k=50$. For this reason, we have listed the E_{nl} values for $k=32$, 33, and 50, to demonstrate both that the levels are still ordered according to k values, and that the sequence p, d, s, f for a given k value continues to hold even in this region of large n and k values.

At present, we do not have an explanation for this remarkable persistence of the energy ordering according to k, and of the sequence p, d, s, f within a given k group. However, we note that even though the radial wave functions for $n=32$, 33, and 50 are, of course, very external, it is probably the small parts of the wave functions which penetrate the Rb$^+$ core and come close to the nucleus that determine the character of the energy ordering, i.e., the observed pattern p, d, s, f. We note that for the 33 levels having $k \leq 14$, there is only a single exception of the type $(k+\lambda)$ for Rb, namely that the $6h$ level with $k=11$ ($E_{6h} = 30\,644$ cm^{-1}) lies in the $k=10$ region. Finally, we note that for Cs, with 40 levels having $k \leq 17$, and the pattern $(h)p, d, s(g)f$, there are nine exceptions of the type $E_{nl}^{(k+\lambda)}$, all of which involve nf levels with $\lambda = +1$.

On the whole, two conclusions can be drawn from the results of Tables II–V.

(1) The energy ordering proceeds predominantly in the order of increasing k values for these *excited states* of the four alkali-metal atoms. This result is in remarkable concordance with the statement of Madelung's Rule A, according to which the *ground states* of the outermost electrons of the chemical elements fill up in the order of increasing k as the atomic number Z is increased.

(2) For each alkali atom, within a given k region, the energy ordering proceeds along a definite pattern characteristic of each atom, which is independent of k, up to the highest k value ($k=50$) for which data are available for the case of Rb (Table IV). This pattern is f, d, p, s for Na (the same as for the periodic table), f, p, d, s for K, and p, d, s, f for both Rb and Cs.

In Table VI, we have listed for each of the four alkalis, the number of levels considered (N_L),

TABLE VI. Summary of the results for the ordering of the k groups for the four alkali-metal atoms: Na, K, Rb, and Cs. The second column lists the number of levels N_L considered; N_E is the number of exceptions of the type $(k+\lambda)$. The last two columns list the values of the ratio N_E/N_L for each atom and the l pattern, as described in the text (Sec. II).

Atom	N_L	N_E	N_E/N_L	Pattern
Na	48	10	0.208	$(h,g)f,d,p,s$
K	38	3	0.079	$(h,g)f,p,d,s$
Rb	45	1	0.022	$(h,g)p,d,s,f$
Cs	40	9	0.225	$(h)p,d,s(g)f$
Total	171	23	0.135	

the number of exceptions of the type $k+\lambda$ (N_E), the ratio N_E/N_L, and the pattern l_1, l_2, l_3, l_4 as given above in conclusion (2). Considering the total number of levels investigated, namely 171, we note that we have a total of 23 exceptions, giving us a ratio $23/171=0.135$.

In Table VII, we have listed the energies $E(k)$ (above the ground level) for the centroids of the different k groups, as a function of $k-k_{\text{min}}$. Here k_{min} is the minimum value of k for the atom considered, i.e., k for the ground state ($n_v s$) of the valence electron. We have $k_{\text{min}}=n_v$, since $l=0$. Thus $k_{\text{min}}=3$ for Na, 4 for K, 5 for Rb, and 6 for Cs. The average $E(k)$ was obtained simply by taking the sum of all values $E_{nl}(k)$ pertaining to a given k, as listed in Tables II–V, and dividing by the number $n_0(k)$ of such energy values.

It can be seen that $E(k)$ increases uniformly with increasing k, or $k-k_{\text{min}}$, as is expected from the previous discussion. For a given value of $k-k_{\text{min}}$, $E(k)$ decreases somewhat with increasing Z, in accordance with the fact that the series limit (ionization potential) also decreases with increasing Z for the alkali-metal atom series. The value of the series limit (for $k\to\infty$) is listed in the last row of the table.

In the preceding tabulations, we have not included the case of lithium Li ($Z=3$). An inspection of the corresponding table of Moore[23] showed at once that for Li, the excited levels are grouped according to the value of n, and with the energy increasing slightly with l for a given n value. For completeness, we have listed the Li excited energy levels in Table VIII, showing both the nl values and the values of k. It is seen that the energy spectrum of the valence electron of Li is essentially hydrogenic.

In as much as for the case of Na already, we have an energy grouping according to the value of k (with a subsidiary sequence f,d,p,s), we can conclude that the grouping according to k and l most probably requires the existence of a core containing a closed shell of non-s electrons, i.e., $2p^6$ for Na. There is also the alternative possibility that the k grouping requires the existence of a sufficiently rapid falloff of the effective Z, namely $Z_p(r)$, in the expression for the potential $V(r)$ seen by the valence electron. Here we use Hartree's notation, i.e., $V(r)=-2Z_p/r$ (Ry) is the potential due to the nucleus + the core electrons. Thus for Li, $Z_p(r)$ decreases only from $Z_p=3$ at $r=0$ to $Z_p=1$ at large r, whereas for Na, the decrease of $Z_p(r)$ is from $Z_p=11$ at $r=0$ to $Z_p=1$ at large r. If this possibility is the actual explanation, the k grouping might be derivable simply from the shape of the effective potential which can be written as

$$V(r)=-\frac{2(Z-1)\chi(r)}{r}-\frac{2}{r}, \qquad (10)$$

where $\chi(r)$ is the Thomas-Fermi function,[24] which has the properties $\chi(0)=1$ and $\chi(\infty)=0$.

On the other hand, if the explanation of the k and $\{l_i\}$ groupings requires the existence of a core containing at least a filled p shell, then the grouping property may be the result of core polarization effects, which would be remarkably similar to those encountered in the study of the nuclear quadrupole antishielding factors[15,17,25] R and γ_∞, and of the inverted fine structure of the nd states of the alkali valence electrons.[26] Both of these effects are caused by the presence of filled np (and nd) shells in the core of the atom.

In order to show the regular behavior of the energy differences between the members of a

TABLE VII. Energy centroids of the various k groups for the excited states of Na, K, Rb, and Cs. k_{min} is the minimum value of k, i.e., the value of n_v, which is n for the valence electron in the ground state $n_v s$. The value of k_{min} is listed in the first row after each element. Thus for Na, with $k_{\text{min}}=3$, the centroid value for $k-k_{\text{min}}=4$ corresponds to $k=7$. All of the levels included in Tables II–V have been weighted equally in obtaining the centroids given in Table VII.

$k-k_{\text{min}}$	Na(3)	K(4)	Rb(5)	Cs(6)
1	21 354	18 529	17 409	17 354
2	30 882	26 521	25 643	23 947
3	35 321	29 398	28 718	26 815
4	36 734	31 285	30 111	28 256
5	38 239	32 010	31 126	28 949
6	38 707	32 612	31 602	29 649
7	39 679	33 167	32 213	30 021
8	39 728	33 778	32 476	30 288
9	40 327	34 033	32 696	30 485
Series limit	41 450	35 010	33 691	31 407

TABLE VIII. Excitation energies E_{nl} for the excited states of the neutral lithium atom, Li. It is seen that the pattern is hydrogenic without exception, that is, levels with the same n value are grouped together, regardless of the value of k. For each n value, the energy values E_{nl} increase uniformly with increasing l.

nl	E_{nl}	k	l
2s	0.00	2	0
2p	14 904	3	1
3s	27 206	3	0
3p	30 925	4	1
3d	31 283	5	2
4s	35 012	4	0
4p	36 470	5	1
4d	36 623	6	2
4f	36 630	7	3
5s	38 300	5	0
5p	39 016	6	1
5d	39 095	7	2
5f	39 105	8	3
6s	39 988	6	0
6p	40 391	7	1
6d	40 437	8	2
7s	40 968	7	0
7p	41 217	8	1
7d	41 247	9	2
8s	41 587	8	0
8p	41 752	9	1
8d	41 771	10	2
9s	42 003	9	0
9p	42 118	10	1
9d	42 131	11	2
10s	42 298	10	0
10p	42 379	11	1
10d	42 389	12	2
11s	42 510	11	0
11p	42 569	12	1
11d	42 578	13	2
12p	42 719	13	1
12d	42 725	14	2
Limit	43 487		

given k group, we have listed in Tables IX and X the values of the energy differences $\Delta_{l_1l_2}$ for Na and Rb, where $\Delta_{l_1l_2}$ is defined as follows

$$\Delta_{l_1l_2} \equiv E(k,l_1) - E(k,l_2)\,. \tag{11}$$

The energy differences $\Delta_{l_1l_2}$ are taken between adjacent levels. Thus for Na (Table IX), with the pattern $(3,2,1,0)$, we have listed the values of Δ_{23}, Δ_{12}, and Δ_{01}. For Rb (Table X), with the pattern $(1,2,0,3)$, we have given the values of Δ_{21}, Δ_{02}, and Δ_{30}. It is seen that the energy differences $\Delta_{l_1l_2}$ themselves maintain the same relative order as k is increased from $k=4$ to $k=14$ for Na and from $k=6$ to $k=50$ for Rb. Thus for Na we find $\Delta_{12} < \Delta_{01} < \Delta_{23}$ for all k values considered, and for Rb we find $\Delta_{30} < \Delta_{02} < \Delta_{21}$ from $k=6$ to $k=50$. The same stability is found for K, where $\Delta_{02} < \Delta_{13} < \Delta_{21}$ throughout the range from $k=5$ to $k=12$, and for Cs, where $\Delta_{21} < \Delta_{02} < \Delta_{30}$ from $k=7$ to $k=12$.

TABLE IX. For the case of Na, this table shows the regular behavior of the energy differences $\Delta_{l_1l_2}(k) \equiv E(k,l_1) - E(k,l_2)$ within a group of levels with constant k. Thus for all values of k for which Δ_{23} is determined, i.e., for $k \geq 7$, we find $\Delta_{23} > \Delta_{01} > \Delta_{12}$.

k	Δ_{23}	Δ_{12}	Δ_{01}
4			8772
5		1098	2930
6		493	1331
7	2448	260	715
8	1329	154	427
9	801	98	276
10	520	66	188
11	357	46	137
12	256	34	100
13	189	26	79
14	147	20	64

Referring again to Tables IX and X, it should be emphasized that we are here dealing with the stability of very small energy differences, and hence with very fine details of the excited energy spectrum. As an example, the values $\Delta_{01} = 188\ \mathrm{cm}^{-1}$, $\Delta_{12} = 66\ \mathrm{cm}^{-1}$, $\Delta_{23} = 520\ \mathrm{cm}^{-1}$ for the $k=10$ group of levels of Na correspond to energy differences of only 23.3×10^{-3} eV, 8.2×10^{-3} eV and 64.5×10^{-3} eV, respectively. (We have 10^{-3} eV $= 8.07\ \mathrm{cm}^{-1}$.)

TABLE X. Values of $\Delta_{l_1l_2}(k)$ for the case of Rb. The table shows that for all cases for which the relevant data exist, we have $\Delta_{21} > \Delta_{02} > \Delta_{30}$.

k	Δ_{21}	Δ_{02}	Δ_{30}
6	6618	779	
7	1935	609	481
8	831	358	231
9	433	218	129
10	256	140	80
11	173	85	52
12	111	67	
32	2.5	2.2	0.7
33	2.4	1.7	0.8
50	0.6	0.5	0.3

III. ADDITIONAL EVIDENCE FROM THE SPECTRA OF THE ALKALINE-EARTH IONS

As additional evidence for the quantum number k, we consider the excited energy spectra of the singly-ionized alkaline-earth atoms,[23] i.e., the ions Mg^+, Ca^+, Sr^+, Ba^+, and Ra^+. These spectra are presented in Tables XI–XV, respectively. The average energies E_{nl} (averaged over the values for $j = l \pm \frac{1}{2}$) are listed in these tables, together with the values of $k = n + l$, and l. The "exceptions" of the type $(k + \lambda)$ are listed as superscripts after the values of E_{nl}, in the same manner as in Tables II–V for the alkali-metal atoms Na, K, Rb, and Cs.

In Table XVI, we have listed for each of the five alkaline-earth ions the number of levels considered (N_L), the number of exceptions (N_E) of the type $(k + \lambda)$, the ratio N_E/N_L, and the pattern $(l_1 l_2 l_3 l_4 l_5)$ of the order in which the l values are ordered for a given (fixed) value of k. It is striking, first of all, that the levels are energy-ordered in the order of increasing k, and that the pattern $(l_1 l_2 l_3 l_4 l_5)$ is maintained for a given k, with very few exceptions. The number of $(k + \lambda)$ exceptions is generally smaller than that for the corresponding alkali-metal atoms. In particular, for Sr^+ $(Z = 38)$, there are no $(k + \lambda)$ exceptions, $N_E = 0$, as compared to $N_E = 1$ for Rb $(Z = 37)$. Also for Ba^+ $(Z = 56)$, there is only one $(k + \lambda)$ exception, $N_E = 1$, as compared to $N_E = 9$ for Cs $(Z = 55)$. The patterns $(l_1 l_2 l_3 l_4 l_5)$ are as follows: (g, f, d, p, s) for Mg^+ and Ca^+, (d, p, f, g, s) for Sr^+, (d, p, g, f, s) for Ba^+, and both (d, p, s, f, g) and (d, p, f, s, g) for Ra^+. Altogether there are 132 levels included in this analysis of the alkaline-earth ionic spectra, with only 16 exceptions, giving a ratio

$$\left(\sum N_E \Big/ \sum N_L\right)_{\text{A-E ions}} = 16/132 = 0.121, \tag{12}$$

which is somewhat lower than the corresponding ratio of exceptions for the neutral alkali-metal atoms, namely

$$\left(\sum N_E \Big/ \sum N_L\right)_{\text{A-M atoms}} = 23/171 = 0.135\,. \tag{13}$$

TABLE XI. Excitation energies E_{nl} (above the ground state) for the excited states of the singly ionized magnesium atom, Mg^+. The values of $k = n + l$ are listed in the third column of the table. The convention with respect to the superscripts (λ) has been explained in the heading of Table II and in the text. The "l pattern", as defined in the text and in Table II is $g, f, d, p, s = 4, 3, 2, 1, 0$, i.e., it is the same as for Na.

nl	E_{nl}	k	l
$3p$	35 730	4	1
$4s$	69 805	4	0
$3d$	71 491	5	2
$4p$	80 641	5	1
$5s$	92 786	5	0
$4d$	93 312	6	2
$5p$	97 464	6	1
$6s$	103 198	6	0
$4f$	93 800$^{(-1)}$	7	3
$5d$	103 421	7	2
$6p$	105 628	7	1
$7s$	108 785	7	0
$5f$	103 690$^{(-1)}$	8	3
$6d$	108 901	8	2
$8s$	112 130	8	0
$6f$	109 063$^{(-1)}$	9	3
$7d$	112 198	9	2
$9s$	114 292	9	0
$6g$	109 073$^{(-2)}$	10	4
$7f$	112 302$^{(-1)}$	10	3
$8d$	114 336	10	2
Limit	121 267		

TABLE XII. Excitation energies E_{nl} for the excited states of the singly ionized calcium atom, Ca^+. The l pattern is $g, f, d, p, s = 4, 3, 2, 1, 0$, i.e., the same as for Na and Mg^+.

nl	E_{nl}	k	l
$3d$	13 687	5	2
$4p$	25 325	5	1
$5s$	52 167	5	0
$4d$	56 851	6	2
$5p$	60 587	6	1
$6s$	70 678	6	0
$4f$	68 057$^{(-1)}$	7	3
$5d$	72 727	7	2
$6p$	74 510	7	1
$7s$	79 450	7	0
$5f$	78 028$^{(-1)}$	8	3
$6d$	80 526	8	2
$8s$	84 303	8	0
$5g$	78 163$^{(-2)}$	9	4
$6f$	83 458$^{(-1)}$	9	3
$7d$	84 937	9	2
$6g$	83 540$^{(-2)}$	10	4
$7f$	86 728	10	3
$8d$	87 675	10	2
$7g$	86 781$^{(-1)}$	11	4
$8f$	88 848	11	3
$9d$	89 490	11	2
Limit	95 748		

Altogether, combining the data from Tables VI

TABLE XIII. Excitation energies for the excited states of the singly ionized strontium atom, Sr^+. The l pattern is $d,p,f,g,s = 2,1,3,4,0$.

nl	E_{nl}	k	l
4d	14 724	6	2
5p	24 250	6	1
6s	47 737	6	0
5d	53 338	7	2
6p	55 962	7	1
4f	60 992	7	3
7s	64 964	7	0
6d	67 547	8	2
7p	68 745	8	1
5f	71 066	8	3
4g	71 358	8	4
8s	73 237	8	0
7d	74 634	9	2
8p	75 312	9	1
6f	76 553	9	3
5g	76 738	9	4
9s	77 858	9	0
8d	78 697	10	2
7f	79 861	10	3
6g	79 984	10	4
10s	80 702	10	0
9d	81 246	11	2
8f	82 006	11	3
7g	82 090	11	4
11s	82 576	11	0
10d	82 952	12	2
9f	83 473	12	3
8g	83 534	12	4
12s	83 880	12	0
11d	84 145	13	2
10f	84 521	13	3
9g	84 567	13	4
13s	84 819	13	0
12d	85 016	14	2
11f	85 295	14	3
10g	85 330	14	4
13d	85 669	15	2
12f	85 884	15	3
Limit	88 964		

and XVI, we have included $\sum N_L = 303$ levels, with a total number of $(k+\lambda)$ exceptions $\sum N_E = 39$, giving a ratio: $39/303 = 0.129$.

It should be noted that we have not included Be^+ in the analysis presented above. The reason is that for Be^+, similarly to Li, the energy ordering is hydrogenic, i.e., $2s, 2p, 3s, 3p, 3d$, etc. (cf. Table VIII). This result for Be^+ was, of course, not surprising in view of the energy ordering for Li which is isoelectronic with Be^+.

However, what was more surprising is that the energy ordering for Al^{2+} is also hydrogenic, as is shown in Table XVII. Thus there is a complete change in the energy sequence of the levels, as Z is increased by only one unit, in going from Mg^+ to Al^{2+}, both of which have 11 electrons. The same hydrogenic ordering is found for the higher members of the isoelectronic sequence, starting with Si^{3+}. This result is somewhat reminiscent of the calculations of Goudsmit and Richards,[2] according to which for the *ground states* of ionized atoms, if the degree of ionization is sufficiently large, the order of level filling becomes hydrogenic instead of following the "$n+l$ rule," i.e., the ordering according to the value of k.

Among the other ions which are isoelectronic with the alkaline-earth ions, we may note the fol-

TABLE XIV. Excitation energies for the excited states of the singly ionized barium atom, Ba^+. The l pattern is $d,p,g,f,s = 2,1,4,3,0$, except for the lowest-lying k group, namely $k=7$, for which the l sequence is $d,p,s,f = 2,1,0,3$.

nl	E_{nl}	k	l
5d	5 355	7	2
6p	21 388	7	1
7s	42 355	7	0
4f	48 387	7	3
6d	46 073$^{(-1)}$	8	2
7p	49 804	8	1
5f	57 529	8	3
8s	58 025	8	0
7d	59 857	9	2
8p	61 536	9	1
5g	63 027	9	4
6f	64 654	9	3
9s	65 683	9	0
8d	66 704	10	2
6g	68 426	10	4
7f	69 239	10	3
10s	70 015	10	0
9d	70 639	11	2
7g	71 682	11	4
8f	72 158	11	3
11s	72 705	11	0
10d	73 114	12	2
8g	73 796	12	4
9f	74 101	12	3
12s	74 492	12	0
11d	74 774	13	2
9g	75 244	13	4
10f	75 445	13	3
12d	75 942	14	2
10g	76 270	14	4
11f	76 422	14	3
Limit	80 687		

TABLE XV. Excitation energies E_{nl} for the excited states of the singly ionized radium atom, Ra^+. The l pattern, as defined in the text and in Table II, is d,p,s,f,g for $k=8$ and $k=9$, and d,p,f,s,g for $k=10$.

nl	E_{nl}	k	l
$6d$	13 079	8	2
$7p$	24 590	8	1
$8s$	43 405	8	0
$5f$	49 150	8	3
$7d$	$49\,042^{(-1)}$	9	2
$8p$	51 797	9	1
$9s$	59 165	9	0
$6f$	59 687	9	3
$5g$	64 151	9	4
$8d$	$61\,878^{(-1)}$	10	2
$9p$	$63\,191^{(-1)}$	10	1
$7f$	66 618	10	3
$10s$	66 838	10	0
$6g$	69 561	10	4
$9d$	$68\,343^{(-1)}$	11	2
$11s$	71 173	11	0
$7g$	72 824	11	4
Limit	81 842		

lowing observations.[23] (1) The ions which are isoelectronic with Mg^+ and Al^{2+} have hydrogenic energy level ordering as would be expected from the results for Al^{2+} (Table XVII). These ions are Si^{3+}, P^{4+}, S^{5+}, Cl^{6+}, Ar^{7+}, Kr^{8+}, Ca^{9+}, Sc^{10+}, Ti^{11+}, and V^{12+}. (2) For the ions which are isoelectronic with Ca^+, namely Sc^{2+}, Ti^{3+}, and V^{4+}, the spectra are more nearly hydrogenic than ordered according to constant k values (i.e., k ordered). (3) For the ions which are isoelectronic with Sr^+, namely Y^{2+}, Zr^{3+}, Nb^{4+}, and Mo^{5+}, the ordering is intermediate between hydrogenic and and k ordering. (4) Finally for La^{2+} which is isoelectronic with Ba^+, we find almost complete k ordering with exception that the $5d$ level, with $k=7$ lies somewhat below $6s$ ($k=6$). The sequence is $5d(7)$, $6s(6)$, $6p(7)$, $7s(7)$, $6d(8)$, $5f(8)$, $8s(8)$, where the value of k has been noted in parentheses.

The preceding results show the direct competition between k ordering and hydrogen-like ordering, as the atoms are progressively more ionized. This competition would be expected directly from the calculations of Goudsmit and Richards[2] on the level filling in ionized atoms.

IV. IMPLICATIONS OF THE PRESENT RESULTS

(1) It appears significant to the present author that the ordering rules A and B of Madelung hold for all Z values which have been presently investigated, i.e., up to $Z=130$ if we include the calculational results of Refs. 19 and 20. Thus for $Z=130$, we have $\alpha Z = 0.95$ and therefore the ordering rules hold throughout the nonrelativistic and the relativistic regions of Z. The same result applies for the k-ordering properties of the excited-state spectra of the alkali-metal atoms, which have been verified up to Cs, $Z=55$, $\alpha Z = 0.40$, and the excited-state spectra of the alkaline-earth ions, which have been analyzed up to Ra^+, $Z=88$, $\alpha Z=0.64$. We note that the quantum number n does not appear directly in either the Schrödinger equation [which contains $l(l+1)$ only] or the Dirac equation which contains the Dirac quantum number $\kappa = -(l+1)$ for $j=l+\frac{1}{2}$ and $\kappa=+l$ for $j=l-\frac{1}{2}$. Since n does not appear in the Schrödinger and Dirac equations, neither do the combinations $k=n+l$ and $q=n-l$. Therefore the property of k as an energy-ordering quantum number can probably not be derived from a consideration of the Schrödinger or Dirac equations alone, but may well be a more general and more fundamental property of the many-body potential function V of N electrons in the field of a nucleus of charge Z. V is given by

$$V = -\sum_{i}^{N} \frac{Ze^2}{r_i} + \sum_{i>j}^{N} \frac{e^2}{r_{ij}} \,. \qquad (14)$$

The k ordering of the excited levels, which is the subject of this paper, seems to hold with relatively fewer exceptions than Madelung's rule B for the filling of the ground-state levels, since we

TABLE XVI. Summary of the results obtained for the alkaline-earth positive ions (Tables XI–XV). The notation is the same as in Table VI. Thus N_L = number of levels considered; N_E = number of "exceptions" of the type $k+\lambda$. The last two columns list the values of the ratio N_E/N_L for each atom and the l pattern, as described in the text. The row denoted by $Total^{(+)}$ gives the total values of N_L and N_E for the positive ions, and the corresponding ratio $\Sigma N_E/\Sigma N_L$. The next row, marked $Total^{(0)}$ gives the corresponding results for the neutral alkali-metal atoms, as obtained from Table VI. The last row gives the corresponding Grand Total = $Total^{(+)} + Total^{(0)}$, and the resulting ratio $\Sigma N_E/\Sigma N_L = 0.129$.

Ion	N_L	N_E	N_E/N_L	Pattern
Mg^+	21	5	0.238	g,f,d,p,s
Ca^+	22	6	0.273	g,f,d,p,s
Sr^+	39	0	0.0	d,p,f,g,s
Ba^+	33	1	0.030	d,p,g,f,s
Ra^+	17	4	0.235	d,p,s,f,g d,p,f,s,g
$Total^{(+)}$	132	16	0.121	
$Total^{(0)}$	171	23	0.135	
Grand Total	303	39	0.129	

TABLE XVII. Excitation energies for the excited states of the doubly ionized aluminum atom, Al^{2+}, which is isoelectronic with Na and Mg^{+}. The table shows clearly that the level pattern is hydrogenic without exception, in the same manner as for Li (Table VIII). Levels with the same n are grouped together, regardless of k. For each n value, the E_{nl} values increase uniformly with increasing l.

nl	E_{nl}	k	l
3*p*	53 839	4	1
3*d*	115 956	5	2
4*s*	126 163	4	0
4*p*	143 685	5	1
4*d*	165 786	6	2
4*f*	167 612	7	3
5*s*	170 636	5	0
5*p*	178 456	6	1
5*d*	188 875	7	2
5*f*	189 875	8	3
5*g*	189 928	9	4
6*s*	191 479	6	0
6*p*	195 635	7	1
6*d*	201 374	8	2
6*f*	201 970	9	3
6*g*	202 001	10	4
6*h*	202 007	11	5
7*s*	202 905	7	0
7*p*	205 360	8	1
7*d*	208 880	9	2
7*f*	209 261	10	3
7*g*	209 282	11	4
7*h*	209 288	12	5
8*d*	213 741	10	2
8*f*	213 992	11	3
8*g*	214 011	12	4
8*h*	214 016	13	5
Limit	229 454		

have for the k ordering, only 39 exceptions in a total of 303 levels, giving a ratio $N_E/N_L = 39/303 = 0.129$ (see Table XVI). By comparison, it appears that three of the rare earths have a 5*d* electron in the ground state as part of the configuration $4f^x5d6s^2$, (La, Ce, and Gd), and there is similar evidence for six of the actinides, where at least one electron is 6*d* in the atomic ground state (Ac, Th, Pa, U, Np, and Cm). Thus we have nine "exceptions" to rule B due to the presence of 5*d* and 6*d* electrons, in a total of 120 atoms ($Z = 1$ to $Z = 120$), and the corresponding ratio of number of exceptions (N_E) to number of atoms (N_A) is therefore $N_E/N_A = 0.075$.

For the atoms immediately following $Z = 120$ (eka - radium), there is believed to be considerable violation of Rule B, since the 6*f* and 7*d* electrons are believed to occur in the lowest atomic states from $Z = 121$ to $Z = 124$, before the 5*g* shell starts to be occupied at $Z = 125$. Thus according to Waber *et al.*,[19] the preferred (lowest-energy) configurations for $Z = 124$, 125, and 126 are $6f^37d$, $5g6f^37d$, and $5g^26f^37d$, respectively (outside the eka-radium $Z = 120$ core).

(2) As has been discussed above, the k-ordering rule already begins to be valid for Na($Z = 11$) and Mg^{+} ($Z = 12$). The fact that it does not hold for the isoelectronic ion Al^{2+} ($Z = 13$) and the higher Z ions in this isoelectronic series (Si^{3+}, P^{4+}, S^{5+}, etc.) is a strong indication that the k-ordering rule applies only if Z is sufficiently large, and the outermost electron is in a *neutral* or *almost neutral* environment. The question of the large Z may be simply a result of the necessity for the rapid fall-off of the (nuclear + electronic) potential $-2Z_p/r$ (Rydbergs), which can also be written in terms of the Thomas-Fermi function $\chi(r)$ [see Eq. (10)]. However, since the effect is not present for Li (and its isoelectronic ions), the k ordering may require the presence of at least one filled p shell ($2p^6$ for Na), and may thus be related to the quadrupole antishielding property of the p (and d) shells[15,17,25] and to the fine-structure inversion of the nd states of the alkali-metal valence electrons.[26]

(3) We have shown that the features of the k ordering and the l patterns of the levels are very general, and persist throughout the entire region of Z (up to $Z \cong 130$) for the ground states, and throughout a very large region of n values for a given Z (up to $n = 50$ for Rb, $Z = 37$). These facts indicate that there may well be a group-theoretical explanation of these properties. This explanation would be a property of the Dirac Hamiltonian including the potential term V of Eq. (14), since the effect persists throughout the relativistic region for both the ground states and the excited states. The explanation would involve a group containing both the principal (radial) quantum number n and the azimuthal quantum number l, since both are simultaneously involved in the definitions of k and q [Eqs. (1) and (2)].

The angular properties of the wave functions involving the quantum numbers l, j, and m (the magnetic quantum number) have been the subject of group-theoretical investigations almost since the beginnings of quantum mechanics, about fifty years ago. On the other hand, the radial properties of the wave functions involving the quantum numbers n and l have been treated by group-theoretical methods only since about 1970. In connection with this development, we should mention the discovery and proof of a new orthogonality property of the hydrogenic radial wave functions by Pasternack and Sternheimer[27] in 1962. This orthogonality property is expressed by the following equation:

$$\int_0^\infty u_{nl}u_{nl'}r^{-s}\,dr=0 \quad \text{for } s=2,3,4\ldots l'-l+1\,. \tag{15}$$

Here we have assumed that $l'>l$, and u_{nl} is r times the normalized radial wave function R_{nl}. Thus both both u_{nl} and $u_{nl'}$ pertain to the same n value, but different values of l. The authors of Ref. 27 proved the property of Eq. (15) by a consideration of the generating function for the associated Laguerre polynomials L_{n+l}^{2l+1}.

In 1970, Armstrong[28] succeeded in obtaining a group-theoretical proof of Eq. (15), which he called a selection rule. The group considered was related to the noncompact groups O(4, 2) and O(2, 1) × O(3). However, in the present context, it should be emphasized that while Armstrong's group pertains to hydrogenic wave functions, the group properties implicit in the k ordering discussed in the present paper pertain to medium and heavy atoms ($Z \gtrsim 10$) with their full complement of Z electrons. In fact the ordering rules A and B and the k ordering rules and l patterns pertain specifically to the ground states and the excited states of the outermost electron of neutral alkali metal atoms (or singly ionized alkaline-earth atoms). Thus the corresponding properties of a global group, or global symmetry scheme, if it exists, must be the properties of the Dirac Hamiltonian with the potential term V of Eq. (14) including the important term

$$\sum_{i>j}^{N} e^2/r_{ij}$$

If such a global group exists, there might be a good reason for calling $k=n+l$ the "global quantum number" of the electronic state. In any case, in view of the results of rules A and B, and the corresponding properties of the energy levels of the excited states (Tables II–V, and XI–XV), the sum $k=n+l$ can certainly be referred to as an "energy-ordering quantum number."

(4) We refer now to the energy-ordered arrangement of the valence electron orbitals, as given in Table I, which results in the revised version of the periodic table of Refs. 2–10. To each k value corresponds a single supershell consisting of the shells listed in the second column of the table. The corresponding sequence of q values ($q=n-l$) is given in the third column. We note that for two consecutive supershells k_0 and $k_e=k_0+1$, where $k_0=$ odd and $k_e=$ even, we have the same number of shells and the same sequence of l values, with only n being larger by one unit for the supershell k_e than for the supershell k_0. The two supershells k_0 and k_e will be referred to as the "block k_e." As an example, the block consisting of $k=3$ and 4 contains the shells $2p$, $3s$, $3p$, and $4s$. We now note that for a given block k_e, all integral values of q from 1 to k_e are represented, e.g., $q=1,2,3,4$ for the block $k_e=4$. Thus for the block k_e, we have

$$q=1,2,3,\ldots k_e-1,k_e\,. \tag{16}$$

The selection rule of Eq. (16) could come about naturally if in some suitable hyperspace, $\vec{k}_e$ would be a three-vector angular momentum, and q would be the magnitude of its projection along the hyper-z axis:

$$q=|k_{e,z}|\,. \tag{17}$$

This would satisfy the usual quantization relation, except for the fact that $q=0$ is not allowed, since $q\geqslant 1$. We may also note that the relation of the quantum numbers l and n is similar to Eq. (16), since we have

$$l+1=1,2,3,\ldots n-1,n\,, \tag{18}$$

so that in a suitable hyperspace we may have an angular momentum $\vec{n}$, and $l+1$ would be the magnitude of its z projection:

$$l+1=|n_z|\,. \tag{19}$$

V. SUMMARY

The order in which the electron shells of the ground states of neutral atoms are filled, as Z is progressively increased, obey two rules (A and B) which were originally discovered by Madelung[1] and have been subsequently rediscovered independently by several authors.[4-9] Rule A involves the sum $n+l$ of the principal quantum number n and the azimuthal quantum number l. In connection with the approximate energy degeneracy of the levels $7d$, $6f$, and $5g$ in the region of $Z\sim 120$ to 130 (superactinide region), we have recently rediscovered the Madelung rules. It then occurred to us that the sum $k\equiv n+l$ might be in the nature of an energy-ordering quantum number for the outermost electrons of neutral or nearly neutral atoms (e.g., singly-ionized atoms). This in turn led us to examine the ordering of the energy levels of the valence electron in the alkali-metal atoms. For all cases except for Li, that is for Na, K, Rb, and Cs, it was found that the order of increasing energies E_{nl} coincides with the order of increasing k values (see Tables II–V). Moreover, for each group of levels having the same k value, i.e., for each k group, the order of increasing excitation energy E_{nl} corresponds to a fixed sequence of l values, which is characteristic of each atom. This sequence of l values has been called the "l pattern." The l pattern of Na (Table II) corresponds to the sequence $(h,g)f,d,p,s$, i.e., $\{l_i\}=(5,4)3,2,1,0$. This sequence is the same as that implied by the Madelung rule B for the order in which new shells appear in the periodic table for a given value of $k=n+l$. Thus the excited spectrum of Na can serve as the prototype of the order of filling of the ground-state levels, as Z is increased progressively in building up the periodic table.

A similar k ordering of the excited energy levels E_{nl} has also been found for the spectra of the singly-ionized alkaline-earth atoms, namely Mg^+, Ca^+, Sr^+, Ba^+, and Ra^+ (see Tables XI–XV). In particular for Mg^+ and Ca^+, the l pattern is $g,f,d,p,s=4,3,2,1,0$, which is the same as the l pattern for Na, and the order of filling of shells in the periodic table for a given supershell k.

For almost all spectra, there are a few "exceptions," of the type $k+\lambda$, i.e., cases in which a level with a given value of $k=k_0$ lies in the region occupied by most levels with $k=k_0+\lambda$, where λ is usually ±1. Table XVI shows that out of a total of 303 levels included in the present analysis, only 39 levels constitute exceptions in the above sense.

The l pattern $p,d,s,f=(1,2,0,3)$ for Rb is shown to persist for all k values from $k=6$ up to $k=50$.

In view of these results for the k ordering of excited states and the fact that Madelung's Rule A holds throughout the relativistic region (up to $Z \cong 130$), we have discussed the possibility that there may be a group-theoretical explanation for the k ordering for both the ground states (variable Z) and the excited states of atoms and ions with one external valence electron (fixed Z, variable n).

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