Physical Chemistry

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1960

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Abstract

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On the Characterization of the Type of Electronic Configuration of Atoms

(Presented by Academician V. N. Kondrat' ev on 26 III 1960)

The question of the type of electronic configuration of atoms is closely connected with the basic concepts of D. I. Mendeleev' s theory of the periodic system, for the periodicity in the change of the chemical and certain physical properties of elements (for example, those related to atomic spectra) is determined by the repetition of electronic configurations of one and the same type among analogous elements. However, up to now the question has remained open as to the existence of any single quantity amenable to a rigorous physical definition, whose values throughout the periodic system would be in unambiguous correspondence with the type of electronic configuration of atoms. We have in mind such a quantity which, being a function of the distribution of electrons in the ground state of atoms, would assume identical values for elements that are electronic analogues.

If one starts from the scheme of the so-called "ideal system of elements" ([1]), which is based on the idea that the normal order of filling of the electronic levels of atoms corresponds to the successive filling of the layers of the electron shell —from smaller values of the principal quantum number n to larger ones—then the type of electronic configuration could be associated with such a quantity as the number of electrons in the outer shell or, in other words, with the number of electrons filling levels with the maximum value of n for atoms of the given element. But in the real periodic system the number of electrons in the outer shell, in the indicated sense of this term, is not a quantity capable of unambiguously characterizing the type of electronic configuration of atoms. This circumstance is due to the fact that, with increasing Z, the actual sequence of filling of the electronic levels of atoms does not correspond to the ideal system, but in reality obeys another regularity, which is revealed by grouping the quantum levels according to the sum of the principal and orbital quantum numbers and is expressed by the rule of successive filling of $(n + l)$-groups ([2]).

On the basis of this rule, solutions were previously obtained for a number of problems relating to the analysis of the dependence between Z and the distribution of atomic electrons ([3–5]). The purpose of the present communication is to show that, by grouping quantum levels according to the sum of the principal and orbital quantum numbers, it is possible to define a certain quantity that is in unambiguous correspondence with the type of electronic configuration of

neutral unexcited atoms of analogous elements throughout the periodic system, and that, on the basis of the rule of successive filling of $(n+l)$-groups, a rational expression can be given for the periodic dependence of this quantity on Z.

We shall use the following notation. Let N_{n+l} be the number of electrons filling, in an atom, the levels with a specified value of the sum of the principal and orbital quantum numbers, and E_{n+l} the number of free, unoccupied–

quantum states occupied by electrons with the same value of $n+l$; we shall call E_{n+l} the **filling deficit** of the $(n+l)$-group [6]. In what follows we shall agree to denote by $\mathcal{E}_{n+l}$ the filling deficit only of those $(n+l)$-groups that have already begun to be filled, i.e.

$$\mathcal{E}_{n+l} = E_{n+l}, \quad \text{if } N_{n+l} > 0. \tag{1}$$

Let us now introduce the notation $\mathcal{E}_k$ for the magnitude of the total filling deficit of all $(n+l)$-groups that have begun to be filled, i.e.

$$\mathcal{E}_k = \sum \mathcal{E}_{n+l}, \tag{2}$$

where the summation is carried out over those values of $n+l$ for which, according to (1), $N_{n+l} > 0$. We shall call the quantity $\mathcal{E}_k$ the configurational index of the electronic structure of normal atoms or, for short, simply the **configurational index**. In accordance with what has been said above, the quantity $\mathcal{E}_k$ may be defined as the **number of electrons lacking in the atom for the completion of all $(n+l)$-groups that have already begun to be filled**. It is not difficult to see that the configurational index $\mathcal{E}_k$ assumes identical values for elements that are electronic analogues (see Table 1).

Table 1

Configurational index $\mathcal{E}_k$ of the electronic structure of normal atoms

$\mathcal{E}_k$	Elements	$\mathcal{E}_k$	Elements	$\mathcal{E}_k$	Elements
0	He,Be,Mg,Ca,Sr,Ba,Ra	11	Co,Rh,Ir	22	Dy,Cf
1	H,Li,Na,K,Rb,Cs,Fr	12	Fe,Ru,Os	23	Tb,Bk
2	Ne,Ar,Kr,Xe,Rn	13	Mn,Tc,Re	24	Gd,Cm
3	F,Cl,Br,J,At	14	Cr,Mo,W	25	Eu,Am
4	O,S,Se,Te,Po	15	V,Nb,Ta	26	Sm,Pu
5	N,P,As,Sb,Bi	16	Ti,Zr,Hf	27	Pm,Np
6	C,Si,Ge,Sn,Pb	17	Sc,Y,Lu	28	Nd,U
7	B,Al,Ga,In,Tl	18	Yb (102)	29	Pr,Pa
8	Zn,Cd,Hg	19	Tm,Mv	30	Ce,Th
9	Cu,Ag,Au	20	Er,Fm	31	La,Ac
10	Ni,Pd,Pt	21	Ho,E		

According to the rule of successive filling of $(n + l)$-groups, the filling of the levels of each $(n + l)$-group is completed by the filling of the s-subgroup (with the formation of the configuration s^2), and this corresponds to the value $\mathcal{E}_k = 0$ for the ground state of the atoms He, Be, Mg, Ca, Sr, Ba, and Ra. The position of helium in this row is justified by the identical type of configuration (s^2), although the analogy of chemical properties compels one to assign helium in the periodic system to another group; this is the only case in which elements with one and the same value of the configurational index occur in two different groups of the Mendeleev system.*

In passing from each of the elements just listed to the beginning of filling, with increasing Z, of the levels of a new $(n + l)$-group in Li, B, Al, Sc, Y, La, and Ac, the value of $\mathcal{E}_k$ increases abruptly, and the increase is the greater the larger the number of n, l-subgroups entering into the composition of the corresponding new $(n + l)$-group. As the levels of each separate $(n + l)$-group are filled, the value of $\mathcal{E}_k$ decreases and again becomes equal to zero when all the levels of this $(n + l)$-group (and of all its preceding ones) prove to be filled–

* We note that in some variants of the table of elements, especially when the aim is to reflect more fully the interrelation between the distribution of atoms by elements and the position of the elements in the system, helium is placed in the second group [7] or simultaneously in the second and zero groups.

···Mathematically, the dependence of $\mathcal{E}_k$ on Z, which follows from the rule of successive filling of $(n+l)$-groups, can be described as follows. Let y be a certain parameter taking integer values that satisfy the condition

$$\frac{1}{6}y^3 + y\left(\frac{1}{2}\cos^2\frac{1}{2}\pi y - \frac{1}{6}\right) < Z \leq \frac{1}{6}(y+1)^3 + (y+1)\left(\frac{1}{2}\sin^2\frac{1}{2}\pi y - \frac{1}{6}\right); \quad (3)$$

then

$$\mathcal{E}_k = \frac{1}{6}(y+1)^3 + (y+1)\left(\frac{1}{2}\sin^2\frac{1}{2}\pi y - \frac{1}{6}\right) - Z. \quad (4)$$

The binomial

$$\frac{1}{6}(y+1)^3 + (y+1)\left(\frac{1}{2}\sin^2\frac{1}{2}\pi y - \frac{1}{6}\right)$$

entering the right-hand side of equation (4) and the right-hand side of inequality (3) is the number of nonidentical quantum states with all values of $n + l$ not exceeding $n+l = y$, while the analogous binomial in the left-hand side of inequality (3) is, correspondingly, the number of nonidentical quantum states with all values of $n + l$ smaller than y ([5,6]). It should be noted that the description of the dependence of $\mathcal{E}_k$ on Z by (4) and (3) is not a combination of successfully

chosen empirical formulas, but is a theoretical consequence of the above definition of the quantity $\mathcal{E}_k$, of the rule of successive filling of $(n+l)$-groups, and of the Pauli exclusion principle.

The values of $\mathcal{E}_k$ calculated from (4) and (3) always (i.e., for any Z within the real system of elements) coincide completely with the empirical data on the distribution of electrons in the ground state of atoms and with the definition of the quantity $\mathcal{E}_k$ as the total filling deficit of all $(n+l)$-groups whose filling has already begun. This agreement is preserved despite the existence of cases of partial rearrangement of electrons between d- and s- or between d- and f-subgroups, associated with small deviations of the actual electron distribution in some d- and f-elements from the distribution predicted by the general rule. These small deviations (such as, for example, d^5s^1 instead of d^4s^2 in chromium, $d^{10}s^1$ instead of d^9s^2 in copper, d^{10} instead of d^8s^2 in palladium, or f^7d^1 instead of f^8 in gadolinium, etc.) never go beyond the set of levels belonging to $(n+l)$-groups whose filling has already begun, and therefore do not affect the value of $\mathcal{E}_k$. Thus, the configurational index $\mathcal{E}_k$ characterizes the type of electronic configuration of atoms in a generalized form, since several such specific configurations, which cannot always be expressed identically—for example, by the number of d and s, or by the number of d and f, electrons—correspond to a definite value of $\mathcal{E}_k$, and therefore do not always correspond to the same symbol of the ground term. At the same time, there are cases in which different values of $\mathcal{E}_k$ indicate a different type of configuration, despite an apparently formal analogy. This applies, in particular, to such elements as Sc, Y, La, Lu, and Ac. In the usual method of denoting the configuration of atoms, all five of these elements may be represented by the symbol d^1s^2. However, for scandium, yttrium, and lutetium $\mathcal{E}_k = 17$, whereas for lanthanum and actinium $\mathcal{E}_k = 31$. Analysis of this case shows the connection of the quantity $\mathcal{E}_k$ with such properties of the electronic shell of atoms which, in the usual method of describing the type of configuration, are omitted from consideration.

The difference between the type of configuration of the atoms Sc, Y, and Lu, on the one hand, and La and Ac, on the other, can be explained by taking into account not only the levels filled with electrons, but also a certain set of "empty" levels. Both in La atoms and in Ac atoms in the ground state ($5d\,6s^2$ and $6d\,7s^2$), among the levels belonging to the $(n+l)$-group whose filling has already begun, there are empty f-levels ($4f$ in La and $5f$ in Ac), which also accounts here for the higher value of $\mathcal{E}_k$. In the atoms Sc, Y, and Lu, however, such, pri-

belonging to an $(n+l)$-group already begun in filling, there are no empty f-levels. This distinction is not formal, since associated with it is the possibility of transition of La and Ac atoms from the ground state d^1 to an energetically very close state f^1, whereas for Sc, Y, and Lu such a possibility is absent, and a transition from the state d^1 to the state f^1 would mean a very strong excitation of the atoms of these elements.

Consequently, a definite value of the configuration index $\mathcal{E}_k$ reflects in the present

case not only the general features of the set of different concrete configurations of one and the same type in analogous elements, but at the same time, as it were, the properties of a certain set of configurations of atoms of one and the same element in the ground state and in states close to the ground state.

In general one may say that, just as the value Z unambiguously determines the belonging of atoms to one or another element, irrespective of differences in mass number, radioactive and other nuclear properties of isotopes of one and the same element, so the value of the configuration index $\mathcal{E}_k$ unambiguously characterizes the type of electronic configuration of atoms in analogous elements, irrespective of the variety of concrete configurations, due not only to a different total number of electrons, but sometimes also to a partial regrouping of electrons between d- and s- or d- and f-subgroups, not going beyond the limits of the $(n + l)$-groups already begun in filling. The introduction of the concept of the configuration index makes it possible in all these cases to draw a clear boundary between the variety of configuration types and one or another variety of concrete configurations within one and the same type.

Received
22 III 1960

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Note: Figure translations are in progress. See original paper for figures.