JUSTIFICATION OF THE RULE FOR SUCCESSIVE FILLING OF (n + l) *GROUPS*

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Submitted to JETP editor February 16, 1961

J. Exptl. Theoret. Phys. (U.S.S.R.) **41**, 465-466 (August, 1961)

It is demonstrated that the rule previously formulated on the basis of a generalization from the empirical data, according to which the filling of the electronic levels of atoms occurs (with increasing atomic number of the element) in a sequence corresponding to increasing values of the sum of the principal and orbital quantum numbers, can be derived theoretically on the basis of the Thomas-Fermi statistical model. A comparison is made of two independently derived values of the interval within which the set of levels with a given value of the sum $n+l$ is filled.

As has been shown previously,[1] the solution of the question of the first appearance of atomic electrons with given l on the basis of statistical theory[2] leads to expressions which not only numerically, but also in their mathematical form, are similar to the analogous expressions arising from the rule of successive filling of $(n+l)$ groups.[3] In this connection the question arises whether this same rule, which was formulated as a result of the generalization of the empirical data concerning the distribution of electrons in electron shells of neutral, unexcited atoms, can also be derived theoretically on the basis of the statistical model of the atom.

Using the equation of the statistical theory[4] for the Thomas-Fermi model

$$N_k = 2\,(6Z/\pi^2)^{1/3}\,k \int [x\varphi_0(x) - (4/3\pi Z)^{2/3}k^2]^{1/2}\,\frac{dx}{x}, \qquad (1)$$

and the approximation[5]

$$\varphi_0(x) = (1 + ax)^{-2}, \qquad a = (\pi/8)^{2/3} \qquad (2)$$

for the function $\varphi_0(x)$, Tietz[6] obtained the following description of the relation between Z and the number N_k of electrons which occupy a level with a given value of the quantum number k in an atom ($k = 1/2, 3/2, 5/2\ldots$ etc.):

$$N_k = 4\,(6Z)^{1/3}\,k\,[1 - (4/3Z)^{1/3}k]. \qquad (3)$$

It is not difficult to see that, taking $k = l + 1/2$, Eq. (3) can be transformed to

$$N_l = 2\,(2l + 1)\,(6Z)^{1/3} - 2\,(2l + 1)^2. \qquad (4)$$

To the limits of the intervals of Z, within which the statistical model predicts the filling of each individual subgroup with given l, there correspond on the surface $N_l = f(Z)$ the points of intersection of the curve N_l with lines parallel to the Z axis at values of the ordinates N_l which are multiples of $2(2l + 1)$. Equation (4) enables one to find the general expression for these points of intersection,

$$N_l = 2\,(2l + 1)\,(x - 1), \text{ if } Z = \tfrac{1}{6}(2l + x)^3, \qquad (5)$$

where x is the order number of the subgroup with given l, whose filling according to this model should occur within the interval

$$\tfrac{1}{6}(2l + x)^3 \leqslant Z \leqslant \tfrac{1}{6}(2l + x + 1)^3. \qquad (6)$$

Since the order number of the subgroup with a given l is equal to $n-l$, and consequently $2l + x = n + l$, Eq. (6) is equivalent to

$$\tfrac{1}{6}(n + l)^3 \leqslant Z \leqslant \tfrac{1}{6}(n + l + 1)^3. \qquad (7)$$

From this it follows that in the statistical model of the atom, for which relations (1), (2), and (3) are valid, filling of a set of subgroups with a given value of $n+l$ should occur within the limits between $Z = (n+l)^3/6$ and $Z = (n+l+1)^3/6$. In other words, this proves that in the statistical model the $(n+l)$ group of quantum levels should be filled successively, starting from groups of levels with smaller values of the sum of principal and orbital quantum numbers to those level groups with larger values of this sum, i.e., precisely in the order which is dictated by the rule of successive filling of $(n+l)$ groups.

The limiting values of Z in (7) are very close to the empirical values, but do not coincide with them precisely; this is related to the statistical character of the theory which is the basis of this model. A more precise description of the limits of the interval within which there is a filling of all the levels with given value of $n+l$ in the electron shells of neutral, unexcited atoms, which follows from the rule of successive filling of $n+l$ groups, has the form

$$\frac{1}{6}(n+l)^3+(n+l)\left[\frac{1}{2}\cos^2\frac{1}{2}\pi(n+l)-\frac{1}{6}\right]$$
$$\leqslant Z\leqslant\frac{1}{6}(n+l+1)^3$$
$$+(n+l+1)\left[\frac{1}{2}\sin^2\frac{1}{2}\pi(n+l)-\frac{1}{6}\right]. \qquad (8)$$

The additional terms appearing in (8) and absent in (7) can here be regarded as corrections to the description (7) obtained on the basis of the statistical model, where one takes account of the integral nature of Z and the condition that Z be kept equal to the total number of electrons in a neutral atom.

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Translated by M. Hamermesh
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