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Migal L.V.
Bondarev V.G.
Bondareva T.P.

COMPUTER MODELING OF PARAMETERS OF THE ELECTRONIC SHELL OF THE ATOM

Belgorod State National Research University,
85 Pobedy St., Belgorod, 308015, Russia

e-mail: Migal@bsu.edu.ru

Abstract
In work results of computer modeling of parameters of an electron shell of atom such as orbital radiuses and constants of shielding are presented. It is shown that for atoms with completely filled electronic subshells, the dependence of the orbital radii from the nuclear charge (atomic number) can be described by application of a computing experiment, and to consider the received equations as a basis for extrapolation of data on orbital radiuses on all range of atomic numbers of elements what gives the chance of creation of the full scheme of dependence of orbital radii on charging number of the nucleus and calculation of the average size of atom.
Keywords: atom; electronic subshell; orbital radius; nuclear charge; constants of shielding.
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Мигаль Л.В.
Бондарев В.Г.
Бондарева Т.П.

КОМПЬЮТЕРНОЕ МОДЕЛИРОВАНИЕ ПАРАМЕТРОВ ЭЛЕКТРОННОЙ ОБОЛОЧКИ АТОМА

Белгородский государственный национальный исследовательский университет,
ул. Победы д. 85, г. Белгород, 308015, Россия

e-mail: Migal@bsu.edu.ru

Аннотация
В работе представлены результаты компьютерного моделирования параметров электронной оболочки атома таких как орбитальные радиусы и константы экранирования. Показано, что для атомов с полностью заполненными электронными подоболочками, зависимость орбитальных радиусов от заряда ядра (атомного номера) можно описать путем применения вычислительного эксперимента, а полученные уравнения рассматривать как основу для экстраполяции данных по орбитальным радиусам на весь диапазон атомных номеров элементов, что даёт возможность построения полной схемы зависимости орбитальных радиусов от зарядового числа ядра и расчета среднего размера атома.
Ключевые слова: атом; электронная подоболочка; орбитальный радиус; заряд ядра; константа экранирования.
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INTRODUCTION

The achievements of recent years in the field of quantum physics make it possible to determine with sufficient accuracy the parameters of the electron shells of atoms, such as the orbital radius, the size of the atom, the screening constant, as well as the energy characteristics of atoms [1-4]. The concept of

the orbital radius is the quantum-mechanical distance calculated from the nucleus to the corresponding main maximum of the radial distribution function of the electron density for the ground state of the atom [2]. Initial information about the values of atomic radii was obtained experimentally by studying the spectral lines of chemical elements [3]. So, when determining atomic radii Pauling [5] suggested that the radius of the atom depends on the most probable distance between the nucleus and the outer electrons and is inversely proportional to the effective charge of the nucleus. Later, Slater [6] constructed his system of atomic radii based on experimental data on interatomic distances with subsequent correction of the results obtained by quantum mechanical calculations. On the basis of qualitative considerations, it can be shown that the size of an atom should depend on the charge of the nucleus and the number of electron shells (the principal quantum number of the outer electrons). However, the difficulties of theoretical interpretation of the properties of many-electron atoms led to the need to replace such atoms with a hydrogen-like system consisting of a nucleus surrounded by internal electrons and having one external electron. The form of this dependence, with respect to the orbital radius r_{orb}, for multielectron atoms is reflected in the formula [7]

$$r_{orb} = K_r \frac{a_0 n^2}{Z - S}, \quad (1)$$

where K_r is the proportionality coefficient; a_0 is the radius of the hydrogen atom; n is the principal quantum number; Z is the nuclear charge; S is the constant of shielding.

The proportionality coefficient K_r is usually expressed here in the form

$$K_r = \frac{3}{2} - \frac{l(l+1)}{2n^2}, \quad (1a)$$

where l is the orbital quantum number.

In 1964, Weber and Cromer [8] calculated the orbital radii of the outer electrons of atoms from the wave functions in the Hartree-Fock-Slater self-consistent field approximation with the Dirac relativistic correction. We also note that subsequently, also with the help of quantum mechanical calculations, Boyd's orbital radii were determined [9], but their values for many elements are almost twice the data of Slater and Weber-Cromer.

Another of the parameters of the electronic structure of an atom is the constant of shielding S. The concept of constant of shielding is a generally accepted method for evaluating the electronic interaction in many-electron atoms. By definition, S is a quantity that compensates for the effect of a part of the nuclear charge on the selected electron due to the presence of previously filled electron shells, and in the study of some properties of the atom and electrons of the unfilled subshell, which can also participate in screening.

Since, as mentioned earlier, different electrons of an atom play different roles in different atomic properties, the screening constants will differ slightly depending on how they are determined. Slater [10] formulated a number of rules of thumb for computing S to give good approximations to atomic orbitals of this type. J. Slater's rules, based on a comparison of theoretical and experimental data, determine the procedure for calculating the effective charge of the nucleus of a free atom. These rules were later refined by a number of authors [11]. At the same time, the calculated results are still incomplete today, which requires a more in-depth consideration by using additional methods for processing known data. Approximate correlations between the values of the considered parameters of the atom make it possible to extrapolate their values to the entire range of atomic numbers [12]. One of these methods is statistical analysis. Applying this approach, we can carry out inter- and extrapolation, taking as a basis the known values of the orbital radii of the closed ones, i.e. completely filled electron shells of atoms.

This paper presents the results of modeling the parameters of the electron shell of free neutral atoms. Here, applying a slightly transformed formula (1) to estimate the orbital radius of a many-electron atom, based on the obtained regression equations, followed by an estimate of the extrapolated values of the orbital radii of completely filled subshells of atoms. The main goal of this work is to construct a diagram of the dependence of the orbital radius on the charge number of the nucleus, which makes it possible to trace the dynamics of the change in the size of the subshells of the atom with an increase in the charge of the nucleus.

1. MODELING

First, let us pay attention to the screening constant, which retains its value within a separate subshell. For the same reason, we will restrict ourselves to considering only closed subshells. Expression (1) includes two calculated parameters: the proportionality coefficient K_r and the screening constant. Taking as a basis the known datasets on orbital radii [8], it is possible to carry out computer simulation, using the methods of statistical analysis, the linearized equation $Z = f(a_0/r_{orb})$, in order to estimate the selected parameters for each of the subshells of the electronic structure of the atom

$$Z = K_r\, n^2\, (a_0/r_{orb}) + S, \qquad (2)$$

where K_r and S act as constants for each individual electron subshell of the atom. Note that the principal quantum number n included in the equation is also constant within an individual electron subshell.

Based on the above mentioned assumptions, let us formulate the task set. Let there be a set of data on orbital radii, including their values for closed electron subshells, limited by the possibilities of calculating numerical values for each of the subshells under consideration. It is required to determine the constants included in Eq. (2) by conducting a computational experiment to construct regression equations for electronic subshells, with subsequent refinement of specific parameter values by varying the initial data. The obtained equations, in the future, can be used to extrapolate the calculated values of the orbital radii for the entire range of possible charge numbers.

Despite the above reservations regarding the orbital radii, it was decided to proceed with the analysis, provided that the known values of the radii given in the literature have been repeatedly discussed and, therefore, their values can be considered verified information. For the statistical analysis, we used tables of the orbital radii of electrons in the atom by Weber and Cromer [8], which are currently considered the most reliable. The information in these tables is not used fully enough to determine the parameters of the electron shell for all atoms. Most often, the tables give the calculated values of the first ten values of the orbital radii, due to the emergence of significant difficulties in calculating the exact values of the orbital radii in the "heavier" atoms. At the same time, the use of these data for specific subshells makes it possible to carry out a statistical analysis based on the above regularity, which reflects the linearity of the dependence of the reciprocal of the orbital radius on the charge of the atomic nucleus. However, we note that the results of calculating the orbital radii are not entirely complete, which requires a more in-depth consideration by using additional methods for processing known data.

To solve the problem, first the parameter K_r is selected so that it, together with the constant of shielding S, would make it possible to apply statistical analysis to construct a linear regression equation $Y=Ax+B$, in which the coefficients will correspond to the values of these parameters K_r and S. Regression analysis of the initial data the values of the orbital radii were performed separately for each electron subshell of the atom.

In order to have a general judgment about the quality of the resulting model, we found the relative deviations of the values of the parameters under consideration, sharply differing in magnitude from the general population, and at the first stage excluded them from further consideration. This procedure was carried out until the regression coefficient reached a value close to one. There are cases when, when carrying out this procedure, the number of values may turn out to be on the limiting boundary – of the order of four. We considered such subshells according to a special, refined procedure, with the involvement of other methods in the analysis of the initial data.

At the next stage, we already proceeded to varying the parameters of the regression equation. This approach is necessary to possibly take into account a number of previously excluded data. As a result of varying the values of K_r and S in the obtained equation, the orbital radii of the atom were calculated, which coincide, within a certain average error, with their experimentally measured values.

At the final stage, obtained by interpolation regression equations of the relationship between the orbital radii of the atom and the parameters affecting them, their values were extrapolated to the entire range of atomic numbers in order to create a complete scheme for changing the orbital radii of the closed electron subshells of the atom from the charge number of the nucleus.

As an example, consider the relationship between the orbital radius r_{orb} and the nuclear charge of an atom Z for a closed 2*s*-subshell, built by taking into account the known values [8] and obtained using the proposed technology presented above. The results of the studies are presented in table 1.

Table 1

Comparison of data on orbital radii obtained in [8] with the results of the application of technology based on regression analysis

Таблица 1

Сравнение данных по орбитальным радиусам, полученных в работе [8], с результатами применения технологии, основанной на регрессионном анализе

Z	r_{orb} (acc. to data [8])	r_{orb} (given article)	Percentage error, %
3	1,586	1,416	10,70
4	1,04	0,991	4,71
5	0,769	0,762	0,89
6	0,62	0,619	0,14
7	0,521	0,521	0,06
8	0,45	0,450	0,05
9	0,396	0,396	0,04
10	0,354	0,354	0,09

Comparison of the results of the computational experiment and the data from [8] shows that the values of the relative error for the first four atoms have significantly higher values than for those presented in the rest of Table 1. This fact is associated with the instability of the position of the electrons of the 2*s*-subshell in the lighter atoms, with the subsequent stabilization of the distances to the nucleus in heavier atoms.

Initially, the first values of r_{orb}, having increased relative errors, were excluded from consideration; however, upon further consideration, it turned out that the value of the orbital radius for an atom with Z = 6 can also be taken into account in the study. The use of equation (2) made it possible to control the curvature of the calculated line (Fig. 1) by changing the constant of shielding S, as well as its displacement relative to the vertical axis, determined by the value of the coefficient K_r.

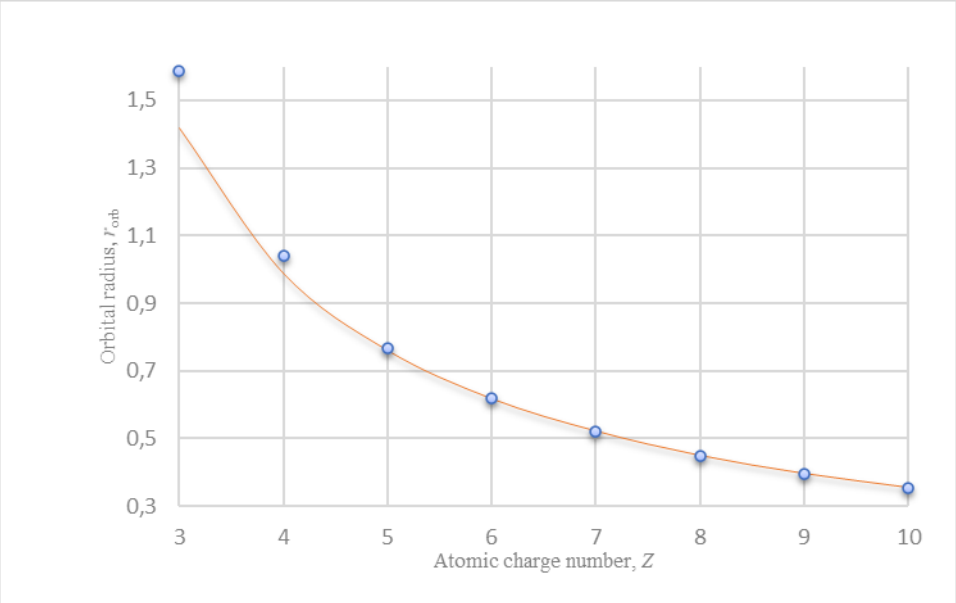

Fig. 1. The graph of the dependence of the orbital radius r_{orb} on the nuclear charge of an atom Z for a closed 2*s*-subshell: ● – according to the data of [8]; red line – according to the values obtained in this work

Рис. 1. График зависимости орбитального радиуса $r_{орб}$ от ядерного заряда атома Z для закрытой 2*s*-подоболочки: ● – по данным работы [8]; красная линия – по значениям, полученным в данной работе

Varying these constants, using the program we developed, allowed us to determine the smallest value for the average relative error, which in our case takes a value equal to 0.7. This average error corresponded to the value of the coefficient K_r =1,56 at S=0,67.

2. RESULTS AND DISCUSSION

Knowing the value of the orbital radius r_{orb} allows using equation (2) to calculate the values of the parameters for the selected subshells of many-electron atoms. The calculation results are presented in table. 2.

Table 2

Calculated values of the parameters of the electron shell of an atom

Таблица 2

Расчетные значения параметров электронной оболочки атома

Subshell No., N_p	Electronic configuration	Coefficient, K_r		Constant of shielding, S		
		Acc to eq. (1a)	In the article	Acc to Slater	In the article	Reference mean error, %
1	$1s^2$	1,5	1,00	0,3	0,178	0,24
2	$2s^2$	1,5	1,56	2,05	0,67	0,07
3	$2p^6$	1,25	1,00	4,15	3,49	0,13
4	$3s^2$	1,5	1,57	9,15	5,68	0,11
5	$3p^6$	1,39	1,41	11,25	8,40	0,05
6	$3d^{10}$	1,17	1,00	21,15	13,70	0,22
7	$4s^2$	1,5	1,50	25,65	17,65	0,04
8	$4p^6$	1,44	1,48	27,75	19,85	0,04
9	$4d^{10}$	1,31	1,21	39,15	27,60	0,18
10	$4f^{14}$	1,13	1,17	50,55	30,46	0,06
11	$5s^2$	1,5	1,38	43,65	32,11	0,06
12	$5p^6$	1,46	1,43	45,75	41,93	0,08
13	$5d^{10}$	1,38	1,17	71,15	53,95	0,08
14	$5f^{14}$	1,26	1,39	62,55	57,05	0,10
15	$6s^2$	1,5	1,13	75,65	60,67	0,04
16	$6p^6$	1,47	1,03	77,75	67,77	0,16
17	$6d^{10}$	1,42	1,00	79,15	73,99	0,03
18	$7s^2$	1,5	1,18	84,8	73,02	0,04

Note: the reference mean error is given for the constant of shielding S calculated in this work.

The analysis of the performed calculation revealed a number of important features. First, we note that the value of the coefficient K_r has a well-defined individual value for each electron subshell. For example, for kainosymmetrics, it takes on a value equal to one. An exception is the 4*f*-subshell, for which the K_r coefficient has a slightly higher value of 1.13. For the subshells following the kainosymmetrics, the value of the coefficient has the largest and almost identical values, numerically close to 1.5.

Second, when considering the screening constants, the obtained values for the 1*s*- and 2*s*-subshells, are striking, which are much smaller than those obtained when calculating according to Slater's rules [10]. If the first case can somehow be compared with the constant of shielding obtained by Pauling (S = 0.188) [5], then the authors have not found a possible explanation for the 2*s*-subshell at the moment. At the same time, all subsequent S values have a fairly satisfactory correlation with the Slater data, which is clearly seen in the graph below (Fig. 3).

Thus, the calculation of the orbital radii in many-electron atoms according to Eq. (1) for the indicated values of the K_r coefficient and the constant of shielding S gives satisfactory agreement with the available experimental data. The average error in the deviation of the calculated values of the constant of shielding here does not exceed 0.24%.

Figure 2 shows in the form of a diagram the curves of the dependence of the orbital radii r_{orb} of the closed electron subshells of the atom on the charge number of the nucleus *Z*.

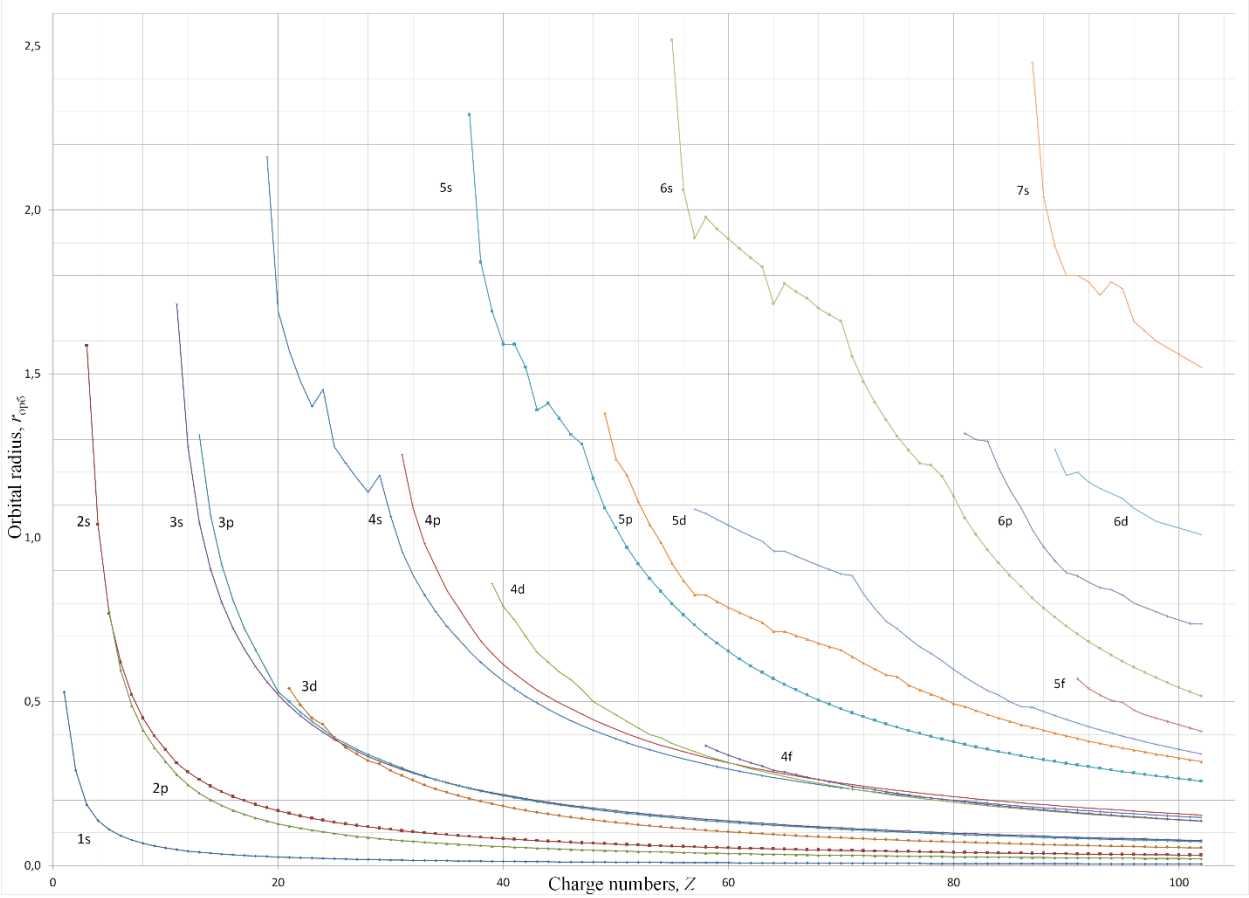

Fig. 2. Scheme of variation of the orbital radii r_{orb} (in angstroms) of closed electron subshells of an atom from the charge number of the nucleus Z

Рис. 2. Схема изменения орбитальных радиусов $r_{орб}$ (в ангстремах) закрытых электронных подоболочек атома от зарядового числа ядра *Z*

As can be seen in the presented graphs of the dependence “orbital radius – nuclear charge”, in addition to the known data on orbital radii [8], also on the continuation of the curves of dependences, the values obtained by calculating by regression equations are located. In addition, we note that here, at large values of the nuclear charge (from Z = 60 and above), the curves are clearly grouped in accordance with the shell model of the atomic structure.

Figure 3 shows the dependence of the parameter *S* on the number of the electron subshell N_p. As you can see, the values of the parameter *S* agree fairly well with the values obtained based on the Slater rules. At the same time, you can also see that the calculated values of the screening constants according to Slater's rules have values slightly higher than those obtained by statistical analysis.

Analysis of the consideration of the concept of the serial number of the subshell Np showed that this parameter, in turn, depends on the principal and orbital quantum numbers, which allows us to represent this dependence as follows

$$N_p = 1 + \frac{n(n-1)}{2} + l \qquad (3)$$

In addition, statistical processing of the data on the dependence of the constant of shielding on the serial number of the subshell allowed us to propose for this dependence the following semi empirical equation

$$S = (N_p - b)^{\pi/2}, \qquad (4)$$

where b – is a constant taking values 1/2 – for Slater data, and 2/3 – according to the data of this work. When constructing equation (3), it was also taken into account that the obtained numerical value of the power equal to 1.571 is quite close to the value 11/7, which can be compared with the value equal to π/2.

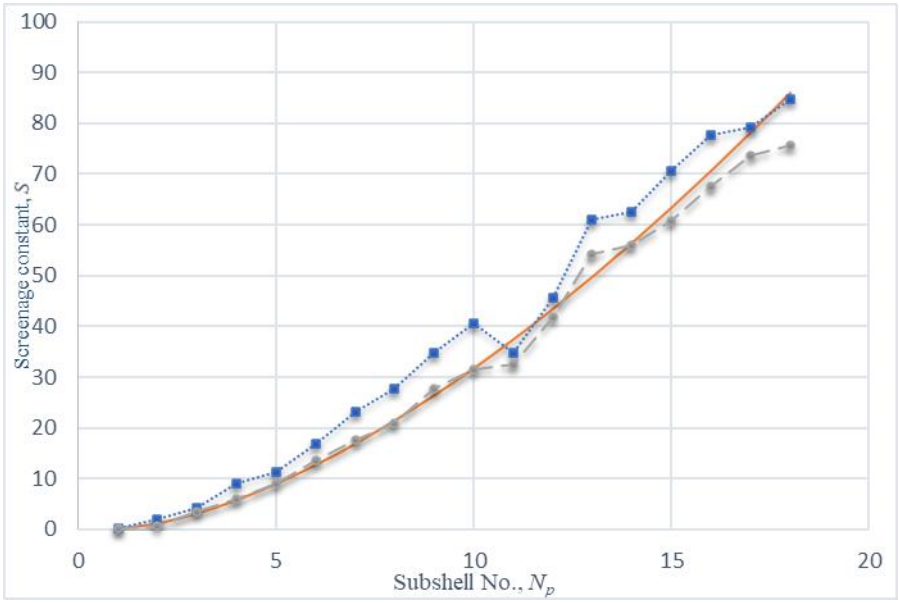

Fig. 3. Dependence of the constant of shielding S on the serial number of the subshell N_p.
● – in this article; ■ – acc. to Slater; red line – according to equation (4) at b=2/3

Рис. 3. Зависимость константы экранирования S от порядкового номера подоболочки N_p.
● – в данной работе; ■ – по Слейтеру; красная линия – по уравнению (4) при b=2/3

When considering the dependence of the coefficient K_r on the subshell sequential number N_p, shown in Fig. 4, it can be unambiguously asserted that the changes in the values of the K_r parameter are periodic in nature, repeating for atoms, starting from the filled subshells with kainosymmetric electrons. In addition, there is almost complete agreement of the calculated data with the theoretical model in the initial part of the graph. The emerging discrepancy in the regions further down the 4*f*-subshell is most likely associated with the effects of lanthanide and actinoid compression.

In the case of subdividing electronic configurations into separate subgroups, at the head of which are kainosymmetrics, then introducing a new quantum number k, for these subgroups, which we call a symmetric quantum number, the coefficient K_r can be written in the form

$$K_r = 1 + \frac{k}{k^2 + 1}. \quad (5)$$

Therefore, the symmetric quantum number k is a quantity that shows the position of the selected subshell in the row of subshells following the kainosymmetrics, and this quantum number can take the following values: 0 (for a subshell with a kainosymmetrics), 1, 2, 3, etc. – for subsequent subshells.

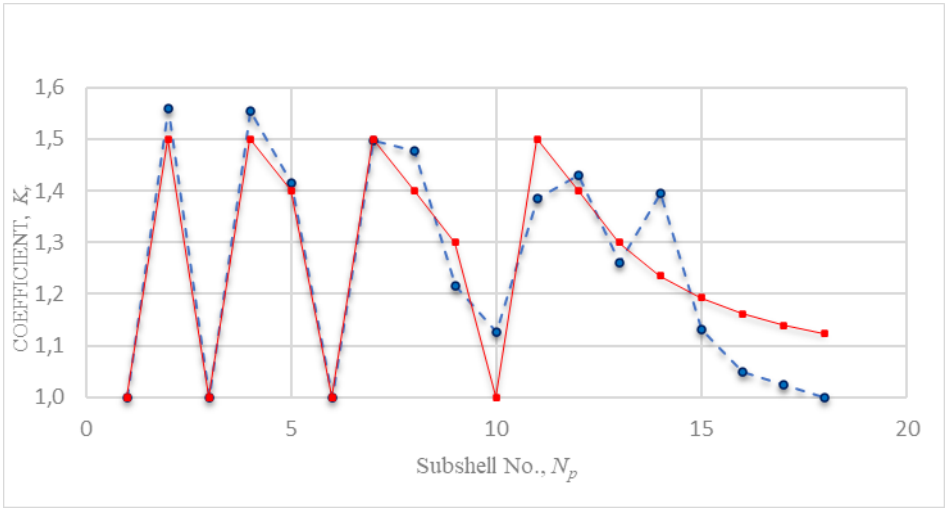

Fig. 4. Dependence of the coefficient K_r on the sequential number of the subshell N_p:
● – calculated data, ■ – according to equation (5)

Рис. 4. Зависимость коэффициента K_r от порядкового номера подоболочки N_p:
● – расчетные данные, ■ – по уравнению (5)

At the end of our study, having included expressions (4) and (5) in formula (1), we finally obtain the equation for calculating the orbital radii of closed subshells that determine the average size of an atom in the following form

$$r_{orb} = \left(1 + \frac{k}{k^2+1}\right) \frac{a_0 n^2}{Z - \left(N_p - b\right)^{\pi/2}}. \qquad (6)$$

Knowing the quantum numbers *n* and *k*, the nuclear charge Z, and the numbers of the subshells N_p under consideration (at *b*=2/3) allows one to calculate the orbital radii r_{orb} for closed subshells of a many-electron atom using Eq. (6). The calculation results are presented in the form of a graph in Figure 5.

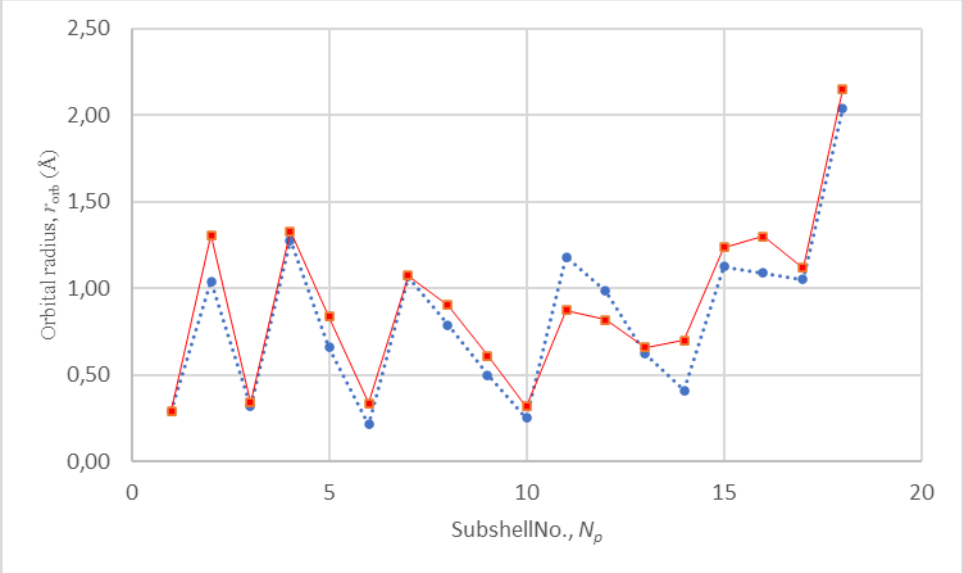

Fig. 5. Dependence of the orbital radius r_{orb} of an atom on the serial number of the closed subshell N_p:
● – data from work [8], ■ – according to the equation (6)

Рис. 5. Зависимость орбитального радиуса $r_{\text{орб}}$ атома от порядкового номера закрытой подоболочки N_p:
● – данные из работы [8], ■ – по уравнению (6)

Note that when considering the dependence of r_{orb} on the subshell sequential number N_p, it is necessary to pay special attention to *s*-subshell, the filling of which takes place in several stages. In this

case, it is desirable to take as a basis only those values of the orbital radii at which the electrons already have a fixed position, that is, they cannot shift in the region of other subshells.

CONCLUSION

As a result of the analysis of the data on the parameters of multielectron atoms, a number of regularities have been revealed that make it possible to make significant adjustments to the traditional concepts of the structure and sequence of formation of the electronic shells of atoms. The essence of the results presented in this work is as follows. By means of computer simulation, a computational experiment was carried out to form regression equations describing the dependence of the orbital radius r_{orb} on the charge number of the nucleus Z, on the basis of which a diagram of the arrangement of the curves $r_{orb}=f(Z)$ was constructed for each of the closed subshells separately. A semi empirical equation is proposed for the dependence of the constant of shielding S on the number of subshells in an atom N_p. The concept of a symmetric quantum number k is introduced, which determines the secondary periodicity of the arrangement of subshells having kainosymmetrics as the main criterion. The form of the dependence of the coefficient K_r on the symmetric quantum number k is determined. An equation is obtained to estimate the average size of an atom.

Thus, the calculation of the average size of closed subshells of atoms according to equation (6) gives satisfactory agreement with the available experimental data.

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Migal Larisa Vladimirovna, associate professor of information and robotic systems, candidate of physical and mathematical sciences, associate professor
Bondarev Vladimir Georgiyevich, teacher of the CEC of general education disciplines, Candidate of Technical Sciences, associate professor
Bondareva Tatyana Pavlovna, senior teacher of department of pediatrics

Мигаль Лариса Владимировна, доцент кафедры информационных и робототехнических систем, кандидат физико-математических наук, доцент
Бондарев Владимир Георгиевич, преподаватель ЦИК общеобразовательных дисциплин, кандидат технических наук, доцент
Бондарева Татьяна Павловна, старший преподаватель кафедры педиатрии