

ESTIMATION OF *LS*-COUPLING VALIDITY WITHIN CONFIGURATION INTERACTION APPROACH*

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Different methods of estimating the *LS*-coupling validity are compared using the results obtained within the configuration interaction approach. The techniques used earlier and proposed in the present paper were applied to evaluate the validity of *LS*-coupling for description of energy levels of the ground and excited configurations of ions of the long isoelectronic sequences of carbon, nitrogen, oxygen, fluorine, and scandium. The performed investigation revealed that the methods proposed in present paper provide the more physically-based results.

Keywords: *LS*-coupling scheme, configuration interaction

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1. Introduction

In theoretical investigations of spectral characteristics of different atoms and ions all calculations are performed using modern software. Thus, the unified standard methods and approaches are applied to all objects. The states of not highly ionized atoms are usually described by the non-relativistic radial wave functions and sequential *LS*-coupling. However, it is known that as the ionization degree grows the *LS*-coupling becomes less pertinent and the possibility to characterize the energy levels by other coupling schemes appears. At the Department of Theory of Atom in the Institute of Theoretical Physics and Astronomy of Vilnius University the works concerning various coupling schemes and the estimation of their validity have been started long ago [1, 2]. However, until the present time the performed researches were mostly based on the single-configuration approach. In paper [3] there was an attempt to apply the existing techniques for estimating the coupling scheme validity on the basis of more precise eigenfunctions obtained within the configuration interaction approach. In the present work a corrected method of the estimation of *LS*-coupling validity is proposed. Within the method it is considered that the multiterm function has been obtained taking into account the correlation effects. In

the next section the methods of calculating the multi-term functions, the ways of estimating the validity of *LS*-coupling for description of the obtained states and their averaging techniques are presented. In Section 3 the results of application of the proposed methods for describing energy levels of the ground and excited configurations of ions of the long isoelectronic sequences of carbon, nitrogen, oxygen, fluorine, and scandium are discussed. The main results are presented in Conclusion.

2. Description of the method

The non-relativistic Hamiltonian describing the main part of interactions in a many-electron atom appears as follows:

$$\begin{aligned}
 H_0 &= H_k + H_Z + H_e \\
 &\equiv -\frac{1}{2} \sum_i \nabla_i^2 - Z \sum_i \frac{1}{r_i} + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}. \quad (1)
 \end{aligned}$$

Here H_k is a kinetic energy operator, H_Z is an operator of the electrostatic interaction with nucleus, H_e is an electron electrostatic interaction operator. The matrix elements of this operator are diagonal by their total

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momentum J and by the total orbital L and spin S momenta,

$$\langle KTLSJ|H_0|K'T'L'S'J\rangle = \delta(LS, L'S') \delta(J, J') \langle KTLS||H_0||K'T'LS\rangle. \quad (2)$$

In order to take into account the relativistic corrections the Breit–Pauli approach is used, where the energy operator appears as

$$H_{BP} = H_0 + H_m + H_D + H_{so} + H_{ss} + H_{oo} + H_{ec} + H_{sc}. \quad (3)$$

Here H_m is a mass-velocity correction operator, H_D an operator of the contact (Darwin) interaction, H_{so} a complete spin–orbit interaction operator, H_{ss} a spin–spin interaction operator, H_{oo} an orbit–orbit interaction operator, H_{ec} an electron-contact interaction operator, H_{sc} a spin-contact interaction operator. The matrix elements of the H_{BP} operator depend on the total momentum J and describe the atomic energy levels. It is possible to isolate a part of the operator

$$H_{LS} = H_0 + H_m + H_D + H_{oo} + H_{ec} + H_{sc}, \quad (4)$$

the matrix elements of which possess the same symmetry properties as the operator H_0 ,

$$\langle KTLSJ|H_{LS}|K'T'L'S'J\rangle = \delta(LS, L'S') \delta(J, J') \langle KTLS||H_{LS}||K'T'LS\rangle. \quad (5)$$

While calculating the energy spectra by the configuration interaction technique within the Breit–Pauli approach the eigenfunctions of the H_{BP} operator are obtained as an expansion of the initial LS -coupling functions:

$$\langle K_0\lambda J| = \sum_{K'T'L'S'} c(K_0\lambda J, K'T'L'S'J) \langle K'T'L'S'J|, \quad (6)$$

where the expansion coefficients are normalized:

$$\sum_{K'T'L'S'} c^2(K_0\lambda LSJ, K'T'L'S'J) = 1. \quad (7)$$

Hereinafter K_0 denotes the investigated configuration, also present in the summation by K' . If the operator H_{LS} is used instead of the operator H_{BP} , the eigenfunctions of the particular intermediate terms may be obtained:

$$\langle K_0\lambda LS| = \sum_{K'T'} a(K_0\lambda LS, K'T'LS) \langle K'T'LS|, \quad (8)$$

where the expansion coefficients are normalized,

$$\sum_{K'T'} a^2(K_0\lambda LS, K'T'LS) = 1. \quad (9)$$

Usually the decision about validity of a coupling scheme is based on the weight (see for example [2, 3]) – the square of the greatest expansion coefficient of the multiterm function (6),

$$P_1(K_0\lambda J) = c_{\max}^2(K_0\lambda J, K_0T'L'S'J). \quad (10)$$

This is totally justified as long as calculations are performed within the single-configuration approximation and the configuration does not contain the terms with the same total momenta L and S . On the other hand, it is impossible to obtain modern precise results without a wide account of correlation effects. The configuration interaction approach is one of the most powerful and widely spread methods. Taking into account the configuration interaction only the interconfiguration matrix elements of the H_0 or H_{LS} operators are usually considered, which are always diagonal by the total orbital L and spin S momenta (5). Hence, this kind of account of correlation effects should not corrupt LS -coupling. However, the configuration interaction may significantly change the greatest weights of the investigated levels, especially in the lightly ionized atoms.

In the present work a new method of estimating the validity of LS -coupling is proposed for the case when calculations are performed within the configuration interaction approach. The method is based on the comparison of the eigenfunction weights obtained diagonalizing the matrices without spin–orbit and analogous terms (8) with the weights calculated taking into account all the relativistic corrections of Breit–Pauli approach. It is proposed to calculate the LS -coupling validity estimation parameter of the particular level within configuration interaction approximation as follows:

$$P_2(K_0\lambda J) = \frac{c_{\max}^2(K_0\lambda J, K_0T'LSJ)}{a^2(K_0\lambda LS, K_0T'LS)}, \quad (11)$$

i. e. it is necessary to take the ratio of the maximum weight obtained using the operator H_{BP} to the weight of the same term calculated with the operator H_{LS} . While writing down both (11) and (10), it has been assumed that K_0 and K' coincide if the coefficient is the highest. In fact this assumption does not always hold true and such situations are discussed in the following section.

Seeking to avoid the separate diagonalization of the H_{LS} operator matrix, another formula of the estimation parameter is proposed. For this purpose it is necessary to perform a summation over all configurations in the

numerator and denominator independently. Only those intermediate momenta T' that exist while forming the total orbital L and spin S momenta of the maximum coefficient must be considered. In this case, in agreement with (9), the denominator sums up to unity and one obtains the following parameter expression:

$$P_3(K_0\lambda J) = \sum_{K'T'} c^2(K_0\lambda J, K'T'LSJ). \quad (12)$$

It is necessary to introduce the generalized parameters in order to avoid the exploration of the properties of separate levels. In paper [2] it has been proposed to perform the following averaging for the levels of the same configuration with equal total momenta:

$$P_i(K_0J) = \frac{1}{m_J} \sum_{\lambda=1}^{m_J} P_i(K_0\lambda J), \quad (13)$$

here m_J denotes the number of levels with the same J . This averaging suits all three definitions of the parameter (10), (11), and (12). Correspondingly, i may signify 1, 2, and 3. In order to obtain the characteristic of the whole configuration the following expression was used in paper [2]:

$$\tilde{P}_i(K_0) = \frac{\sum_J (2J+1) P_i(K_0J)}{\sum_J (2J+1)}. \quad (14)$$

The same expression was used in work [3] for calculating the parameters $\tilde{P}_1(K_0)$. On the other hand, the averaged LS -coupling validity parameter of the whole configuration may be derived directly from the parameters of separate levels using the standard quantum-mechanical averaging:

$$P_i(K_0) = \frac{\sum_{\lambda J} (2J+1) P_i(K_0\lambda J)}{\sum_{\lambda J} (2J+1)}. \quad (15)$$

As it is seen, the expressions (14) and (15) are different. In order to pass from (14) to (15) it is necessary to include the number of the levels with the same total momenta, m_J , into the summation in the numerator and denominator. The consequences of this change of the definition are discussed in the next section.

3. Discussion of the results

The investigations of the ground and excited configurations of various isoelectronic sequences have been performed seeking to distinguish the different methods

of estimation of LS -coupling validity. The isoelectronic sequences of carbon, nitrogen, oxygen, fluorine, and scandium were explored. The ions starting from the first one up to $Z = 25, \dots, 30$ were included into calculations while investigating the isoelectronic sequences of the atoms of the second period. In the case of the scandium isoelectronic sequence with the ground configuration containing three d -electrons the calculations were performed for the nucleus charges from 24 up to 34. The neutral scandium and its first ions have not been investigated because of the well-known degeneracy of $3d$ - and $4s$ -electrons, which makes the mixing of the $4s^23d$, $4s3d^2$, and $3d^3$ configurations so extreme that the estimation of the coupling scheme validity loses its meaning.

All configuration interaction calculations have been performed on the basis of the transformed radial orbitals with the variable parameter, the same as it is done in paper [3]. The properties of these orbitals are described in work [4] and the application of the whole method is discussed in the reviews [5, 6]. Small sets of admixed configurations were used in order to shorten the calculation time. Only the configurations with the averaged weight exceeding 10^{-4} were taken into account applying the technique [7, 8]. The influence of the admixed configurations with lower weights cannot significantly change LS -coupling. The computer codes [9–11] were used besides the unpublished programs of the Department of Theory of Atom when performing these calculations.

The results of the calculations showed that the values of the parameters $P_2(K_0)$ obtained using the ratio of two weights (11) are in good coincidence with the parameters $P_3(K_0)$ achieved by the summation of the weights of the terms with the same LS momenta (12). In almost all the cases the differences between the parameters make up only several tenths or even hundredths of a percent. Only in the case of the configuration $2s2p^23s$ of the oxygen sequence, when the charge of the nucleus is higher than 25, the differences between the parameters significantly exceed 1%. Due to this reason in almost all the graphs below only the parameter $P_2(K_0)$ is presented since the curves representing $P_2(K_0)$ and $P_3(K_0)$ practically merge into one.

In the graphs showing the dependence of the parameters of the coupling scheme validity on the charge of the nucleus the following data are presented: the parameter of the whole configuration obtained from the maximum weight of the multiterm function (10) and averaged using the expressions (13) and (14) – \tilde{P}_1 (denoted in the graph by A); the parameter of the whole configuration

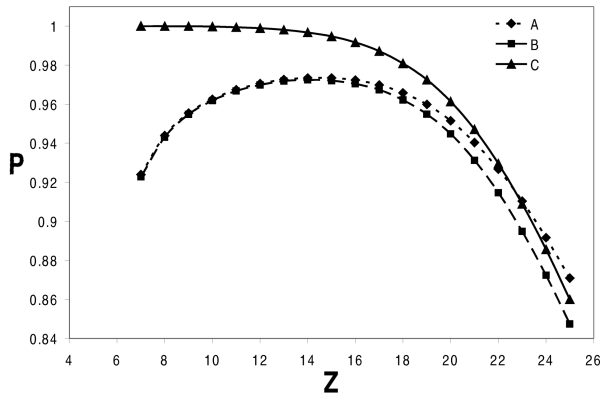


Fig. 1. The LS -coupling validity parameters for the configuration $1s^2 2s^2 2p^2$. A for $\tilde{P}_1(2p^2)$, B for $P_1(2p^2)$, C for $P_2(2p^2)$.

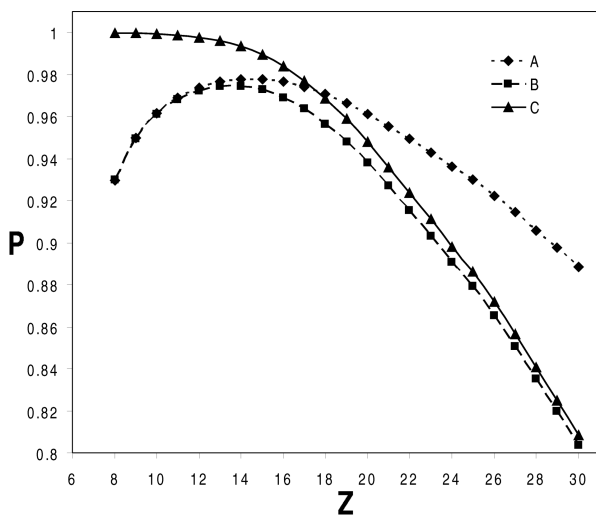


Fig. 2. The LS -coupling validity parameters for the configuration $1s^2 2s^2 2p^3$. A for $\tilde{P}_1(2p^3)$, B for $P_1(2p^3)$, C for $P_2(2p^3)$.

calculated from the maximum weight of the multiterm function (10) and averaged using the standard quantum-mechanical formula (15) – P_1 (denoted by B); the parameter of the whole configuration obtained from the ratio of the two weights (11) and averaged using the standard quantum-mechanical formula (15) – P_2 (denoted by C).

The data obtained in the case of the ground configurations of the carbon and oxygen isoelectronic sequences are presented in Figs. 1 and 2. As it is seen from the graphs, in the beginning of the isoelectronic sequences \tilde{P}_1 and P_1 parameters almost coincide and grow as the ionization degree increases. Such a behaviour contradicts the known fact that LS -coupling “becomes worse” as the ionization degree grows. At the same time the parameter P_2 calculated by the expressions proposed in the present paper behaves in agreement with the known laws. The difference between \tilde{P}_1

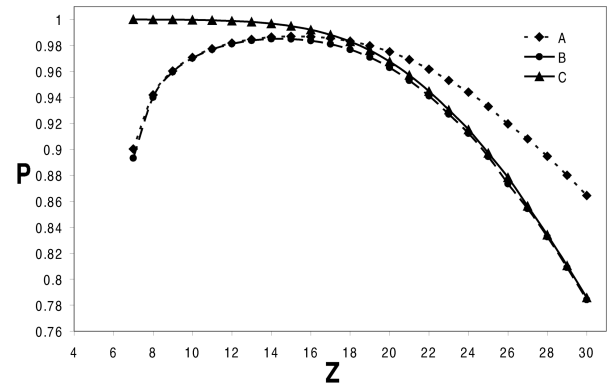


Fig. 3. The LS -coupling validity parameters for the configuration $1s^2 2s 2p^3$. A for $\tilde{P}_1(2s 2p^3)$, B for $P_1(2s 2p^3)$, C for $P_2(2s 2p^3)$.

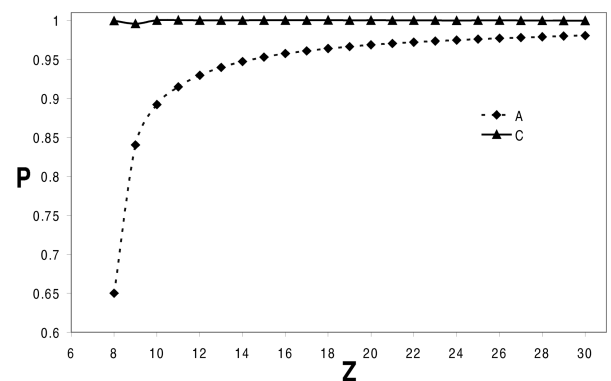


Fig. 4. The LS -coupling validity parameters for the configuration $1s^2 2p^5$. A for $\tilde{P}_1(2p^5)$, C for $P_2(2p^5)$.

and P_1 becomes more pronounced as the ionization degree grows.

The parameters of the configurations formed by excitation of the electrons from $2s$ - to $2p$ -shells are presented in the Figs. 3 and 4. In the case of the configuration $2s 2p^3$ of the carbon isoelectronic sequence (Fig. 3) the behaviour of the curves is the same as in the case of the ground configurations. The graphs of the configuration $2p^5$ of the nitrogen isoelectronic sequence (Fig. 4) are very different. In this case the values of the parameters \tilde{P}_1 and P_1 almost merge to one, and the parameter P_2 is equal to unity practically all the time. The reason for this is very simple – the investigated configuration contains only 2 levels with different total momenta J . In such situation the expression of averaging (14) and (15) provide the same results; the eigenfunctions practically do not change and LS -coupling remains pure. The growth of the parameter P_1 demonstrates only the increase of the correlation effects as the ionization degree rises. On the basis of this graph it is simple to understand, why the parameter \tilde{P}_1 starts growing in comparison with the parameter P_1 . As the ionization degree grows, the influence of the correlation effects de-

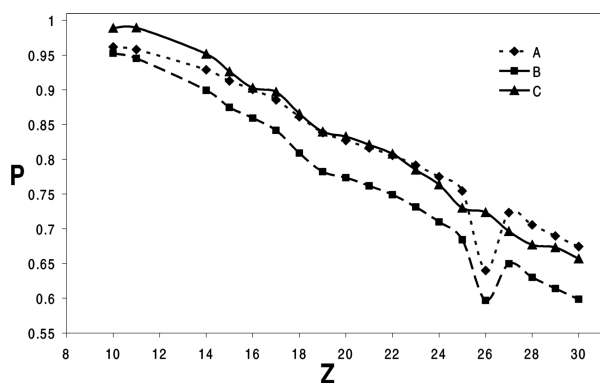


Fig. 5. The LS -coupling validity parameters for the configuration $1s^2 2s^2 2p^4 3p$. A for $\tilde{P}_1(2p^4 3p)$, B for $P_1(2p^4 3p)$, C for $P_2(2p^4 3p)$.

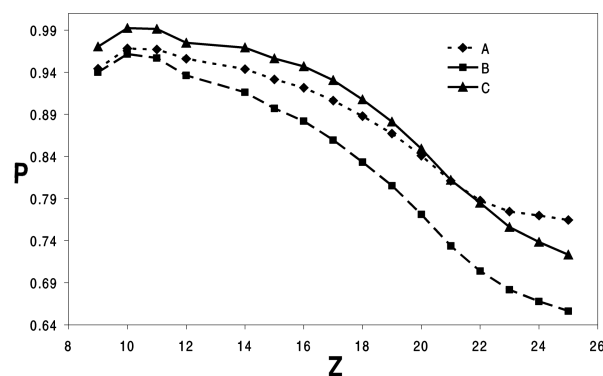


Fig. 7. The LS -coupling validity parameters for the configuration $1s^2 2s^2 2p^3 3d$. A for $\tilde{P}_1(2p^3 3d)$, B for $P_1(2p^3 3d)$, C for $P_2(2p^3 3d)$.

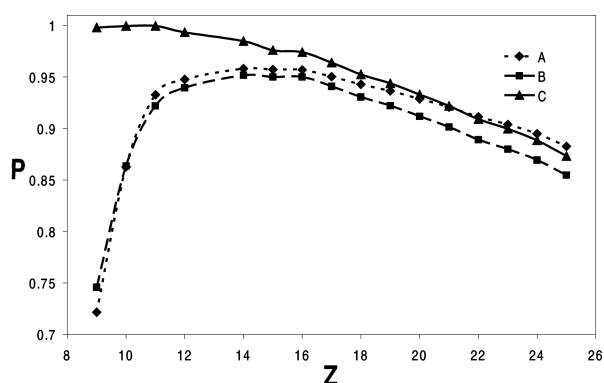


Fig. 6. The LS -coupling validity parameters for the configuration $1s^2 2s^2 2p^4 3s$. A for $\tilde{P}_1(2s 2p^4 3s)$, B for $P_1(2s 2p^4 3s)$, C for $P_2(2s 2p^4 3s)$.

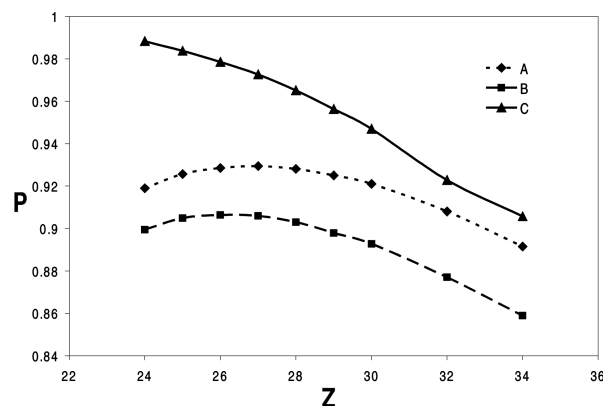


Fig. 8. The LS -coupling validity parameters for the configuration $3d^3$ of the scandium isoelectronic sequence. A for $\tilde{P}_1(3d^3)$, B for $P_1(3d^3)$, C for $P_2(3d^3)$.

increases. Consequently, the influence of the levels possessing the total momenta J , which are few within the configuration, is overestimated while averaging by expression (14). Because of this the parameter \tilde{P}_1 may exceed the parameter P_2 by its value. It is seen from the parameters of the configuration $2s^2 2p^2$ (Fig. 1) that this superiority is not very significant. Meanwhile, in the case of the configuration $2s^2 2p^3$ the parameters \tilde{P}_1 and P_1 diverge from each other very early and \tilde{P}_1 becomes notably greater than P_2 . This can be explained simply: the configuration $2s^2 2p^2$ contains five levels, 1S_0 , $^3P_{0,1,2}$, and 1D_2 , and only one of them (3P_1) can remain pure; the configuration $2s^2 2p^3$ has also five levels, $^4S_{3/2}$, $^2P_{1/2,3/2}$, and $^2D_{3/2,5/2}$, and three of those mix among themselves, but two remain pure. In the second case the averaging without taking account of the true number of the levels with the same J (14) leads to the significantly larger deviation from the reality.

The results for the configurations formed by excitation of electrons from the $2s$ - and $2p$ -shells to $3l$ -shells are presented in Figs. 5–7. The same tendencies as before are seen here. Some irregularities are observed in

all graphs. They are caused by the fact that the configurations of such type strongly interact, since they are energetically close, and, in the case of the particular charges of the nucleus, some levels suddenly come close to each other, which causes the strong mixing of the functions. These effects can increase the number of levels assigned to the particular configuration and correspondingly decrease the number of levels of another configuration. In this situation applying the expression (11) for calculations of the parameter of the separate level may become problematic. Then it is better to use the definition (12). The problems of identification of the levels are the reason for deviation of the values of parameters $P_2(K_0)$ and $P_3(K_0)$ of the configuration $2s 2p^2 3s$ mentioned in the beginning of this section.

The parameters of the scandium isoelectronic sequence are presented in Figs. 8 and 9. The whole investigated nuclear charge region belongs to the highly charged ions (the charge of the nucleus of the neutral scandium is equal to 21). As it is seen from the

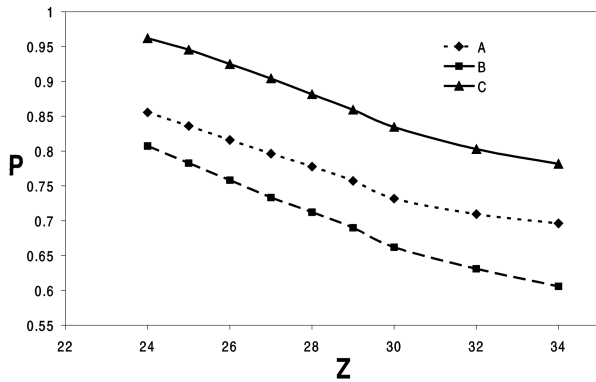


Fig. 9. The LS -coupling validity parameters for the configuration $3d^2 4d$ of the scandium isoelectronic sequence. A for $\bar{P}_1(3d^2 4d)$, B for $P_1(3d^2 4d)$, C for $P_2(3d^2 4d)$.

Fig. 8 describing the ground configuration, the transition to the investigation of d -shells does not affect the behaviour of the charts. The only difference is the stronger deviations between the parameters P_2 and P_1 . One may expect such a behaviour, since the significance of the correlation effects is much higher for $3d$ -electrons compared to $2p$ -electrons. The investigation of the excited configuration $3d^2 4d$ (Fig. 9) shows the same tendency as before. There two last values of the parameter P_2 are taken from the results calculated for the parameter P_3 because of the problems with identification of the levels. It is interesting that in this graph all the values decrease, the same as in the case of the configuration $2p^4 3p$ (Fig. 5). It may be caused by the fact that these configurations are obtained from the ground one by excitation of an electron without changing its orbital momentum. The configurations of such kind strongly interact with the ground one and consequently they are often distinguished by special properties.

The calculations have been performed for much more configurations than presented in the graphs. However, no fundamental differences from the discussed above have been noticed.

4. Conclusion

The parameters of estimating the LS -coupling validity, obtained for the single-configuration approach, are not suitable for calculations within the configuration interaction approach. In order to ensure the reliability of the averaged values of the parameters it is recommended to use the standard quantum-mechanical averaging, but not the expression (14), since the values calculated using that expression may be unfoundedly overestimated. Two ways of calculation of the parameters proposed in the present paper (the weight ratio (11) and

the summing of the weights (12)) provide almost the same results. The dependence of values of the parameters calculated by these formulas on the nuclear charge is in good agreement with the well-known behaviour of single-configuration calculations and from the physical point of view proposed expressions provide the more justified results.

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LS RYŠIO GRYNUMO ĮVERTINIMAS KONFIGŪRACIJŲ SUPERPOZICIJOS ARTINYJE

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Santrauka

Lyginami skirtingi *LS* ryšio grynumo įvertinimo metodai tikrinėms energijos operatoriaus funkcijoms, gaunamoms konfigūracijų superpozicijos artinyje. Naudoti anksčiau ir šiame darbe pristatyti metodai taikomi vertinant *LS* ryšio tinkamumą pagrindinių ir su-

žadintų konfigūracijų lygmenims aprašyti ilgose anglies, azoto, deguonies, fluoro ir skandžio izoelektroninėse sekose. Atlikti tyrimai parodė, kad šiame darbe siūlomi metodai duoda labiau pagrįstus fizikiniu požiūriu rezultatus.