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Volume 129 November 2013 ISSN 0022-4073
website: http://www.elsevier.com/locate/jqsrt
ELSEVIER

Journal of
Quantitative
Spectroscopy &
Radiative
Transfer

Editors-in-Chief: M.P. Mengüç, M.I. Mishchenko and L.S. Rothman

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Journal of Quantitative Spectroscopy & Radiative Transfer 129 (2013) 131–144

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Average characteristics of the configuration interaction in atoms and their applications

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A R T I C L E I N F O

Article history:
Received 3 May 2013
Received in revised form
3 June 2013
Accepted 6 June 2013
Available online 15 June 2013

Keywords:
Configuration interaction
Average characteristic
Wave function basis
Isoelectronic sequence
Tungsten ions
Atomic spectra

A B S T R A C T

The average characteristics of the configuration interaction (CI) present the perspective, but yet little used method for the estimation and investigation of CI effects in atoms. This work is the first attempt to give the systematic view on such characteristics. Their general, but rather simple explicit expressions are presented. The application of these characteristics for the investigation of CI effects in atoms is illustrated by calculation results for practically important cases of configurations with a symmetric exchange of symmetry, $(sd)^N$ complex and some ground configurations. It is shown that the average weight of one configuration in the expansion of the wave functions of the other configuration as well the average shift of energy level of configuration due to its interaction with the levels of distant configuration present useful characteristics for the selection of wave function basis. The average characteristics can also be applied for the estimation of CI regularities in the isoelectronic and isonuclear sequences, the determination of the types of CI.

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1. Introduction

The configuration interaction is the most widely used method for taking into account correlations between electrons in the calculations of atomic spectra. *Configuration mixing* would be more accurate term, however, *configuration interaction*, especially its CI abbreviation, is well-established historically. Correlations between electrons play a rather different role for various elements, numbers of electrons in open shells and ionization degrees of atoms. The comprehensive reviews of CI with an analysis of correlation effects for various configurations were given in widely used monographs [1,2]; some regularities of the CI method were discussed in [3–10]; many other works are indicated in references therein.

For the estimation of CI effects, the investigation of their regularities and influence on atomic spectra, the average characteristics can be used [8,11,12]. As it is known, the CI method converges rather slowly on increasing the configuration basis. Thus, the average characteristics of CI can be successfully applied for the selection of the most important configurations, admixed to the considered configuration [13]. Consequently, further development of this method is an actual task.

The aim of our work is to give the systematic view on the average characteristics of CI in atoms, to present their explicit expressions for a wide class of configurations and to demonstrate their usefulness for the atomic calculations.

The main methods, used for derivation of the average characteristics of CI and its influence on atomic spectra, are the second quantization representation [14] and group-diagrammatic method [15–17,12]. In Section 2, these methods are shortly described. Various average characteristics of CI in atoms, mainly obtained by the group-diagrammatic method, are considered and their expressions are presented in Section 3. The usefulness of these average characteristics for the investigation of CI regularities is demonstrated by their application to the configurations with a symmetric exchange of symmetry (one electron is filling the vacancy in

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0022-4073/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jqsrt.2013.06.003

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the lower shell and the other electron is excited to the empty shell without the change of the principal quantum number [18])

$$nl^{4l+1}n(l+1)^{N+1}+nl^{4l+2}n(l+1)^{N-1}n(l+2), \tag{1}$$

to the complex of $(\mathrm{sd})^N$ configurations

$$nd^N+nd^{N-1}(n+1)\mathrm{s}+nd^{N-2}(n+1)\mathrm{s}^2, \tag{2}$$

as well as to some configurations with one open shell. The CI with a symmetric exchange of symmetry is considered in the ions of tungsten, which spectra are important for the modeling of tokamak plasma [19]. The interaction within $(\mathrm{sd})^N$ complex is investigated for the neutral atoms and first ions, where the configurations of this complex strongly overlap and interchange their positions [1].

The results of calculations presented in this work were obtained using the original computer code for the calculation of the average characteristics of atomic spectra [20] with the quasirelativistic Hartree–Fock–Cowan wave functions [1].

2. Methods of derivation of expressions for the average characteristics

The summation over spin angular parts of matrix elements can be performed under usual assumption that the single set of radial orbitals is used for all terms of configuration. However, the direct summation of matrix elements is hardly possible because their expressions contain, except for the simple configurations, the fractional parentage coefficients, having non-standard form.

The derivation of matrix elements sums over many-electron quantum numbers is possible in the second quantization representation. Then the antisymmetrization property is transferred from the wave functions to the electron creation and annihilation operators obeying the anticommutation rules. The Hamiltonian and other operators are expressed in terms of these one-electron operators. For example, the operator of the Coulomb interaction between electrons is represented as follows:

$$H^e=\frac{1}{2}\sum_{\nu\xi\varsigma\eta}a^+_\nu a^+_\xi\langle\nu\xi|h^e|\varsigma\eta\rangle a_\eta a_\varsigma, \tag{3}$$

where the operator a^+_ν creates an electron in the single-electron state $\nu\equiv nlm\mu$ and a_ν annihilates an electron in the same state. The quantity in the brackets is the matrix element of two-electron Coulomb operator h^e. This element has the meaning of the amplitude of transition from one atomic state to the other state under the action of operator h^e.

The sum of the product of two interconfiguration matrix elements of operator H^e over the states of one configuration can be represented:

$$\begin{aligned}&\sum_{\Gamma'}\langle K\Gamma|H^e|K'\Gamma'\rangle\langle K'\Gamma'|H^e|K\Gamma\rangle\\&\quad\to\frac{1}{4}\sum_{\Gamma'}\langle K\Gamma|\sum_{\nu\xi\varsigma\eta}a^+_\nu a^+_\xi\langle\nu\xi|h^e|\varsigma\eta\rangle a_\eta a_\varsigma|K'\Gamma'\rangle\\&\quad\times\langle K'\Gamma'|\sum_{\nu'\xi'\varsigma'\eta'}a^+_{\nu'}a^+_{\xi'}\langle\nu'\xi'|h^e|\varsigma'\eta'\rangle a_{\eta'}a_{\varsigma'}|K\Gamma\rangle,\end{aligned} \tag{4}$$

where Γ and Γ' denote many-electron states. The averaging should be performed over all many-electron quantum numbers, including the projections of total momenta.

In Eq. (4), the sums over single-electron states are restricted to those excitations that connect the considered configurations K and K'. Thus, the expression $\sum_{\Gamma'}|K'\Gamma'\rangle\langle K'\Gamma'|$ can be removed using the closure theorem, even though the states $|K'\Gamma'\rangle$ do not form a complete set [14]. This occurs because the missing states cannot be connected to the states $|K\Gamma\rangle$ and hence give zero matrix elements. Then applying the anticommutation rules for the creation and annihilation operators all $\mathbf{a}^+$ are carried out to the left and operators $\mathbf{a}$ on the right in order to reduce the total operator into the normal form. The two-electron matrix elements are also transformed using the formulas for sums of Wigner coefficients and $3nj$ coefficients. In such a way the sum in Eq. (4) can be represented as a matrix element of some effective operator H^{eff}. Of course, the summation over Γ' can be performed only by the introduction of the operator more complex than the Hamiltonian H. The effective operator consists of several parts acting on different numbers of electrons (they appear as a result of the application of anticommutation rules). The most complex part is the four-electron operator. The matrix element of H^{eff} is expressed using the mathematical apparatus of irreducible tensors [1,21].

The second quantization representation was also applied to derive some expressions for the average characteristics of energy level spectra and transition arrays as well as for their changes due to CI [11,22,23]. Using this representation, the dependence of average quantities on the numbers of electrons in the shells was determined, and then the coefficients in the polynomials at the powers of N_i were obtained from the explicit expressions for some simple configurations. However, such a method becomes insufficient to find more complex formulae.

In [15,16], the general method for the evaluation of the operator averages for the fermion systems was proposed. It was applied and elaborated for the summation of atomic quantities over all many-electron quantum numbers [12]; its outline is presented in [17]. This method uses the properties of irreducible representations of higher continuous groups: special orthogonal group SO_{8l+5} and its unitary subgroup U_{4l+2}. These groups are inconvenient for the classification of states due to a large number of repeating terms, but are useful for finding expressions for the sums of atomic quantities over all many-electron quantum numbers, whereas each irreducible representation of the unitary group appears once and only once in a given irreducible representation of the special orthogonal group.

The sum of matrix elements is expressed in terms of an unitary scalar coefficient, having a simple algebraic expression, and a vacuum expectation. Separate terms of the sum can be represented by special diagrams. The contribution of every diagram consists of the N factor including all dependence on the electron numbers in shells and the so-called minimal sum of one- or two-electron matrix elements of operators corresponding to the considered quantities. This method is implemented in the special heuristic computer code [20].

In this work we will restrict our consideration to the non-relativistic or quasirelativistic approximation. It preserves the

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LS coupling scheme within shells which usually is more realistic than *jj* coupling scheme used in the relativistic approximation. The relativistic effects can be taken into account rather accurately, even for heavy atoms, by the calculation of quasirelativistic radial orbitals [1,24].

3. Main characteristics of CI

3.1. The sums of squares of interconfiguration matrix elements over the states of one configuration

The main quantity of the CI is the interconfiguration matrix element (ICME). It can obtain both positive and negative values, thus, in the calculation of average CI characteristics it is necessary to take its square. The cumulative influence of all states γ' of configuration K' on the state γ of configuration K is described by the sum of the ICME squares over γ'. Using the second quantization representation this sum can be presented in the form of the matrix element of an effective operator H^{eff}:

$$\sum_{\gamma'}\langle K\gamma|H|K'\gamma'\rangle^2=\langle K\gamma|H^{eff}|K\gamma\rangle. \tag*{5)}$$

Here and further on many-electron states are denoted by the Greek letters.

In the case of configuration K, containing only one open shell, the explicit expression of matrix element of H^{eff} was obtained by direct summation of ICME in [7]. The general expressions of effective operator for all types of CI were presented in [12]. The matrix elements of H^{eff} for some particular configurations were given in [25,26].

The effective operator, corresponding to the Coulomb interaction between electrons, has four-electron, three-electron and two-electron parts; they all contain summations over ranks. At all ranks, equal to zero, the operator becomes a purely scalar operator and its matrix element does not depend on many-electron quantum numbers. Due to this peculiarity the sum (5) for some pairs of configurations becomes an invariant not-dependent on the state γ. Such cases can be determined without consideration of the particular form of H^{eff} only on the ground of the following reasoning.

The effective operator, like the Hamiltonian, has the total zero rank. In the space of a closed shell only part of operator with all zero ranks gives contribution to the matrix element. Thus, the element of H^{eff} becomes term-independent, when the electrons are excited only from the closed shells of configuration K (it can contain also passive open shells do not involved in the excitations). The invariance property can be extended to configuration K containing also one active open shell, if H^{eff} acts only on one electron of this shell. Then in the matrix element of effective operator all ranks become zero in the space of the other closed shell (or other such shells). Consequently, the sum (5) does not depend on many-electron quantum numbers for the pairs of configurations, which fulfill the following conditions: (i) configurations K and K' are related by two-electron excitations; (ii) one excitation is from the open shell of K or to this shell; it can also be open in K' configuration; (iii) the other active shells of configuration K are closed. Two simple cases, corresponding to the excitation from the closed shell, should be added too. Both configurations K and K' can contain any number of passive open shells.

These conditions are fulfilled for the following K–K' pairs (configuration K is indicated the first, the K and K' cannot be interchanged):

$$\begin{aligned}
&K_0l_1^{4l_1+2}l_2^{N_2}-K_0l_1^{4l_1}l_2^{N_2+1}l_3\\
&K_0l_1^{4l_1+2}l_2^{N_2}-K_0l_1^{4l_1+1}l_2^{N_2-1}l_3^2\\
&K_0l_1^{4l_1+2}l_2^{N_2}-K_0l_1^{4l_1+1}l_2^{N_2-1}l_3l_4\\
&K_0l_1^{4l_1+2}l_2^{4l_2+2}l_3^{N_3}-K_0l_1^{4l_1+1}l_2^{4l_2+1}l_3^{N_3+1}l_4\\
&K_0l_1^{4l_1+2}-K_0l_1^{4l_1}l_2l_3\\
&K_0l_1^{4l_1+2}-K_0l_1^{4l_1}l_2^2.
\end{aligned} \tag{6}$$

Here K_0 means closed or open passive shells. In this and most of the subsequent formulae, l_i stands instead of n_il_i in the notations of shells, if there is no necessity to indicate directly a principal quantum number.

In all cases (6) the matrix element of H^{eff} equals the constant C, which value can be determined on performing in Eq. (5) the additional summation over γ:

$$\sum_{\gamma\gamma'}\langle K\gamma|H|K'\gamma'\rangle^2=Cg(K), \tag{7}$$

where $g(K)$ is the statistical weight of configuration K. Thus,

$$\sum_{\gamma'}\langle K\gamma|H|K'\gamma'\rangle^2=C=\frac{\sum_{\gamma\gamma'}\langle K\gamma|H|K'\gamma'\rangle^2}{g(K)} \tag{8}$$

The explicit formulae for the total sum of ICME squares will be given in the next subsection of this paper.

Eq. (8) is valid for the pairs of configurations (6), corresponding to the excitation not only to the discrete state, but also to the continuum one. Transposition of open and closed shells in the 1st and 4th configurations of the set (6) gives the following pairs [27]:

$$\begin{aligned}
&K_0l_1^{N_1}l_2^{4l_2+2}-K_0l_1^{N_1+1}l_2^{4l_2}\varepsilon l\\
&K_0l_1^{N_1}l_2^{4l_2+2}l_3^{4l_3+2}-K_0l_1^{N_1+1}l_2^{4l_2+1}l_3^{4l_3+1}\varepsilon l,
\end{aligned} \tag{9}$$

where ε is the energy of free electron. Then Eq. (8) can be applied for the derivation of the expression for the partial Auger width:

$$\Gamma_A(K\gamma J-K'\varepsilon l)=\sum_{\gamma'J'j}\langle K\gamma J|H|K'\gamma'J'\varepsilon ljJ\rangle^2. \tag{10}$$

Here l and j are the quantum numbers of Auger electron; the total quantum number J is excluded from γ. The wave function of Auger electron is normalized into the unit flux of electrons, and the atomic units are used. The term-independence of some class of partial Auger widths was established and their expressions were given in [27,28].

It is possible also to determine the pairs of configurations when the corresponding effective operator contains at most two-electron part. It takes place for configurations K, containing one open active shell, when two electrons from this shell are excited in configuration K'.

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3.2. Sums of the squares of ICME over states of both configurations

The expressions for the sums over all many-electron quantum numbers are easily derived employing the group-diagrammatic method. In the nonrelativistic approximation the contribution to ICME for the two-electron excitation is given only by the operator H^e of the Coulomb interaction between electrons. When two electrons are excited from one shell to another shell, the following expression is obtained [12]:

$$\sum_{\gamma\gamma'}\langle K_0 l_1^{N_1} l_2^{N_2}\gamma|H^e|K_0 l_1^{N_1-2} l_2^{N_2+2}\gamma'\rangle^2 = g(K_0)\binom{4l_1}{N_1-2}\binom{4l_2}{N_2}M(l_1l_1,l_2l_2), \tag{11}$$

where the quantity in the brackets on the right-hand side of the equation is the binomial coefficient and $M(l_1l_1,l_2l_2)$ is the minimal sum of two-electron matrix elements. Its general expression is the following:

$$\begin{aligned} M(l_1l_2,l_3l_4) &= \sum_{LS}[L,S]\langle l_1l_2LS|h^e|l_3l_4LS\rangle^2 \\ &= 16N_{l_1,l_2}^2N_{l_3,l_4}^2\sum_{kk'}\left\{\frac{\delta(k,k')}{2k+1}\left[\mathfrak{R}^k(l_1l_2,l_3l_4)^2+\mathfrak{R}^k(l_1l_2,l_4l_3)^2\right]\right. \\ &\quad \left. -(-1)^{k+k'}\begin{Bmatrix} l_1 & l_3 & k \\ l_2 & l_4 & k' \end{Bmatrix}\mathfrak{R}^k(l_1l_2,l_3l_4)\mathfrak{R}^{k'}(l_1l_2,l_4l_3)\right\}. \end{aligned} \tag{12}$$

Here $[x, y,\ldots]\equiv(2x+1)(2y+1)\ldots$, N_{l_1,l_2} is the normalization constant:

$$N_{l_1,l_2}\equiv N_{n_1l_1,n_2l_2} = \begin{cases} 1/2 \ \text{for the equivalent electrons}\ (n_1=n_2,\ \ l_1=l_2); \\ 1/\sqrt{2}\ \text{for the nonequivalent electrons;} \end{cases} \tag{13}$$

$\mathfrak{R}^k$ is the radial integral R^k of the Coulomb interaction multiplied by the one-electron reduced matrix elements of spherical harmonic $C^{(k)}$:

$$\begin{aligned} \mathfrak{R}^k(l_1l_2,l_3l_4) &\equiv \mathfrak{R}^k(n_1l_1n_2l_2,n_3l_3n_4l_4) \\ &= R^k(n_1l_1n_2l_2,n_3l_3n_4l_4)\langle l_1||C^{(k)}||l_3\rangle\langle l_2||C^{(k)}||l_4\rangle. \end{aligned} \tag{14}$$

When excitations involve three or four shells, the sum gets:

$$\sum_{\gamma\gamma'}\langle K_0 l_1^{N_1} l_2^{N_2} l_3^{N_3}\gamma|H^e|K_0 l_1^{N_1-2} l_2^{N_2+1} l_3^{N_3+1}\gamma\rangle^2 = g(K_0)\binom{4l_1}{N_1-2}\binom{4l_2+1}{N_2}\binom{4l_3+1}{N_3}M(l_1l_1,l_2l_3), \tag{15}$$

$$\begin{aligned} &\sum_{\gamma\gamma'}\langle K_0 l_1^{N_1} l_2^{N_2} l_3^{N_3} l_4^{N_4}\gamma|H^e|K_0 l_1^{N_1-1} l_2^{N_2+1} l_3^{N_3+1} l_4^{N_4-1}\gamma\rangle^2 \\ &= g(K_0)\binom{4l_1+1}{N_1-1}\binom{4l_2+1}{N_2}\binom{4l_3+1}{N_3}\binom{4l_4+1}{N_4-1} \\ &\quad \times M(l_1l_4,l_2l_3). \end{aligned} \tag{16}$$

Only the Coulomb interaction may be taken into account at single-electron excitation with a change of orbital quantum number:

$$\begin{aligned} &\sum_{\gamma\gamma'}\langle K_0 l_1^{N_1} l_2^{N_2}\gamma|H^e|K_0 l_1^{N_1-1} l_2^{N_2+1}\gamma'\rangle^2 \\ &= g(K_0)\left[\binom{4l_1-1}{N_1-2}\binom{4l_2+1}{N_2}M(l_1l_1,l_1l_2)\right. \\ &\quad \left.+\binom{4l_1+1}{N_1-1}\binom{4l_2-1}{N_2-1}M(l_1l_2,l_2l_2)\right] \\ &\quad +\sum_{i\subset K_0}\frac{g(K_0)}{g(l_i^{N_i})}\binom{4l_i}{N_i-1}\binom{4l_1+1}{N_1-1}\binom{4l_2+1}{N_2} \\ &\quad \times M(l_il_1,l_il_2), \quad l_1\neq l_2. \end{aligned} \tag{17}$$

However, the summation over all shells of K_0 appears.

When interacting configurations differ by a state of one electron with the same orbital quantum number, additionally the one-electron operators of potential and kinetic energy as well as the spin-orbit operator give contributions to the double sum. The expressions for these additional parts are given in [12].

The separate cases of the formula (15) and (16) present the total Auger transition rates at the decay of states with one inner vacancy:

$$\sum_{\gamma\gamma'}\langle K_0 l_1^{4l_1+1} l_2^{N_2}\gamma|H^e|K_0 l_1^{4l_1+2} l_2^{N_2-2}\gamma\varepsilon l\gamma'\rangle^2 = g(K_0)\binom{4l_2}{N_2-2}M(l_2l_2,l_1\varepsilon l), \tag{18}$$

$$\sum_{\gamma\gamma'}\langle K_0 l_1^{4l_1+1} l_2^{N_2} l_3^{N_3}\gamma|H^e|K_0 l_1^{4l_1+2} l_2^{N_2-1} l_3^{N_3-1}\gamma\varepsilon l\gamma'\rangle^2 = g(K_0)\binom{4l_2+1}{N_2-1}\binom{4l_3+1}{N_3-1}M(l_2l_3,l_1\varepsilon l). \tag{19}$$

These formulae can be used for the extrapolation of Auger transition rates for the other configurations of the same element under the assumption that the values of radial integrals and the minimal sum approximately do not depend on the configuration.

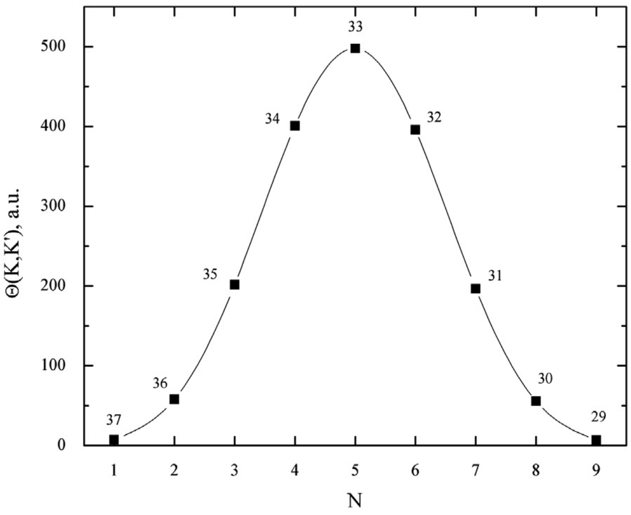

Fig. 1. Sum of the squares of interconfiguration matrix elements $\Theta(K,K')\equiv\sum\langle K\gamma|H|K'\gamma'\rangle^2$ between configurations $4p^54d^{N+1}$ and $4p^64d^{N-1}4f$ in the W^{q+} isonuclear sequence. The value of ionization degree q=29–37 is indicated near the curve.

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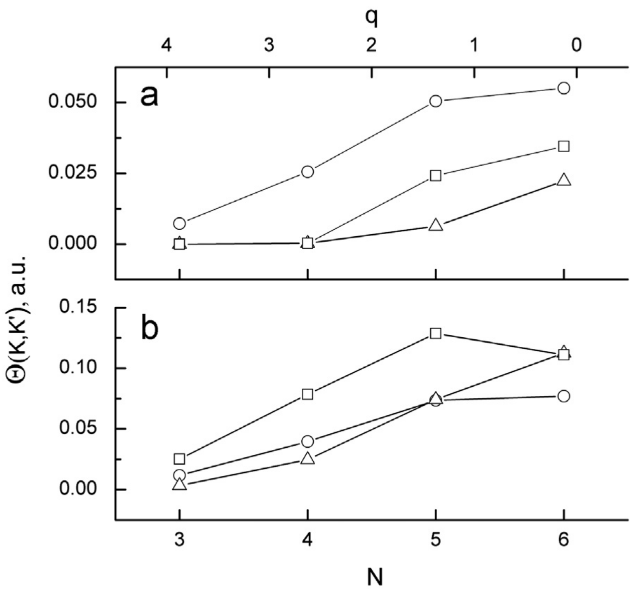

Fig. 2. Sum of the squares of interconfiguration matrix elements $\Theta(K,K')\equiv\sum_{\gamma\gamma'}\langle K\gamma|H|K'\gamma'\rangle^2$ between configurations nd^N and $nd^{N-2}(n+1)s^2$ (○); nd^N and $nd^{N-1}(n+1)s$ (□); $nd^{N-1}(n+1)s$ and $nd^{N-2}(n+1)s^2$ (△) in the isonuclear sequences at $n=3$ for Cr^{q+} (a) and $n=4$ for Mo^{q+} (b), $q=0$–4.

The sums of the squares of ICME for some strongly interacting configurations are presented in Figs. 1 and 2. The value of such a sum depends on the number of interacting states, which is expressed in terms of the binomial coefficients. At the two-electron excitation with a symmetric exchange of symmetry (1), the variation of sum with filling the same open shell is determined by one binomial coefficient $\binom{4l}{N-1}$, thus, the considered quantity obtains its maximum for the half-filled shell $N=2l+1$ (Fig. 1). For the single-electron excitation with a change of orbital quantum number (2) the variation of such a sum is less smooth and its maximum tends to be shifted to a larger number of electrons (Fig. 2) due to the additional terms having more complex dependence on a number of electrons. The value of sum also strongly depends on the overlap of radial orbitals of active electrons and consequently indicates the strength of CI. Especially large value of this sum for configurations (1) at $l=2$ (Fig. 1) indicates that this correlation effect is one of the strongest in atoms. On the other hand, the CI in the $(nd(n+1)s)^N$ complex increases with n due to the contraction of radial orbitals in the homologous sequence.

3.3. *Configuration interaction zone and two types of CI.*

Usually various states of considered configuration interact differently with the states of other configuration. Such a peculiarity of configuration K interaction with configuration K' can be characterized by the average energy of configuration K obtained using a weight, equal to the square of ICME:

$$E^{av}_{K'}(K)=\frac{\sum\limits_{\gamma\gamma'}\langle K\gamma|H|K\gamma\rangle\langle K\gamma|H|K'\gamma'\rangle^2}{\sum\limits_{\gamma\gamma'}\langle K\gamma|H|K'\gamma'\rangle^2}. \tag{20}$$

in this equation the summation over γ' is acting only on the ICME. The application of Eq. (8) shows that there exists a class of configurations K', which interaction with K corresponds to the simple equality:

$$\frac{\sum\limits_{\gamma\gamma'}\langle K\gamma|H|K\gamma\rangle\langle K\gamma|H|K'\gamma'\rangle^2}{\sum\limits_{\gamma\gamma'}\langle K\gamma|H|K'\gamma'\rangle^2}=\frac{\sum_{\gamma}\langle K\gamma|H|K\gamma\rangle}{g(K)} \tag{21}$$

or

$$E^{av}_{K'}(K)=E_{av}(K), \tag{22}$$

where $E_{av}(K)$ is the average energy of configuration K. The Eq. (22) means that every state of configuration K interacts equally with the whole array of states of configuration K'. Such pairs are indicated in the set (6). The interchange of the role of two configurations in the pair shows that the equality

$$E^{av}_{K}(K')=E_{av}(K') \tag{23}$$

is fulfilled for the following pairs of K–K' (K' is the excited, located higher with respect to K configuration):

$$K_0l_1^{N_1}l_2^{4l_2}l_3\text{–}K_0l_1^{N_1-1}l_2^{4l_2+2}$$
$$K_0l_1^{N_1}l_2^{4l_2+1}l_3^{4l_3+1}l_4\text{–}K_0l_1^{N_1-1}l_2^{4l_2+2}l_3^{4l_3+2}. \tag{24}$$

It follows from the comparison of (6) and (24) sets that both conditions (22) and (23) cannot be fulfilled simultaneously. Surely, more often various states of configuration play different role in the CI, and the shift

$$\Delta E^{av}_{K'}(K)=E^{av}_{K'}(K)-E_{av}(K) \tag{25}$$

can obtain rather large values, even constituting an essential part of an energy spectrum interval. Especially it is typical of the configurations with a symmetric exchange of symmetry which belong to the same complex of configurations. Some regularities of the interaction of such configurations will be considered in the next section.

For the description of the influence of configuration K' on the configuration K, the concept of interaction zone can be introduced, it means the main part of energy level spectrum of configuration K taking part in the interaction with configuration K'. Such an effective zone is determined by its statistical moments. The quantity $E^{av}_{K'}(K)$ presents its first moment – the average energy of the zone. Its second moment is the variance, which is defined with respect to the average energy:

$$\sigma^2_{K'}(K)=\frac{\sum_{\gamma\gamma'}\left[\langle K\gamma|H|K\gamma\rangle-E^{av}_{K'}(K)\right]^2\langle K\gamma|H|K'\gamma'\rangle^2}{\sum_{\gamma\gamma'}\langle K\gamma|H|K'\gamma'\rangle^2}. \tag{26}$$

This quantity contains the information on the width of interaction zone. It can be estimated from the approximate formula:

$$\Delta E_{K'}(K)=2\sqrt{2\ln 2\;\sigma^2_{K'}(K)}. \tag{27}$$

It should be noted, that this equation can become very approximate at small number of levels.

Moreover, the higher moments of zone, containing the higher degrees of the difference between the matrix element and the average energy, can be introduced. The

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explicit formula for $\sigma^2_{K'}(K)$ is obtained employing the group-diagrammatic method. The expression of $\sigma^2_{K'}(K)$ is more complex in comparison with the average energy, thus, it was derived and calculated using the special computer code [20]. This method enables one to obtain the formulae for the higher moments too.

The expressions for the average energy of zone at the two-electron excitation and at the single-electron excitation with a change of orbital quantum number are given in the Appendix. The more complex formula for the Brillouin excitation was obtained in [13].

In the case of the first configuration K for the pairs (6) as well as for the second configurations K' for the pairs (24) the CI zone coincides with the energy level spectrum of configuration. This follows from the fact (also directly obtained from Eq. (8)), that not only average energies of configuration and zone, but also all their higher statistical moments coincide. For example, such a zone corresponds to the interaction of configuration p^6d^N with configurations $p^5d^{N-1}pd$, $p^4d^{N+1}d$ and $p^4d^Np^2$. However, for the configurations of the other type the intervals of CI zone and energy level spectrum can differ significantly (Fig. 3). Consequently, the concept of zone can be useful for investigation of the regularities of CI interaction in atoms.

3.4. Average distance between two interacting configurations

The average energy distance between configurations can be approximately estimated by the difference of their average energies. More exact expression is obtained taking into account the energy differences only between interacting states as well as the magnitudes of relating them ICME [12]:

$$E_{av}(K,K') = \frac{\sum_{\gamma\,\gamma'}[\langle K\gamma|H|K\gamma\rangle - \langle K'\gamma'|H|K'\gamma'\rangle]\,\langle K\gamma|H|K'\gamma'\rangle^2}{\sum_{\gamma\,\gamma'}\langle K\gamma|H|K'\gamma'\rangle^2}. \tag{28}$$

It is convenient to define $E_{av}(K,K')$ as a positive quantity, then K means higher and K' lower configuration. According to Eq. (20), the average energy distance is expressed in terms of the average energies of CI zones already considered in the previous section:

$$E_{av}(K,K') = E^{av}_{K'}(K) - E^{av}_{K}(K'). \tag{29}$$

This characteristic presents well-defined average energy distance even between overlapping and intersecting configurations. It can be applied for the configurations belonging to $(nd(n+1)s)^N$ complex. At $n=3$, the energy levels of all three configurations strongly overlap, but $E_{av}(K,K')$ indicates, that in neutral atoms the average distance between interacting levels is smallest for the $3d^{N-2}4s^2$ and $3d^{N-1}\,4s$ configurations and thus their interaction is strongest (Fig. 4a). The intersection of $3d^N$ and $3d^{N-2}\,4s^2$ configurations takes place on going from neutral atoms to first ions and of $3d^N$ and $3d^{N-1}4s$ configurations on increasing the ionization degree q from 1 to 2. The corresponding data for similar configurations with $n=4$ and 5 also enables one to analyze their interaction in the isonuclear sequence (Figs. 4b and c). At $n=4$, the strongest

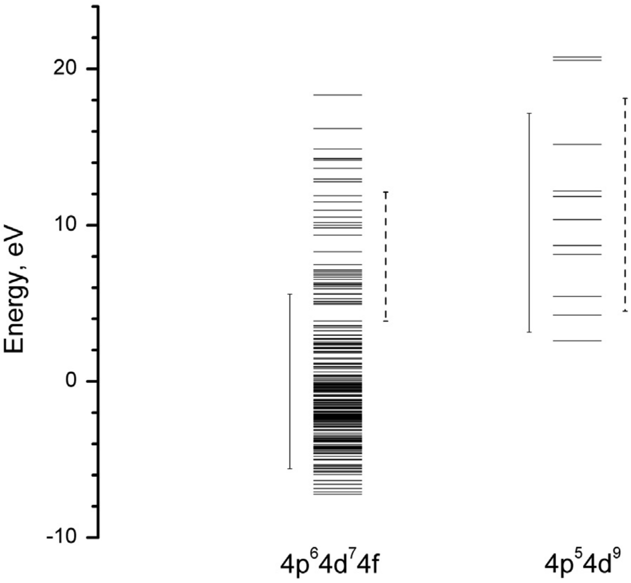

Fig. 3. Energy level spectra and CI zones for configurations $4p^54d^9$ and $4p^64d^74f$ of Sn^{6+}. The interval of zone, determined from Eq. (27), is shown by broken line on the right-hand side of the spectrum. For the comparison the interval of energy level spectrum, determined from the same approximate Eq. (27), is indicated by the solid line on the other side of the spectrum.

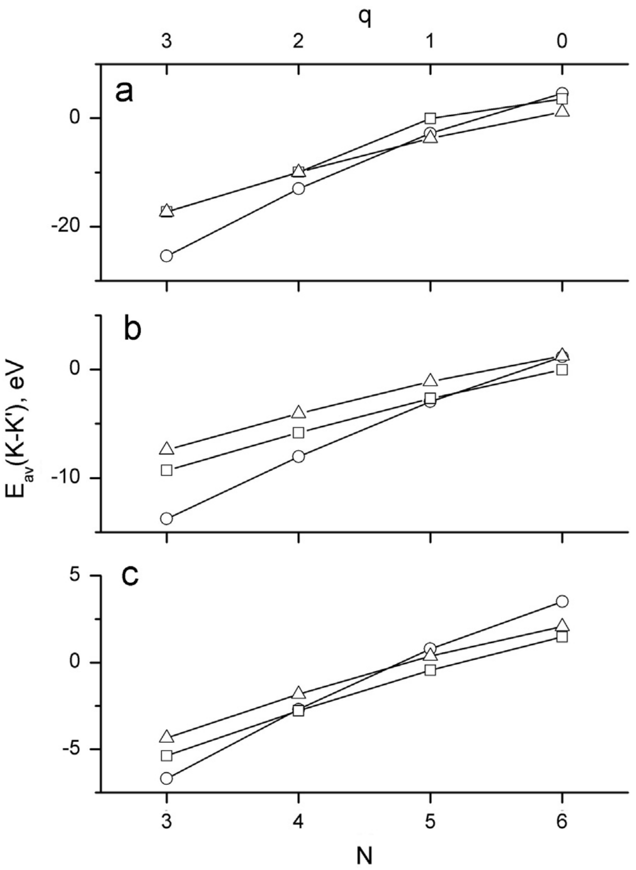

Fig. 4. Average energy between the levels of interacting configurations nd^N and $nd^{N-2}(n+1)s^2$ (○); nd^N and $nd^{N-1}(n+1)s$ (□); $nd^{N-1}(n+1)s$ and $nd^{N-2}(n+1)s^2$ (Δ) in the isonuclear sequences at $n=3$ for Cr^{q+} (a), $n=4$ for Mo^{q+} (b) and n=5 for W^{q+} (c), q=0-3.

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CI is a characteristic typical of neutral atoms, while at $n=5$ of single ions. In all cases the $E_{av}(K,K')$ changes faster with ionization degree between configurations differing by two 3d electrons.

3.5. Average shift of the energy level due to its interaction with the levels of distant configuration

In the second order of the perturbation theory the shift of the energy of state γ due to its interaction with all states of configuration K' or CI correction is expressed:

$$\Delta E(K\gamma,K') = \sum_{\gamma'} \frac{\langle K\gamma|H|K'\gamma'\rangle^2}{E(K\gamma)-E(K'\gamma')}. \tag{30}$$

the same expression gives the shift of the energy level.

If the excited configuration K' is energetically distant from configuration K, the denominator in Eq. (30) can be approximately replaced by the average distance between $K\gamma$ and configuration K' (this quantity is defined similarly as in Eq. (28), but only with one summation over γ'). Then the shift equals

$$\Delta E(K\gamma,K') = \frac{\langle K\gamma|H^{eff}|K\gamma\rangle}{E_{av}(K\gamma,K')}. \tag{31}$$

While averaging $\Delta E(K\gamma,K')$ over the states of configuration K and introducing the positive average distance $E_{av}(K',K)=-E_{av}(K,K')$, the mean value of the shift for levels or states of configuration K is obtained [12]:

$$\Delta E_{av}(K,K') = -\frac{\sum_{\gamma\,\gamma'}\langle K\gamma|H|K'\gamma'\rangle^2}{g(K)E_{av}(K',K)}. \tag{32}$$

Here the already introduced quantities are used. This average characteristic gives the simple estimation of the contribution of various distant configurations on the adjustment of energy levels for the considered configuration. In Tables 1 and 2 it is illustrated by the results of calculation for Mo^{3+} $3d^4$ and Se $4p^4$ taking into account various excited configurations. The relative error of $\Delta E_{av}(K,K')$ calculation in comparison with its value, obtained by matrix diagonalization, usually does not exceed one percent.

3.6. Configuration interaction strength

In order to select the optimal set of the most important configurations for the calculation of considered electronic configuration it is useful to introduce also the other measure of CI. It can be related to the weight coefficient in the expansion of wave function. In the first order of the perturbation theory such a coefficient is proportional to ICME between two interacting states and inversely proportional to the energy distance between them. In order to avoid the compensation effects on averaging such a measure, the squares of quantities should be taken. Thus, the configuration interaction strength (CIS) can be defined as follows:

$$T(K,K') = \frac{\sum_{\gamma\,\gamma'}\langle K\gamma|H|K'\gamma'\rangle^2}{E_{av}(K,K')^2}. \tag{33}$$

At first it was introduced with the difference of average energies of configurations in the denominator [29]. Later the difference of average energies was replaced by more accurate average distance between two interacting configurations $E_{av}(K,K')$ [12]. Also the variant of CIS with a variance of the distances between the interacting states was considered [8,12], but this quantity has more complex expression.

$T(K,K')$ approximately equals the sum of squares of expansion coefficients of wave functions of configuration K' in all wave functions of configuration K. In order to obtain the average weight of all states of configuration K' in the expansion of the wave functions of configuration K the $T(K,K')$ should be divided by the statistical weight $g(K)$ of configuration K:

$$a^2(K,K')_{av} = \frac{T(K,K')}{g(K)} \approx \frac{1}{g(K)} \sum_{\gamma\,\gamma'} a^2(K\gamma,K'\gamma'). \tag{34}$$

Here $a(K\gamma,K'\gamma')$ is the expansion coefficient in the two-configuration approximation. Such an average weight of one state of configuration K' in the expansion of the wave functions of configuration K is obtained via the additional division of Eq. (34) by statistical weight $g(K')$.

The values of the average weight, CI strength $T(K,K')$ as well as of other average characteristics for Mo^{3+} $3d^4$ and Se $4p^4$ configurations interacting with some set of the excited configurations are presented in Tables 1 and 2. In order to check the accuracy of the estimation of average weights by Eq. (34), their exact values obtained by the diagonalization of energy matrix are given too and the difference in percent is indicated. Our calculations for other configurations as well as some results presented in [13,30] confirm that the relative error of $a^2(K,K')$ estimation usually does not exceed several percent for energetically distant and even neighboring configurations. Thus, such an average characteristic is useful for the selection of CI basis, except overlapping configurations, which usually are well-known (for this reason the $3d^24s^2$ and $3d^34s$ configurations are not presented in Table 1).

3.7. Shift of the average energy of emission spectrum due to CI

The average energy of the array of electric dipole transitions between the levels of two configurations is defined [11]:

$$E^e_{av}(\tilde K,K') = \frac{\sum_{\tilde\gamma\gamma'}\left[\langle\tilde K\tilde\gamma|H|\tilde K\tilde\gamma\rangle-\langle K'\gamma'|H|K'\gamma'\rangle\right]S(\tilde K\tilde\gamma,K'\gamma')}{\sum_{\tilde\gamma\gamma'}S(\tilde K\tilde\gamma,K'\gamma')}, \quad \tilde K\equiv K_1+K_2, \tag{35}$$

where $S(K\gamma,K'\gamma')$ is the line strength. At equal population of all initial states and transition energy essentially exceeding the sum of widths of energy level spectra of both configurations, Eq. (35) gives the average energy of emission spectrum. Then the influence of CI on emission spectrum is described as the difference of average energies, calculated in the CI and in the single-configuration (SC) approximations:

$$\Delta E = E^{CI}_{av}-E^{SC}_{av}. \tag{36}$$

This quantity can be derived explicitly, but only for the total array of transitions between the sets of interacting

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Table 1

Average characteristics $E_{K'}^{av}(K)$ (20), $E_{av}(K,K')$ (28), $\Delta E(K,K')$ (32), $T(K,K')$ (33) and $a^2(K,K')_{av}$ (34) corresponding to the interaction of configuration K=$3p^6\ 3d^4$ for Mn^{3+} with various excited configurations K'.

(K')	$E_{K'}^{av}(K)$(eV)	$E_{av}(K')$(eV)	$E_K^{av}(K')$(eV)	$E_{av}(K',K)$(eV)	$T(K,K')$	Average energy level shift			Average weight		
						Obtained by matrix diagonalization	$\Delta E_{av}(K,K')$(eV)	Error in %	Obtained by matrix diagonalization	Calculated using CI strength from eq. (34)	Error in %
$3s^23p^43d^6$	0.43	106.61	121.19	120.76	2.37E+00	−1.3496	−1.3616	0.89	1.10E-02	1.13E-02	2.68
$3s3p^63d^5$	0.73	89.93	92.26	91.53	3.10E-01	−0.1347	−0.1349	0.14	1.47E-03	1.47E-03	0.42
$3s^23p^43d^54d$	0	136.3	146.02	146.02	1.99E-01	−0.1388	−0.1385	−0.21	9.55E-04	9.49E-04	−0.61
$3s^23p^53d^34p4d$	0	109.41	116.1	116.1	1.42E-01	−0.0785	−0.0783	−0.27	6.79E-04	6.74E-04	−0.8
$3s^23p^63d^24d^2$	0.32	68.6	72.33	72.01	1.21E-01	−0.0415	−0.0415	−0.03	5.77E-04	5.76E-04	−0.1
$3s^23p^53d^44\ f$	−0.17	88.52	99.5	99.67	1.09E-01	−0.0521	−0.0519	−0.45	5.28E-04	5.20E-04	−1.36
$3s^23p^53d^45\ f$	−0.17	93.6	104.51	104.68	7.30E-02	−0.0366	−0.0364	−0.43	3.52E-04	3.48E-04	−1.3
$3s^23p^63d^24d5d$	0.33	78.35	81.47	81.13	6.92E-02	−0.0267	−0.0267	−0.06	3.30E-04	3.29E-04	−0.17
$3s^23p^43d^55d$	0	144.9	154.04	154.04	6.27E-02	−0.0461	−0.046	−0.27	3.01E-04	2.99E-04	−0.8
$3s^03p^63d^6$	1.26	182.12	183.41	182.15	5.98E-02	−0.0518	−0.0519	0.02	2.85E-04	2.85E-04	0.05
$3s^23p^63d^24p^2$	1.28	46.51	47.52	46.24	5.16E-02	−0.0114	−0.0114	−0.24	2.47E-04	2.46E-04	−0.71
$3s^23p^43d^44p^2$	0	152.73	158.46	158.46	4.72E-02	−0.0357	−0.0356	−0.26	2.27E-04	2.25E-04	−0.79
$3s^23p^53d^34p5d$	0	119.01	123.76	123.76	4.72E-02	−0.0279	−0.0278	−0.29	2.27E-04	2.25E-04	−0.85
$3s3p^53d^54p$	0	162.18	174.92	174.92	3.96E-02	−0.033	−0.033	−0.12	1.89E-04	1.89E-04	−0.35
$3s^23p^53d^34d5p$	0	126.39	130.8	130.8	3.59E-02	−0.0224	−0.0223	−0.26	1.72E-04	1.71E-04	−0.76
$3s3p^63d^34s4d$	0	140.44	144.37	144.37	3.04E-02	−0.0209	−0.0209	−0.04	1.45E-04	1.45E-04	−0.11
$3s3p^6\ 3d4s$	−0.04	103.47	103.48	103.51	2.61E-02	−0.0139	−0.0129	−7.46	1.34E-04	1.24E-04	−7.44
$3s^23p^53d^34s4p$	0	90.37	95.27	95.27	2.58E-02	−0.0118	−0.0117	−0.55	1.25E-04	1.23E-04	−1.61

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Table 2

Average characteristics $E_{K'}^{av}(K)$ (20), $E_{av}(K,K')$ (28), $\Delta E(K,K')$ (32), $T(K,K')$ (33) and $a^2(K,K')_{av}$ (34) corresponding to the interaction of configuration $K{=}4s^24p^4$ for Se with various excited configurations K'.

(K')	$E_{K'}^{av}(K)$(eV)	$E_{av}(K')$(eV)	$E_{K}^{av}(K')$	$E_{av}(K',K)$(eV)	$T(K,K')$	Average energy level shift			Average weight		
						Obtained by matrix diagonalization	$\Delta E_{av}(K,K')$(eV)	Error in %	Obtained by matrix diagonalization	Calculated using CI strength from Eq. (34)	Error in %
$4s^24p^24d^2$	0.08	21.07	22.76	22.68	9.36E-02	−0.1408	−0.1415	0.44	6.16E-03	6.24E-03	1.32
$4s^24p^24d5d$	0.08	22.36	24.24	24.16	4.52E-02	−0.0727	−0.0727	0.08	3.00E-03	3.01E-03	0.24
$4s4p^44d$	−0.15	21.4	23.86	24.01	4.20E-02	−0.0678	−0.0672	−0.81	2.87E-03	2.80E-03	−2.52
$4s^04p^6$	2.65	27.73	27.73	25.07	3.24E-02	−0.0524	−0.0541	3.12	1.97E-03	2.16E-03	9.57
$4s4p^45d$	−0.15	22.24	24.6	24.75	2.07E-02	−0.0345	−0.0341	−0.94	1.42E-03	1.38E-03	−2.89
$4s^24p^24d6d$	0.09	22.85	24.32	24.23	2.03E-02	−0.0328	−0.0328	−0.1	1.36E-03	1.35E-03	−0.3
$4s^24p^24d5s$	0.11	19.02	19.79	19.68	1.08E-02	−0.0142	−0.0142	−0.03	7.21E-04	7.20E-04	−0.09
$4s4p^46d$	−0.15	22.61	24.92	25.07	1.07E-02	−0.0181	−0.0179	−1	7.37E-04	7.14E-04	−3.08
$4s^24p^25p^2$	0.1	20.84	21.74	21.64	6.07E-03	−0.0088	−0.0088	−0.12	4.06E-04	4.05E-04	−0.37
$4s^24p^25d^2$	0.09	25.36	26.07	25.98	5.78E-03	−0.01	−0.01	−0.14	3.87E-04	3.86E-04	−0.41
$4s^24p^25d6d$	0.09	26.29	27	26.91	3.49E-03	−0.0063	−0.0063	−0.15	2.34E-04	2.33E-04	−0.43
$4s4p^35s5p$	0	30.89	33.18	33.18	3.33E-03	−0.0075	−0.0074	−1.12	2.30E-04	2.22E-04	−3.4
$4s4p^34d5p$	0	32.75	35.37	35.37	3.25E-03	−0.0077	−0.0077	−0.83	2.22E-04	2.17E-04	−2.49
$4s^24p^25s^2$	0.44	17.29	17.8	17.36	3.01E-03	−0.0035	−0.0035	−0.03	2.01E-04	2.00E-04	−0.09
$4s^04p^55p$	0	35.97	36.05	36.05	2.45E-03	−0.0059	−0.0059	−0.05	1.64E-04	1.63E-04	−0.15
$4s^24p^25p6p$	0.11	22.8	23.58	23.47	2.38E-03	−0.0037	−0.0037	−0.14	1.60E-04	1.59E-04	−0.42
$4s^24p^25s5d$	0.11	20.64	20.84	20.73	2.18E-03	−0.003	−0.003	−0.11	1.46E-04	1.46E-04	−0.32
$4s^24p^24d6s$	0.11	21.81	22.11	22	1.85E-03	−0.0027	−0.0027	−0.08	1.23E-04	1.23E-04	−0.22

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configurations. Often the transitions from two interacting configurations into single configuration are considered. Then follows:

$$\Delta E_{CI}(K_0 l_1^{N_1-1} l_2^{N_2+1} l_3^{N_3} + K_0 l_1^{N_1} l_2^{N_2-1} l_3^{N_3+1} \rightarrow K_0 l_1^{N_1} l_2^{N_2} l_3^{N_3})$$
$$= \frac{2}{4l_2+1}\left[\frac{(4l_1+2)d^2_{l_2,l_3}}{N_1(4l_2+2-N_2)} + \frac{(4l_3+2)d^2_{l_1,l_2}}{N_2(4l_3+2-N_3)}\right]^{-1} d_{l_1,l_2} d_{l_3,l_2}$$
$$\times \sum_k \left[\frac{2\delta(k,1)}{3} - \begin{Bmatrix} l_1 & l_2 & k \\ l_3 & l_2 & 1 \end{Bmatrix}\right] \mathfrak{R}^k(l_1 l_3, l_2 l_2), \tag{37}$$

where d_{l_1,l_2} is the reduced matrix element of the dipole transition operator

$$d_{l_1,l_2} \equiv d_{n_1 l_1, n_2 l_2} = \langle n_1 l_1 || d^{(1)} || n_2 l_2 \rangle = -\langle l_1 || C^{(1)} || l_2 \rangle \langle n_1 l_1 | r | n_2 l_2 \rangle \tag{38}$$

and the quantity in the braces of Eq. (37) is the 6*j* coefficient. The separate case of Eq. (37) at $N_1 = 4l_1+1$ was derived in [11] and for any N_1 in [23,31].

When four open shells are involved in the transitions, one gets [31,12]:

$$\Delta E_{CI}(K_0 l_1^{N_1-1} l_2^{N_2+1} l_3^{N_3} l_4^{N_4} + K_0 l_1^{N_1} l_2^{N_2} l_3^{N_3-1} l_4^{N_4+1} \rightarrow K_0 l_1^{N_1} l_2^{N_2} l_3^{N_3} l_4^{N_4})$$
$$= \left[\frac{2(2l_3+1)(2l_4+1)d^2_{l_1,l_2}}{N_3(4l_4+2-N_4)} + \frac{2(2l_1+1)(2l_2+1)d^2_{l_3,l_4}}{N_1(4l_2+2-N_2)}\right]^{-1} d_{l_1,l_2} d_{l_4,l_3}$$
$$\times \sum_k \left[\frac{2\delta(k,1)}{3}\mathfrak{R}^k(l_3 l_2, l_4 l_1) + (-1)^k \begin{Bmatrix} l_1 & l_2 & 1 \\ l_4 & l_3 & k \end{Bmatrix} \mathfrak{R}^k(l_3 l_2, l_1 l_4)\right]. \tag{39}$$

The shift of spectrum from one initial configuration to two interacting configurations can be obtained from Eqs. (37) and (39) using the vacancy-electron symmetry of averages [12]:

$$\Delta E_{CI}(K_0 l_1^{N_1-1} l_2^{N_2+1} l_3^{N_3} + K_0 l_1^{N_1} l_2^{N_2-1} l_3^{N_3+1} \rightarrow K_0 l_1^{N_1} l_2^{N_2} l_3^{N_3})$$
$$\rightarrow -\Delta E_{CI}(K_0 l_1^{4l_1+2-N_1} l_2^{4l_2+2-N_2} l_3^{4l_3+2-N_3}$$
$$-K_0 l_1^{4l_1+3-N_1} l_2^{4l_2+1-N_2} l_3^{4l_3+2-N_3} + K_0 l_1^{4l_1+2-N_1} l_2^{4l_2+3-N_2} l_3^{4l_3+1-N_3}), \tag{40}$$

$$\Delta E_{CI}(K_0 l_1^{N_1-1} l_2^{N_2+1} l_3^{N_3} l_4^{N_4} + K_0 l_1^{N_1} l_2^{N_2} l_3^{N_3-1} l_4^{N_4+1} \rightarrow K_0 l_1^{N_1} l_2^{N_2} l_3^{N_3} l_4^{N_4})$$
$$\rightarrow -\Delta E_{CI}(K_0 l_1^{4l_1+2-N_1} l_2^{4l_2+2-N_2} l_3^{4l_3+2-N_3} l_4^{4l_4+2-N_4}$$
$$-K_0 l_1^{4l_1+3-N_1} l_2^{4l_2+1-N_2} l_3^{4l_3+2-N_3} l_4^{4l_4+2-N_4}$$
$$+K_0 l_1^{4l_1+2-N_1} l_2^{4l_2+2-N_2} l_3^{4l_3+3-N_3} l_4^{4l_4+1-N_4}) \tag{41}$$

The results of ΔE_{CI} shift calculation from strongly interacting configurations (1) and (2) to the ground configuration for ions of tungsten are presented in Figs. 5 and 6. It follows from the analysis of the shift equation for these transitions that ΔE_{CI} always obtains a positive value [11]. It means that configuration mixing enhances the shorter wavelength transitions from the higher excited configuration and quenches the longer wavelength transitions from the lower configuration. Usually it is related to the essential narrowing of the emission spectrum [11,32]. The presence of multipliers N_i $(4l+2-N_i)$ in Eqs. (37) and (39) determines their symmetry with respect to the half-filled shell, but it is distorted by the increase of radial integrals in the isonuclear sequence. Moreover, due to this increase of integrals for the higher ionization degrees the ΔE_{CI} shift obtains larger value for transitions (2) at smaller value of principle quantum number *n*.

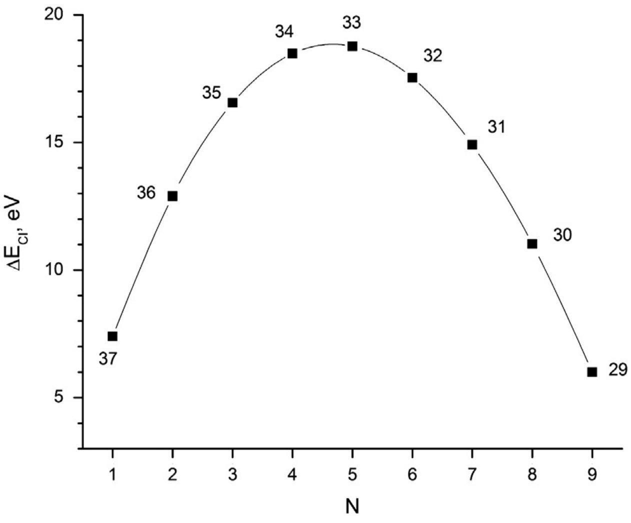

Fig. 5. Shift of the average energy of emission spectrum due to CI for the transitions $(4p^5 4d^{N+1} + 4p^6 4d^{N-1} 4f)$–$4p^6 4d^N$ in the W^{q+} isonuclear sequence, $q=29$–37. The value of ionization degree is indicated near the curve.

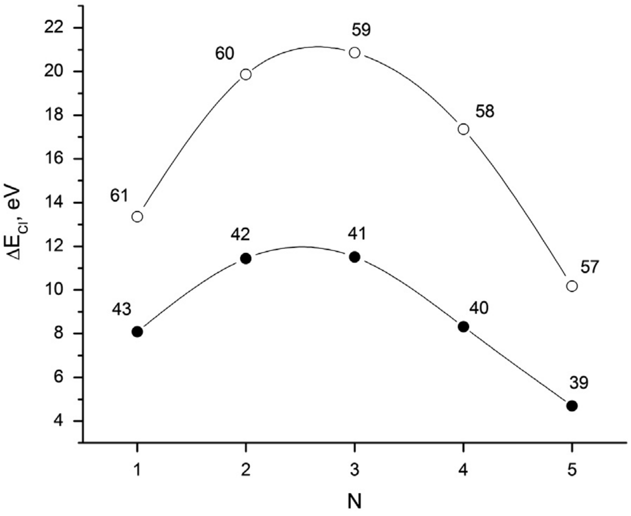

Fig. 6. Shift of the average energy of emission spectrum due to CI for the transitions $(4s4p^{N+1}+4s^2 4p^{N-1} 4d)$–$4s^2 4p^N$ in the W^{q+} isonuclear sequence, $q=39$–43 (●) and for the transitions $(3s3p^{N+1}+3s^2 3p^{N-1} 3d)$ $-3s^2 3p^N$ in the W^{q+} isonuclear sequence, $q=57$–61 (○). The value of ionization degree is indicated near the curve.

The shift of the average energy of Auger spectrum has more complex form. Its explicit expressions will be presented in a separate paper.

4. Conclusions

The advantage of the average CI characteristics in atoms is mainly determined by the presence of their rather simple explicit expressions. In this work, they are presented for a wide class of configurations. The given calculation results illustrate the usefulness of these characteristics for the selection of configurations the most important for the considered configuration as well as for the investigation of the regularities of CI effects in the isoelectronic and isonuclear sequences. The

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sums of interconfiguration matrix elements and the strength of CI can be used to compare various correlation effects. The CI strength, divided by the statistical weight of configuration, presents the useful characteristic for the estimation of average weights in the expansion of wave functions and consequently for the selection of CI bases. The CI zone gives the possibility to determine the main part of the energy level spectrum taking part in the interaction with the other configuration and to distinguish the type of configuration, which levels equally influence all levels of the other configuration. The average shift of energy level due to its interaction with the levels of other configuration presents simple, but rather accurate characteristic for the estimation of the contribution of various distant configurations on the adjustment of energy levels for the considered configuration. The shift of the average energy of emission or Auger spectrum due to CI enables one to investigate the influence of CI on such spectra.

Acknowledgment

This work was partially supported by the Contract of Association between EURATOM and Lithuanian Energy Institute within the framework of the European Fusion Development Agreement no. FU07-CT-20007-00063. The authors would like to thank A. Kupliauskienė for reading the manuscript and making the valuable comments.

Appendix. Expressions for the average energy distance between two interacting configurations

The average energy distance between two interacting configurations $E_{av}(K,K')$ (28) is the main characteristic of CI in atoms; also the configuration interaction strength (33) and the average shift of the energy level due to its interaction with the levels of distant configuration (32) are expressed in terms of this quantity. It was introduced in [12], and the expressions for various pairs of configurations were given in [13]. However, the minimal sums can be presented in more compact form, preferable for the realization in computer code and some other improvements made. Furthermore, in the case of single-electron excitation with a change of orbital quantum number three terms have been added which were omitted in [13]. In our work all formulae were rederived using the heuristic computer code [20]. In this Appendix the expressions for $E_{av}(K,K')$ are presented for all main types of configurations, except Brillouin excitation.

When configurations K and K' differ by quantum numbers of two electrons, the sum $\sum_{\gamma\gamma'}\langle K\gamma|H|K'\gamma'\rangle^2$ contains only one minimal sum. In order to present the formula for $E_{av}(K,K')$ in a compact form this quantity was expressed as follows:

$$E_{av}(K,K') = E_{av}(K) - E_{av}(K') + \frac{O_{K'}(K) - O_K(K')}{M(l_il_j,l_ul_v)}, \tag{A.1}$$

where $E_{av}(K)$ is the average energy of configuration, $M(l_il_j,l_ul_v)$ is the minimal sum (12) (in the notations of shells, l_i stands instead of n_il_i). We will present the formulae for $O_{K'}(K)$. The similar expression for $O_K(K')$ is obtained by the transposition of shells in configuration K' and using the corresponding numbers of electrons in the shells.

(i) Two-electron pair excitation:

$$K \equiv K_0 l_1^{N_1} l_2^{N_2}, \quad K' \equiv K_0 l_1^{N_1-2} l_2^{N_2+2}$$

(K_0 means the open or closed shells having the same number of electrons in both configurations).

$$O_{K'}(K) = \frac{(4l_1+2-N_1)(4l_1+1-N_1)}{4l_1(4l_1-1)} D_1(l_1l_1) + \frac{N_2(N_2-1)}{4l_2(4l_2-1)} D_1(l_2l_2) + \frac{(4l_1+2-N_1)N_2}{4l_1 4l_2} D_2(l_1l_2). \tag{A.2}$$

Here D_1 and D_2 are the minimal sums expressed in terms of two-electron matrix elements [17]:

$$D_1(l_al_b) \equiv D_1(Kl_al_b;Kl_il_j,K'l_ul_v) = \frac{1}{8}\sum_{LS}[L,S]V^{LS}_{l_al_b,l_al_b}\left(V^{LS}_{l_il_j,l_ul_v}\right)^2, \tag{A.3}$$

$$D_2(l_al_b) \equiv D_2(Kl_al_b;Kl_il_j,K'l_ul_v) = -\sum_{Q_1Q_2}[Q_1,Q_2]\overline{V}^{Q_1Q_2}_{l_al_b,l_al_b}\left(\overline{V}^{Q_1Q_2}_{l_il_j,l_ul_v}\right)^2. \tag{A.4}$$

The extended notations of minimal sums indicate the configurations, which radial orbitals are used for the calculation of matrix elements. $V^{LS}$and $\overline{V}^{Q_1Q_2}$ are defined:

$$V^{LS}_{l_1l_2,l_3l_4} = \frac{1}{2}N^{-1}_{l_1l_2}N^{-1}_{l_3l_4}\langle l_1l_2LS|\hat{h}^e|l_3l_4LS\rangle, \tag{A.5}$$

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$$\overline{V}^{Q_1Q_2}_{l_1l_2,l_3l_4} = \sum_{LS}[L,S](-1)^{l_1+l_2+L+S+1}\begin{Bmatrix} l_1 & l_2 & L \\ l_4 & l_3 & Q_1 \end{Bmatrix}\begin{Bmatrix} 1/2 & 1/2 & S \\ 1/2 & 1/2 & Q_2 \end{Bmatrix} V^{LS}_{l_1l_2,l_3l_4}, \tag{A.6}$$

where $\hat{h}^{e}$ is the traceless Coulomb interaction operator, $N^{-1}_{l_il_j}$ is the normalization constant (13), [x, y,…]≡(2x+1)(2y+1)… In separate cases, corresponding to the interaction between electrons in the same configuration, $V^{LS}_{l_1l_2,l_3l_4}$ is expressed:

$$V^{LS}_{l_1l_1,l_1l_1} = \left[1+(-1)^{L+S}\right]\sum_{k>0}\left[(-1)^{L}\begin{Bmatrix} l_1 & l_1 & L \\ l_1 & l_1 & k \end{Bmatrix} + \frac{1}{(2l_1+1)(4l_1+1)}\right]\langle l_1||C^{(K)}||l_1\rangle^2 F^k(l_1,l_1), \tag{A.7}$$

$$\begin{aligned} V^{LS}_{l_1l_2,l_1l_2} = {} & \sum_{k>0}(-1)^{l_1+l_2+L}\begin{Bmatrix} l_1 & l_2 & L \\ l_2 & l_1 & k \end{Bmatrix}\langle l_1||C^{k}||l_1\rangle\langle l_2||C^{k}||l_2\rangle F^k(l_1,l_2) \\ & +\sum_{k}\left[(-1)^{S}\begin{Bmatrix} l_1 & l_2 & L \\ l_1 & l_2 & k \end{Bmatrix} + \frac{1}{2(2l_1+1)(2l_2+1)}\right]\langle l_1||C^{(k)}||l_2\rangle^2 G^k(l_1,l_2). \end{aligned} \tag{A.8}$$

The formula for V^{LS}, corresponding to interconfiguration matrix element between the l_i and l_j electrons of configuration K and l_u, l_v electrons of configuration K'gets:

$$V^{LS}_{l_il_j,l_ul_v} = (-1)^{l_j+l_u}\sum_{k}[(-1)^{L}\begin{Bmatrix} l_i & l_j & L \\ l_v & l_u & k \end{Bmatrix}\mathfrak{R}^k(l_il_j,l_ul_v) + (-1)^{S}\begin{Bmatrix} l_i & l_j & L \\ l_u & l_v & k \end{Bmatrix}\mathfrak{R}^k(l_il_j,l_vl_u)]. \tag{A.9}$$

In Eqs. (A.7)–(A.9), F^k and G^k are the standard Slater integrals and $\mathfrak{R}^k$ is the general radial integral of the Coulomb interaction along with the one-electron reduced matrix elements (14).

It should be noted that for avoiding uncertainties of the type 0 divided by 0 in Eq. (A.2) and the other expressions for $O_{K'}$ *(K)*, the multipliers in the numerator should be cancelled with the identical multipliers in the denominator for the particular N_i before specifying quantum numbers l_i. The application of such a rule enables one to avoid of the additional multiplier which ensures the validity of formulae for configuration with s shell.

(ii) Two-electron paired-unpaired excitation:

$$K \equiv K_0 l_1^{N_1} l_2^{N_2} l_3^{N_3},\ K' \equiv K_0 l_1^{N_1-2} l_2^{N_2+1} l_3^{N_3+1}$$

$$\begin{aligned} O_{K'}(K) = {} & 2\frac{(4l_1+2-N_1)(4l_1+1-N_1)}{4l_1(4l_1-1)}D_1(l_1l_1) + 4\frac{N_2N_3}{(4l_2+1)(4l_3+1)}D_1(l_2l_3) + \frac{(4l_1+2-N_1)N_2}{4l_1(4l_2+1)}D_2(l_1l_2) \\ & + \frac{(4l_1+2-N_1)N_3}{4l_1(4l_3+1)}D_2(l_1l_3). \end{aligned} \tag{A.10}$$

(iii) Two-electron unpaired excitation:

$$K \equiv K_0 l_1^{N_1} l_2^{N_2} l_3^{N_3} l_4^{N_4},\ \ K' \equiv K_0 l_1^{N_1-1} l_2^{N_2-1} l_3^{N_3+1} l_4^{N_4+1}$$

$$\begin{aligned} O_{K'}(K) = {} & \frac{(4l_1+2-N_1)(4l_2+2-N_2)}{(4l_1+1)(4l_2+1)}D_1(l_1l_2) + \frac{N_3N_4}{(4l_3+1)(4l_4+1)}D_1(l_3l_4) + \frac{(4l_1+2-N_1)N_3}{(4l_1+1)(4l_3+1)}D_2(l_1l_3) \\ & + \frac{(4l_2+2-N_2)N_3}{(4l_2+1)(4l_3+1)}D_2(l_2l_3) + \frac{(4l_1+2-N_1)N_4}{(4l_1+1)(4l_4+1)}D_2(l_1l_4) + \frac{(4l_2+2-N_2)N_4}{(4l_2+1)(4l_4+1)}D_2(l_2l_4). \end{aligned} \tag{A.11}$$

(iv) Single-electron excitation with a change of orbital quantum number

$$K \equiv K_0 l_1^{N_1} l_2^{N_2},\ \ K' \equiv K_0 l_1^{N_1-1} l_2^{N_2+1},\ \ (l_1 \neq l_2)$$

This case is more complex, because the additional contributions corresponding to various interactions between shells appear. The sum of the squares of interconfiguration matrix elements also contain several terms, so the eq. (A.1) should

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be replaced by the following one:

$$E_{av}(K,K') = E_{av}(K) - E_{av}(K') + \frac{O'_{K'}(K) - O'_{K}(K')}{\sum\limits_{\gamma\gamma'} \langle K\gamma|H|K'\gamma'\rangle^2}. \tag{A.12}$$

Thus, every term of $O'_{K'}(K)$ contains simple multipliers which cannot be canceled with the similar multipliers from the sum in the denominator. Additionally, more complex notation of the minimal sum, indicating also the quantum numbers of electrons in the interconfiguration matrix element, should be used.

If the core K_0 contains only closed shells, $O'_{K'}(K)$ has the expression:

$$\begin{aligned}
O'_{K'}(K) = {} & 2\frac{N_1(N_1-1)(4l_1+2-N_1)(4l_1+1-N_1)(4l_1-N_1)(4l_2+2-N_2)}{(4l_1+2)(4l_1+1)4l_1(4l_1-1)(4l_1-2)(4l_2+2)} D_1(l_1l_1; l_1l_2, l_1l_1) \\
& +4\frac{N_1(4l_1+2-N_1)N_2(4l_2+2-N_2)(4l_2+1-N_2)(4l_2-N_2)}{(4l_1+2)(4l_1+1)(4l_2+2)(4l_2+1)4l_2(4l_2-1)} D_1(l_1l_2; l_1l_2, l_2l_2) \\
& +2\frac{N_1N_2(N_2-1)(N_2-2)(4l_2+2-N_2)(4l_2+1-N_2)}{(4l_1+2)(4l_2+2)(4l_2+1)4l_2(4l_2-1)(4l_2-2)} D_1(l_2l_2; l_1l_2, l_2l_2) \\
& +4\frac{N_1(N_1-1)(N_1-2)(4l_1+2-N_1)N_2(4l_2+2-N_2)}{(4l_1+2)(4l_1+1)4l_1(4l_1-1)(4l_2+2)(4l_2+1)} D_1(l_1l_2; l_1l_1, l_1l_2) \\
& +\frac{N_1(N_1-1)(4l_1+2-N_1)(4l_1+1-N_1)N_2(4l_2+2-N_2)}{(4l_1+2)(4l_1+1)4l_1(4l_1-1)(4l_2+2)(4l_2+1)} D_2(l_1l_2; l_1l_1, l_1l_2) \\
& +\frac{N_1(N_1-1)(N_1-2)(4l_1+2-N_1)(4l_1+1-N_1)(4l_2+2-N_2)}{(4l_1+2)(4l_1+1)4l_1(4l_1-1)(4l_1-2)(4l_2+2)} D_2(l_1l_1; l_1l_1, l_1l_2) \\
& +\frac{N_1(4l_1+2-N_1)N_2(N_2-1)(4l_2+2-N_2)(4l_2+1-N_2)}{(4l_1+2)(4l_1+1)(4l_2+2)(4l_2+1)4l_2(4l_2-1)} D_2(l_1l_2; l_1l_2, l_2l_2) \\
& +\frac{N_1N_2(N_2-1)(4l_2+2-N_2)(4l_2+1-N_2)(4l_2-N_2)}{(4l_1+2)(4l_2+2)(4l_2+1)4l_2(4l_2-1)(4l_2-2)} D_2(l_2l_2; l_1l_2, l_2l_2) \\
& +2\frac{N_1(N_1-1)(4l_1+2-N_1)N_2(4l_2+2-N_2)(4l_2+1-N_2)}{(4l_1+2)(4l_1+1)4l_1(4l_2+2)(4l_2+1)4l_2} D_2(l_1l_2; l_1l_1, l_1l_2; l_2l_2, l_2l_1).
\end{aligned} \tag{A.13}$$

In the last term the more general notation of minimal sum D_2 is used:

$$D_2(l_al_b; l_il_j, l_ul_v; l_rl_s, l_pl_q) \equiv D_2(Kl_al_b; Kl_il_j, K'l_ul_v; K'l_rl_s, Kl_pl_q) = -\sum_{Q_1Q_2} [Q_1, Q_2]\, \overline{V}^{Q_1Q_2}_{l_al_b, l_al_b} \overline{V}^{Q_1Q_2}_{l_il_j, l_ul_v} \overline{V}^{Q_1Q_2}_{l_rl_s, l_pl_q}. \tag{A.14}$$

When the core K_0 contains open shells, the following additional terms, corresponding to the interaction with these shells appear:

$$\begin{aligned}
\Delta O'_{K'}(K) = {} & 8\frac{N_1(4l_1+2-N_1)(4l_2+2-N_2)}{(4l_1+2)(4l_1+1)(4l_2+2)} \sum_p \frac{N_p(4l_p+2-N_p)(4l_p+1-N_p)}{(4l_p+2)(4l_p+1)4l_p} D_1(l_1l_p; l_2l_p, l_1l_p) \\
& +8\frac{N_1N_2(4l_2+2-N_2)}{(4l_1+2)(4l_2+2)(4l_2+1)} \sum_p \frac{N_p(N_p-1)(4l_p+2-N_p)}{(4l_p+2)(4l_p+1)4l_p} D_1(l_2l_p; l_1l_p, l_2l_p) \\
& +\frac{N_1N_2(4l_2+2-N_2)}{(4l_1+2)(4l_2+2)(4l_2+1)} \sum_p \frac{N_p(4l_p+2-N_p)(4l_p+1-N_p)}{(4l_p+2)(4l_p+1)4l_p} D_2(l_2l_p; l_1l_p, l_2l_p) \\
& +\frac{N_1(4l_2+2-N_2)}{(4l_1+2)(4l_2+2)} \sum_p \frac{N_p(N_p-1)(4l_p+2-N_p)(4l_p+1-N_p)}{(4l_p+2)(4l_p+1)4l_p(4l_p-1)} D_2(l_pl_p; l_1l_p, l_pl_2) \\
& +\frac{N_1(4l_1+2-N_1)N_2(4l_2+2-N_2)}{(4l_1+2)(4l_1+1)(4l_2+2)(4l_2+1)} \sum_p \frac{N_p(4l_p+2-N_p)}{(4l_p+2)(4l_p+1)} D_2(l_1l_2; l_1l_p, l_pl_2) \\
& +\frac{N_1(4l_1+2-N_1)(4l_2+2-N_2)}{(4l_1+2)(4l_1+1)(4l_2+2)} \sum_p \frac{N_p(N_p-1)(4l_p+2-N_p)}{(4l_p+2)(4l_p+1)4l_p} D_2(l_1l_p; l_1l_p, l_2l_p) \\
& +2\frac{N_1(N_1-1)(4l_1+2-N_1)(4l_2+2-N_2)}{(4l_1+2)(4l_1+1)4l_1(4l_2+2)} \sum_p \frac{N_p(4l_p+2-N_p)}{(4l_p+2)(4l_p+1)} D_2(l_1l_p; l_1l_1, l_1l_2; l_pl_2, l_pl_1) \\
& +2\frac{N_1N_2(4l_2+2-N_2)(4l_2+1-N_2)}{(4l_1+2)(4l_2+2)(4l_2+1)4l_2} \sum_p \frac{N_p(4l_p+2-N_p)}{(4l_p+2)(4l_p+1)} D_2(l_2l_p; l_1l_2, l_2l_2; l_2l_p; l_pl_2, l_pl_1).
\end{aligned} \tag{A.15}$$

The summation over p includes open shells of core. In the last two terms the Eq. (A.14) for D_2 is used.

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