



Global characteristics of atomic spectra and their use for the analysis of spectra. IV. Configuration interaction effects

To cite this article: S Kučas *et al* 1997 *Phys. Scr.* **55** 667

View the [article online](#) for updates and enhancements.

You may also like

- [Resonant vacuum ultraviolet photoemission of atomic Fe, Co and Ni](#)
E Schmidt, H Schroder, B Sonntag et al.
- [XUV spectra of laser-produced zirconium plasmas](#)
Bowen Li, Takeshi Higashiguchi, Takamitsu Otsuka et al.
- [Length and velocity form calculations of generalized oscillator strengths of dipole, quadrupole and monopole excitations of argon](#)
L Gomis, I G Faye, S Diallo et al.

Global Characteristics of Atomic Spectra and their use for the Analysis of Spectra. IV. Configuration Interaction Effects

S. Kučas,* V. Jonauskas and R. Karazija

Institute of Theoretical Physics and Astronomy, A. Goštauto 12, 2600 Vilnius, Lithuania

Received August, 26, 1996; accepted in revised form October 26, 1996

Abstract

Changes of the moments of atomic spectrum due to configuration interaction (CI), the CI strength, the average shift of the energy of a level due to its interaction with all levels of distant configuration and other global characteristics of CI effects in atoms are systematised and their expressions presented. The results of the calculation of these characteristics for the energy level spectra of the $3s3p^3 + 3s^23p3d$ configurations in Si isoelectronic series, $3p^53d^N + 3p^63d^{N-2}4p + 3p^63d^{N-2}4f$ ($N = 5, 6, 7, 8$) in Cr, Mn, Fe and Co isoelectronic series, $ns^2np^N + np^{N+2}$ at $n = 2 - 5$ and $N = 2 - 4$ in neutral atoms as well as for the characteristic emission spectra corresponding to the $3p^53d^9 + 3d^74p \rightarrow 3d^8$ transitions as well as for the Auger $M_{4,5}N_{1,2,3}$ spectra in Kr and $N_{4,5}O_{1,2,3}$ in Xe are given and compared with the same characteristics of the more complete experimental spectra.

1. Introduction

The global characteristics of atomic spectra can be useful for the investigation of configuration interaction (CI) effects in atoms, their influence on the structure of spectra. The shift of the average energy of characteristic emission spectrum, corresponding to the transitions between two complexes of configurations, has been introduced in [1] and its expressions for the various types of transitions have been given in [2–4]. In addition some formulae have been obtained for the change of the variance of spectrum in [2–4]. These characteristics were applied for the study of the narrowing of spectrum due to CI [1, 2]. The CI between two configurations can be characterized by the CI strength [5, 4], the average energy shift of the level of one configuration due to its interaction with the levels of other configuration [6] and other global characteristics. The general method for obtaining explicit expressions for all such characteristics has been developed in [4, 7], and realized in the computer code.

In the preceding papers of this series the global characteristics of the energy level [8], characteristic emission [9], and Auger [10] spectra were considered mainly in the single-configuration approximation, though a few examples were given in the CI approximation too. The aim of this work is to present the more systematic results on the use of global characteristics for the study of CI effects in such spectra. The calculations have been performed taking into account configuration interaction in the limited basis of single-configuration wave functions (CI approximation). The Hartree-Fock method with relativistic corrections (Cowan code [11]) has been used for the evaluation of radial integrals.

2. Moments of the spectra in CI approximation

Let us call the whole of n interacting configurations under consideration as the complex of configurations:

$$\mathcal{K} = K_1 + K_2 + \dots + K_n, \quad (1)$$

where the script $\mathcal{K}$ denotes the complex and the print K_i denotes the i th configuration of this complex.

The moments of the energy level spectrum, corresponding to the complex of interacting configurations, or of the emission or the Auger spectrum, corresponding to the transitions between two such complexes, are defined similarly as in the single-configuration approximation [8–10], but the summation over the states of a configuration is extended over the states of a complex or to the double sum over configurations and their states. Thus the moments of spectrum in CI approximation can be expressed in terms of the averages of operator products in single-configuration approximation [4, 7]. It is necessary to note that the explicit expressions of the moments in CI approximation can be obtained only for the all complex of interacting configurations but not for the single-configuration or the separate group of them.

The initial (α_k) or centered (μ_k) moment of the spectrum in CI approximation can be separated into two parts: the moment α_k^{sum} or μ_k^{sum} calculated in single-configuration approximation neglecting the interconfiguration matrix elements between the configurations of complex and the change of the moment due to CI:

$$\alpha_k^{\text{CI}} = \alpha_k^{\text{sum}} + \Delta\alpha_k^{\text{CI}}, \quad (2)$$

$$\mu_k^{\text{CI}} = \mu_k^{\text{sum}} + \Delta\mu_k^{\text{CI}}. \quad (3)$$

The changes of initial moments $\Delta\alpha_k^{\text{CI}}$ have more simple expressions than $\Delta\mu_k^{\text{CI}}$, thus we shall present the formulae for the first ones. Then the centered moments in any approximation can be obtained using their relation with the initial moments:

$$\mu_k = \sum_{p=0}^k (-1)^p \binom{k}{p} \alpha_{k-p} \alpha_1^p, \quad (4)$$

where $\binom{k}{p}$ is the binomial coefficient.

The average energy of the complex of configurations is not shifted due to the interaction between them ($\Delta\alpha_1^{\text{CI}} = 0$).

* kucas@itpa.lt

The change of the second initial moment for the energy level spectrum of the complex of configurations can be presented:

$$\begin{aligned}\Delta\alpha_2^{CI}(\mathcal{K}) &= \frac{2}{g(\mathcal{K})} \sum_{i < j} g(K_i) \langle H_{ij} H_{ji} \rangle^{K_i} \\ &= \frac{2}{g(\mathcal{K})} \sum_{i < j} M(K_i, K_j),\end{aligned}\quad (5)$$

where $g(K_i)$ and $g(\mathcal{K})$ are the statistical weights of configuration K_i and complex $\mathcal{K}$, the quantity in the brackets denotes the average of the product of operators with respect to configuration K_i . The operator H_{ij} is the Hamiltonian in the second quantization form, describing the interaction between configurations K_i and K_j and the summation is carried out over all pairs of configurations in the complex. The shift is expressed in terms of the sum over the squares of interconfiguration matrix elements:

$$M(K_i, K_j) = \sum_{\gamma\gamma'} \langle K_i \gamma | H | K_j \gamma' \rangle^2. \quad (6)$$

The explicit formulae of this quantity have been obtained in [12] (the nonrelativistic approximation) and in [6] (the relativistic approximation). The results in nonrelativistic approximation for various pairs of configurations are presented in Appendix I.

The changes of the third and the fourth initial moments are expressed in terms of the averages of products of operators as follows [4]:

$$\begin{aligned}\Delta\alpha_3^{CI}(\mathcal{K}) &= \frac{3}{g(\mathcal{K})} \left\{ \sum'_{ij} \langle H_i H_{ij} H_{ji} \rangle^{K_i} \right. \\ &\quad \left. + 2 \sum'_{i < j < k} \langle H_{ij} H_{jk} H_{ki} \rangle^{K_i} \right\} g(K_i),\end{aligned}\quad (7)$$

$$\begin{aligned}\Delta\alpha_4^{CI}(\mathcal{K}) &= \frac{2}{g(\mathcal{K})} \left\{ \sum'_{i < j} \langle H_{ij} H_{ji} H_{ij} H_{ji} \rangle^{K_i} \right. \\ &\quad + 2 \sum'_{ij} \langle H_i H_{ij} H_{ji} H_i \rangle^{K_i} \\ &\quad + 2 \sum'_{i < j} \langle H_i H_{ij} H_j H_{ji} \rangle^{K_i} \\ &\quad + 4 \sum'_{\substack{i \\ j < k}} \langle H_i H_{ij} H_{jk} H_{ki} \rangle^{K_i} \\ &\quad + 2 \sum'_{\substack{i \\ j < k}} \langle H_{ij} H_{ji} H_{ik} H_{ki} \rangle^{K_i} \\ &\quad \left. + \sum'_{\substack{i < j \\ kl}} \langle H_{ij} H_{jk} H_{kl} H_{li} \rangle^{K_i} \right\} g(K_i).\end{aligned}\quad (8)$$

Here H_i denotes the Hamiltonian acting in the space of configuration K_i . The prime at the symbol of sum means, that the equal values of summation indexes are excluded. In order to apply the group diagrammatic summation method for the expressing of averages all the operators contained in (7), (8) must be presented in the irreducible form with respect to the special orthogonal group SO_{8l+5} and its unitary subgroup U_{4l+2} [13, 4]. The operator H_i , corresponding to the interaction within configuration K_i , is reduced by subtracting the average energy of configuration $\bar{E}(K_i)$. The operator H_{ij} is irreducible, if the configurations K_i and K_j differ by quantum numbers of two electrons, but it contains the single-electron part in the case of two configurations which differ by quantum numbers of one elec-

tron [4]. The expressions for the averages of the products of three and four irreducible operators have been given in [7, 10].

As in the preceding papers [9, 10], the moments of the characteristic emission and the Auger spectra are determined under the assumption that populations of the initial levels of considered transitions are proportional to their statistical weights. For the emission spectrum the additional assumption is made, that the strength of line can be used as a weighting factor instead of the probability of transition [14, 4].

The concretization of general formula for the first initial moment of characteristic emission spectrum and its expression in terms of the single configuration averages gives the formula for the change (shift) of the average energy

$$\begin{aligned}\Delta\bar{E}_{CI}(\mathcal{K} \rightarrow \mathcal{K}') &= 2S(\mathcal{K}, \mathcal{K}')^{-1} \\ &\quad \times \left[\sum_q g(K'_q) \sum_{i < j} \langle \mathcal{D} H_{ij} \mathcal{D}^+ \rangle^{K'_q} \right. \\ &\quad \left. - \sum_i g(K_i) \sum_{p < q} \langle \mathcal{D} H_{pq} \mathcal{D}^+ \rangle^{K_i} \right],\end{aligned}\quad (9)$$

where $\mathcal{D}$ is the operator of electric dipole transition and $\mathcal{D}^+$ is its Hermitian conjugated operator, $g(K)$ is the statistical weight of configuration K , the indexes i, j label the configurations of initial complex $\mathcal{K}$ and p, q label the configurations of the final complex $\mathcal{K}'$. The total transition strength between complexes $\mathcal{K}$ and $\mathcal{K}'$ is equal to the sum of the total transition strength between all pairs of configurations:

$$S(\mathcal{K}, \mathcal{K}') = \sum_{i, p} S(K_i, K_p). \quad (10)$$

In the same way the change of the second initial moment is presented:

$$\begin{aligned}\Delta\alpha_2(\mathcal{K} \rightarrow \mathcal{K}') &= S(\mathcal{K}, \mathcal{K}')^{-1} \left\{ \sum_p g(K'_p) \left[2 \sum'_{ij} \langle \mathcal{D}^+ H_i H_{ij} \mathcal{D} \rangle^{K'_p} \right. \right. \\ &\quad + \sum'_{ij} \langle \mathcal{D}^+ H_{ij} H_{ji} \mathcal{D} \rangle^{K'_p} \\ &\quad + \sum'_{ijl} \langle \mathcal{D}^+ H_{ij} H_{jl} \mathcal{D} \rangle^{K'_p} \Big] \\ &\quad + \sum_i g(K_i) \left[2 \sum_{pq} \langle \mathcal{D}^+ H_p H_{pq} \mathcal{D} \rangle^{K_i} \right. \\ &\quad + \sum'_{pq} \langle \mathcal{D}^+ H_{pq} H_{qp} \mathcal{D} \rangle^{K_i} \\ &\quad + \sum'_{pqr} \langle \mathcal{D}^+ H_{pq} H_{qr} \mathcal{D} \rangle^{K_i} \Big] \\ &\quad \left. - 2 \sum'_{ij} g(K_i) \sum'_{pq} \langle H_{ij} \mathcal{D}_{jp}^+ H_{pq} \mathcal{D}_{qi} \rangle^{K_i} \right\}.\end{aligned}\quad (11)$$

The prime at the sum has the same meaning as in eq. (8). The expressions for the shifts of moments of the Auger spectrum can be obtained directly from (9), (11) replacing the one-electron operator of radiative transition $\mathcal{D}$ by the two-electron operator of Auger transition (in the nonrelativistic approximation by the operator of Coulomb interaction).

The formulae for the averages of the products of operators given in terms of minimal sums [9, 10] are valid also in CI approximation. The simple explicit expressions for the

shift $\Delta\bar{E}_{\text{CI}}$ of emission spectrum in terms of the radial integrals have been given in [3, 4].

The symmetry of averages in the spin and angular spaces with respect to replacement of electrons by vacancies [13, 4] leads to the relations between the shifts for some conjugated types of transitions. For example, the following equalities can be obtained (the radial orbitals are supposed to be frozen) [4]:

$$\begin{aligned} \Delta\bar{E}_{\text{CI}}(K_0 l_1^{N_1} l_2^{N_2} l_3^{N_3} + K_0 l_1^{N_1+1} l_2^{N_2-2} l_3^{N_3+1}) \\ \rightarrow K_0 l_1^{N_1+1} l_2^{N_2-1} l_3^{N_3}) \\ = -\Delta\bar{E}_{\text{CI}}(K_0 l_1^{4l_1+1-N_1} l_2^{4l_2+3-N_2} l_3^{4l_3+2-N_3}) \\ \rightarrow K_0 l_1^{4l_1+2-N_1} l_2^{4l_2+2-N_2} l_3^{4l_3+2-N_3} \\ + K_0 l_1^{4l_1+1-N_1} l_2^{4l_2+4-N_2} l_3^{4l_3+1-N_3}), \end{aligned} \quad (12)$$

$$\begin{aligned} \Delta\sigma_{\text{CI}}^2(K_0 l_1^{N_1} l_2^{N_2} l_3^{N_3} \rightarrow K_0 l_1^{N_1+1} l_2^{N_2-1} l_3^{N_3} \\ + K_0 l_1^{N_1} l_2^{N_2+1} l_3^{N_3-1}) \\ = \Delta\sigma_{\text{CI}}^2(K_0 l_1^{4l_1+1-N_1} l_2^{4l_2+3-N_2} l_3^{4l_3+2-N_3} \\ + K_0 l_1^{4l_1+2-N_1} l_2^{4l_2+1-N_2} l_3^{4l_3+3-N_3} \\ \rightarrow K_0 l_1^{4l_1+2-N_1} l_2^{4l_2+2-N_2} l_3^{4l_3+2-N_3}), \end{aligned} \quad (13)$$

where K_0 means all passive shells. For these conjugated transitions the spin-angular coefficients at the radial integrals have the same expressions.

3. Global characteristics of CI effects in atoms

Besides the change of the moment of energy level spectrum some other global characteristics which characterize CI effects and their influence on the energy level spectrum can be introduced.

In the lowest order of perturbation the interaction of two levels is proportional to the absolute value of the matrix element between these levels and inversely proportional to the energetic distance between them. Thus, the following quantity, the configuration interaction strength, can be used as a measure of CI between two configurations K and K' [5, 4]:

$$T(K, K') = \frac{\sum_{\gamma\gamma'} \langle K\gamma | H | K'\gamma' \rangle^2}{\sigma^2(K, K')}, \quad (14)$$

where the summation is performed over all states γ and γ' of both configurations. $\sigma^2(K, K')$ is the variance of the energy distances between interacting levels of configurations K and K'

$$\begin{aligned} \sigma^2(K, K') \\ = \frac{\sum_{\gamma\gamma'} [\langle K\gamma | H | K\gamma \rangle - \langle K'\gamma' | H | K'\gamma' \rangle]^2 \langle K\gamma | H | K'\gamma' \rangle^2}{\sum_{\gamma\gamma'} \langle K\gamma | H | K'\gamma' \rangle^2}. \end{aligned} \quad (15)$$

The CI strength of two configurations, which differ by quantum numbers of two electrons or by one electron with different l , can be expressed in terms of the averages of irreducible Hamiltonians ($\mathcal{H}_K$ acting within configuration K'

and $\mathcal{H}_{KK'}$ acting between configurations K, K'):

$$\begin{aligned} T(K, K') = M(K, K')^2 \{ g(K) \langle \mathcal{H}_{KK'} \mathcal{H}_K \mathcal{H}_{K'} \mathcal{H}_{K'K} \rangle^K \\ + g(K') \langle \mathcal{H}_{K'K} \mathcal{H}_K \mathcal{H}_{K'} \mathcal{H}_{KK'} \rangle^{K'} \\ - 2g(K) \langle \mathcal{H}_K \mathcal{H}_{KK'} \mathcal{H}_{K'} \mathcal{H}_{K'K} \rangle^K \\ + M(K, K') [\bar{E}(K) - \bar{E}(K')] \\ \times [2\bar{E}(K, K') - \bar{E}(K) + \bar{E}(K')] \}^{-1}. \end{aligned} \quad (16)$$

Here $M(K, K')$ is defined by (6), $\bar{E}(K)$ and $\bar{E}(K')$ are the average energies of configurations K, K' and $\bar{E}(K, K')$ is the average energy distance between the interacting levels of these configurations

$$\begin{aligned} \bar{E}(K, K') \\ = \frac{\sum_{\gamma\gamma'} [\langle K\gamma | H | K\gamma \rangle - \langle K'\gamma' | H | K'\gamma' \rangle] \langle K\gamma | H | K'\gamma' \rangle^2}{\sum_{\gamma\gamma'} \langle K\gamma | H | K'\gamma' \rangle^2}. \end{aligned} \quad (17)$$

For all pairs of configurations, except the configurations differing by principal quantum number of one electron, the following formulae are valid

$$\begin{aligned} \bar{E}(K, K') = \bar{E}(K) - \bar{E}(K') + M(K, K')^{-1} g(K) \\ \times [\langle \mathcal{H}_K \mathcal{H}_{KK'} \mathcal{H}_{K'K} \rangle^K - \langle \mathcal{H}_{KK'} \mathcal{H}_{K'} \mathcal{H}_{K'K} \rangle^{K'}], \end{aligned} \quad (18)$$

$$\begin{aligned} \sigma^2(K, K') = M(K, K')^{-1} g(K) \{ \langle \mathcal{H}_K \mathcal{H}_K \mathcal{H}_{KK'} \mathcal{H}_{K'K} \rangle^K \\ - 2\langle \mathcal{H}_K \mathcal{H}_{KK'} \mathcal{H}_{K'} \mathcal{H}_{K'K} \rangle^K \\ + \langle \mathcal{H}_{KK'} \mathcal{H}_{K'} \mathcal{H}_{K'} \mathcal{H}_{K'K} \rangle^{K'} \} \\ + [\bar{E}(K) - \bar{E}(K')] [2\bar{E}(K, K') + \bar{E}(K) - \bar{E}(K')]. \end{aligned} \quad (19)$$

The CI strength $T(K, K')$, divided by the number of levels of configuration K interacting with the levels of configuration K' approximately has the meaning of the square of mixing coefficient at the wave function of configuration K' in the expansion of the wave function of configuration K .

The $T(K, K')$ can be approximately calculated using the difference of the average energies $\bar{E}(K) - \bar{E}(K')$ instead of $\sigma(K, K')$ [5].

In the second order of perturbation theory the shift of the energy for the level γ of configuration K due to its interaction with all levels of the distant configuration K' is presented

$$\Delta E(K\gamma, K') = \sum_{\gamma'} \frac{\langle K\gamma | H | K'\gamma' \rangle^2}{E(K\gamma) - E(K'\gamma')}. \quad (20)$$

The difference of energies (in the zero order) in the denominator can be approximately replaced by the average energy between the level $K\gamma$ and interacting with it levels of configuration K' (this quantity is defined similarly to (17), but only with one sum over γ'):

$$\begin{aligned} \Delta E(K\gamma, K') \\ \approx \bar{E}(K\gamma, K')^{-1} \sum_{\gamma'} \langle K\gamma | H | K'\gamma' \rangle \langle K'\gamma' | H | K\gamma \rangle. \end{aligned} \quad (21)$$

Then the summation can be accomplished in the second quantization representation [15, 16, 4].

The average shift of the energy level of configuration K due to its interaction with configuration K' is expressed [4]:

$$\Delta \bar{E}(K, K') = \frac{1}{g(K)} \sum_{\gamma} \Delta E(K\gamma, K') \approx \frac{M(K, K')}{g(K)\bar{E}(K, K')}, \quad (22)$$

where $M(K, K')$ is the sum of the squares of matrix elements (6) and $\bar{E}(K, K')$ is the average energy (17).

4. Investigation of CI with symmetric exchange of symmetry and other many-electron effects

One of the most important configuration interaction types in atoms is the so-called CI with symmetric exchange of symmetry [17]: the orbital quantum number of one electron is decreased by 1 and of the other electron is increased by 1. This interaction is strongest, when the principal quantum number of electrons does not change. Usually such configurations are obtained by creating a vacancy in a subvalent shell:

$$nl^{4l+1}n(l+1)^N + nl^{4l+2}n(l+1)^{N-2}n(l+2). \quad (23)$$

The variation of the global characteristics of the energy level spectrum for the complex of two configurations

$$3s3p^3 + 3s^23p3d \quad (24)$$

is shown in Fig. 1. The square root of the variance (the mean deviation of the levels from the average energy) $\sigma(\mathcal{K})$ characterizes the width of the spectrum. The skewness κ_1 describes the asymmetry of the spectrum and the excess κ_2 is related with the density of levels in the main part of the spectrum, these dimensionless quantities are expressed in terms of centered moments:

$$\kappa_1 = \mu_3/(\sigma^2)^{3/2}, \quad \kappa_2 = \mu_4/(\sigma^2)^2 - 3. \quad (25)$$

In neutral atoms the levels of the $3s^23p3d$ configuration are located in the lower part of the array of the $3s3p^3$ configuration [18]. On going to the first ions the $3s^23p3d$ configuration is shifted upwards with respect to the $3s3p^3$ [the average energy $\bar{E}(3s^23p3d)$ becomes higher than $\bar{E}(3s3p^3)$]. It causes the change of the sign for skewness and excess of this complex going from Si I to P II. Further in the isoelectronic series they vary monotonically.

The inclusion of CI between both configurations changes significantly the values of global characteristics and draw the values of skewness and excess nearer to the values of experimental spectra. The correspondence between characteristics of theoretical and experimental spectra remains qualitative due to the incompleteness of experimental spectra (for the spectra of various ions only 88–60% of states are registered), the use of the single-configuration radial orbitals and the approximate account of the relativistic effects for the higher ions. The exclusive deviation of all three characteristics for the experimental spectrum of Ge VIII is caused by the doubtful classification of the highest level of considered complex as the $3p3d\ ^3F_3$ in the rather old investigation [20].

The CI strength of $3s3p^3$ and $3s^23p3d$ configurations has a distinct maximum for the first ions, for which the distance between interacting levels is shortest, and then monotonically approaches to some rather large asymptotic value [Fig. 2(a)]. On the other hand the CI strength between the

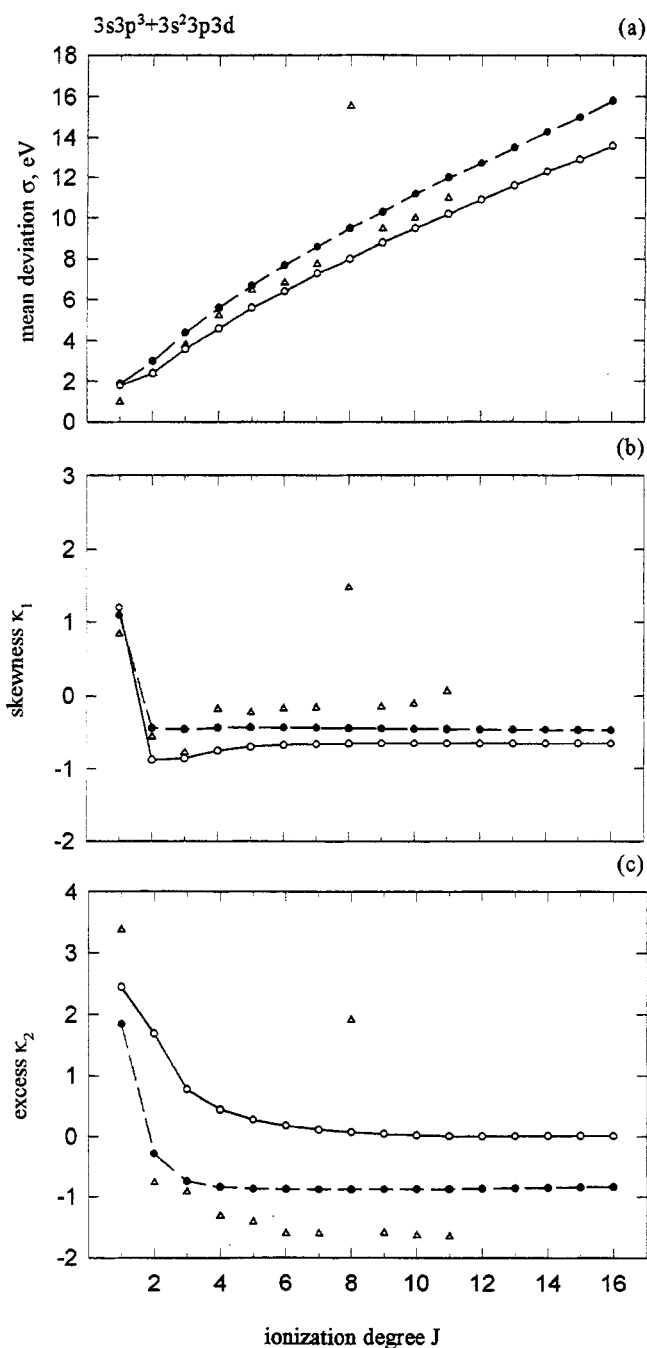


Fig. 1. Mean deviation (square root of variance) σ (a), skewness κ_1 (b) and excess κ_2 (c) for the complex of configurations $3s3p^3 + 3s^23p3d$ in the Si isoelectronic series. The solid line represents values in the single-configuration approximation, the dashed line in the two-configuration CI approximation, and triangles show the corresponding values for the experimental energy level spectra [18, 19].

$3s3p^3$ and the excited $3s^23pnd$ ($n = 4, 5$) configurations shows only a small increase for the neutral atoms and first ions. The replacement of the mean distance between interacting levels by the difference of average energies becomes less accurate for more neighbouring configurations. Such approximation gives a very sharp maximum for the strongly overlapping configurations.

The sum of the squares of interconfiguration matrix elements $M(K, K')$ as well as the mean deviation between the interacting levels of configurations $\sigma(K, K')$ show a different dependence on the ionization degree for $n = 3$ and $n = 4, 5$ [Fig. 2(b)–(c)]. The average shift of the energy of levels for the $3s3p^3$ configuration due to its interaction with $3s^23pnd$

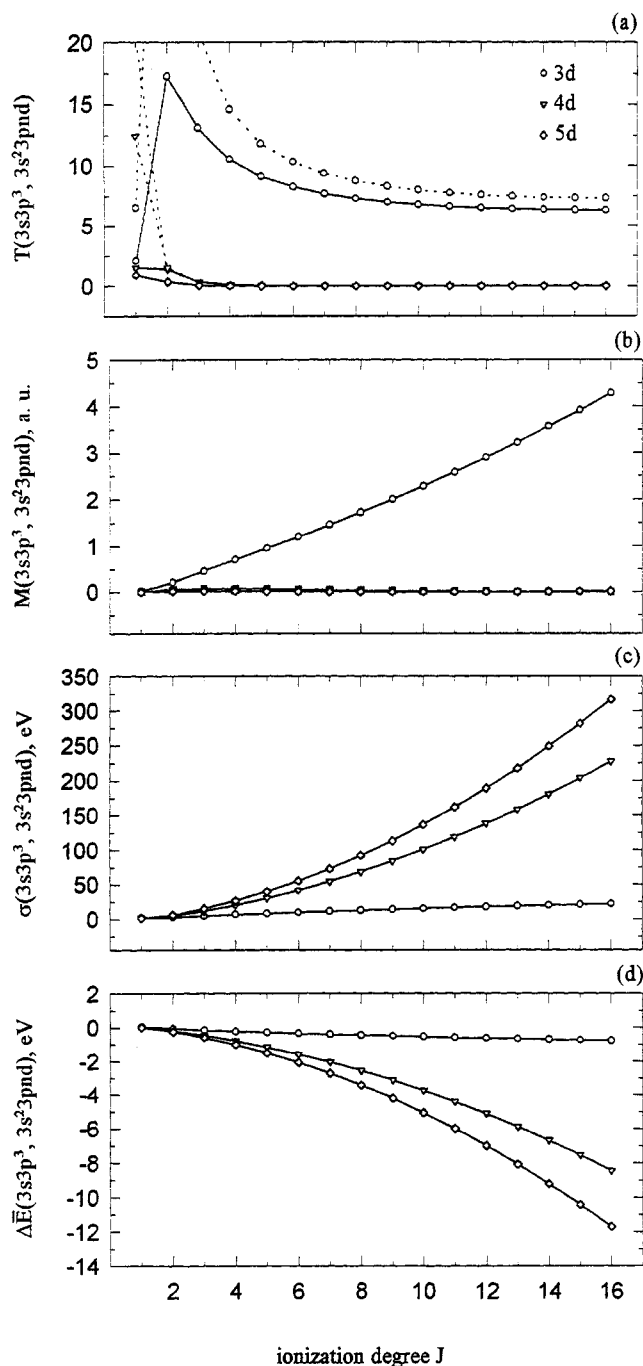


Fig. 2. CI strength $T(K, K')$ (a), sum of the squares of interconfiguration matrix elements $M(K, K')$ (b), the mean deviation between interacting levels $\sigma(K, K')$ (c) and the average shift of the energy of level $\Delta \bar{E}(K, K')$ for configurations $K = 3s3p^3$, $K' = 3s^23pnd$ ($n = 3, 4, 5$) in the Si isoelectronic series. $T(K, K')$ calculated from (14) is shown by the solid line, and approximated replacing $\sigma(K, K')$ by $\bar{E}(K) - \bar{E}(K')$ is represented by the dotted line.

($n = 3, 4, 5$) is directly proportional to $-\sigma(3s3p^3, 3s^23pnd)$ [Fig. 2(d)].

The configurations with different principal quantum numbers of one or two electrons interact strongly in the isoelectronic series only in the vicinity of the certain ionization degree, where they change their positions. Further in the series such configurations are separated energetically and the interaction between them decreases rapidly. This is clearly shown (Fig. 3) by the variation of the CI strength for various pairs of configurations from the complex:

$$3p^53d^9 + 3p^63d^74p + 3p^63d^74f. \quad (26)$$

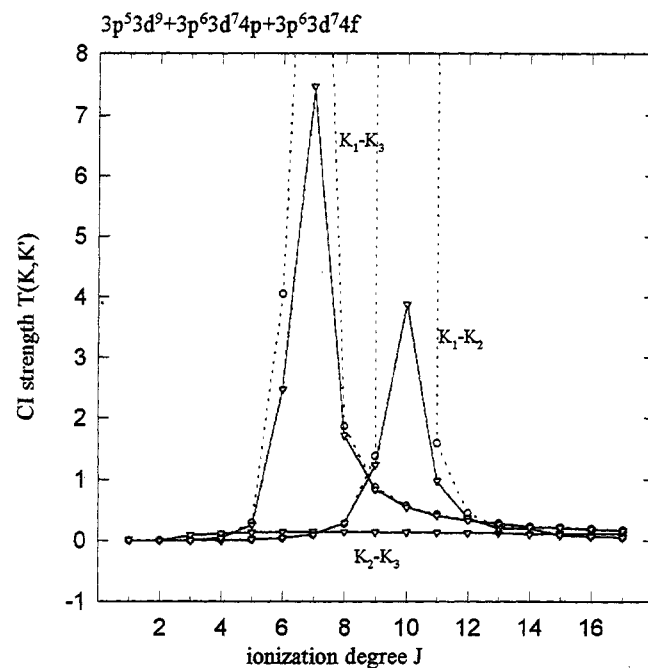


Fig. 3. Variation of the CI strength $T(K, K')$ for the all pairs of configurations from the $3p^53d^9 + 3p^63d^74p + 3p^63d^74f$ complex in the Ni isoelectronic series. The meaning of the solid and dotted lines is the same as in Fig. 2.

For such critical ionization degree the global characteristics of spectrum show an anomalous behavior (Fig. 4). The mean deviation σ as well as the width of complex obtains minimum values at the maximum overlap of configurations. On the other hand the skewness describing the asymmetry of spectrum changes its sign when both configurations interchange their places. The excess obtains its minimum value.

The dependence of the global characteristics for the $3p^53d^N + 3p^63d^{N-2}4f$ complex on the number of electrons in the d^N shell (Fig. 4) can be related with the complexity of spectrum. For the almost filled shell ($N > 2l + 1$) the mean deviation σ increases with the number of vacancies in the shell, when the number of levels of spectrum and its spread increases. The variation of κ_1 and κ_2 is less expressed for the smaller number of electrons: the deviation of their values from the zero value of normal distribution tends to diminish when increasing the complexity of spectrum. For the simplest configurations with $N = 10$ the skewness reaches the value 10 and the excess even the extremely high value 90. Similarly for the partially filled $3d^N$ shell the variation of κ_1 and κ_2 is more expressed for the simpler spectra at the smaller number of electrons N .

The same regularities in the variation of global characteristics take place for the $3p^53d^N + 3p^63d^{N-2}4p$ isoelectronic series.

The changes of the moments due to CI for the $3p^53d^N + 3p^63d^{N-2}4l$ ($l = 1, 3$) complexes are essentially smaller than for the complex (24). Probably in the case of multilevel spectrum the different shifts of various levels due to CI are partially canceled, when the summation is performed evaluating the global characteristics of spectrum.

As follows from the previous examples, the CI strength strongly depends on the average energy distance between the interacting levels. The correlation between the CI strength $T(K, K')$ (14) and the average energy $\bar{E}(K, K')$ (17)

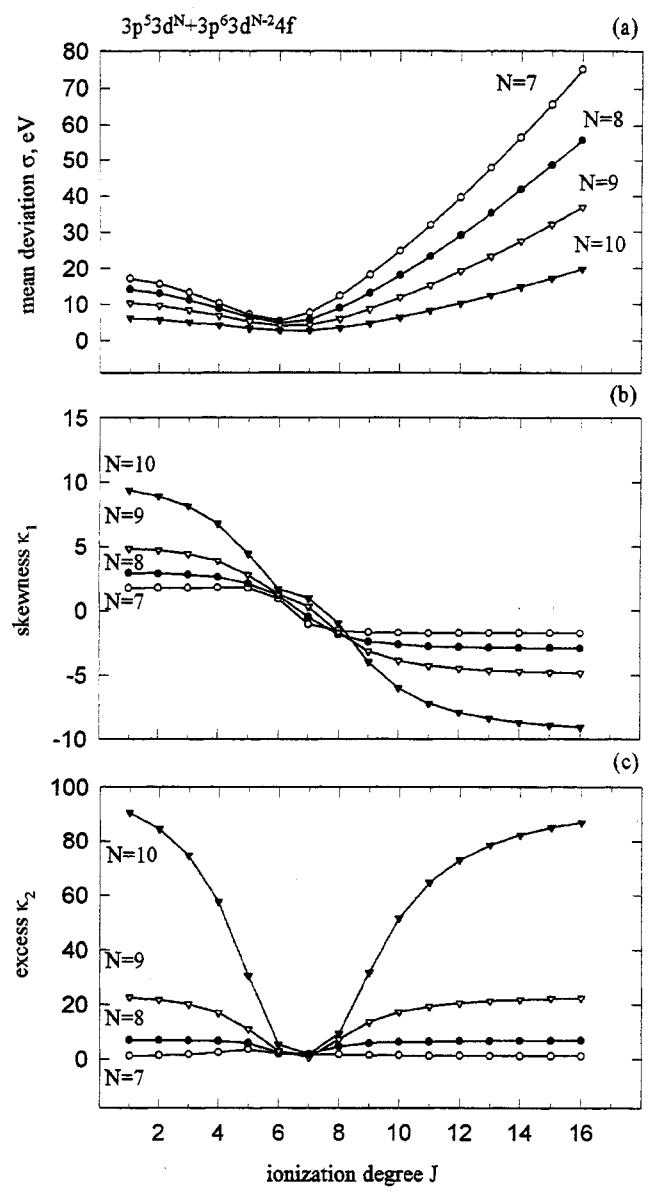


Fig. 4. Dependence of the mean deviation σ (a), skewness κ_1 (b) and excess κ_2 (c) on the ionization degree and the number of electrons N in the $3d^N$ shell (indicated near the curve) for the $3p^5 3d^N + 3p^6 3d^{N-2} 4f$ configurations.

Table I. Global characteristics for the Kr $M_{4,5}N_1N_{2,3}$ and Xe $N_{4,5}O_1O_{2,3}$ Auger spectra

Element	Global characteristics	Theoretical spectrum				Experimental spectrum [22]
		a	b	c	d [22]	
Kr	σ	2.77	4.69	4.66	5.73	5.48
	κ_1	1.41	0.30	0.32	0.17	-0.22
	κ_2	0.30	-1.49	-1.46	-1.52	-1.06
Xe	σ	1.73	4.53	4.53	4.44	3.31
	κ_1	1.95	0.49	0.49	0.38	-0.36
	κ_2	4.03	-1.31	-1.30	-1.43	-0.43

Initial $3d^{-1}$ vacancy for Kr and $4d^{-1}$ for Xe.
Final configurations:
a - single configuration approximation for Kr $4s4p^5$ and Xe $5s5p^5$;
b - CI approximation for Kr $4s4p^5 + 4s^2 4p^3 4d$ and Xe $5s5p^5 + 5s^2 5p^3 5d$;
c - CI approximation for Kr $4s4p^5 + 4s^2 4p^3 4d + 4s^2 4p^3 5s$ and Xe $5s5p^5 + 5s^2 5p^3 5d + 5s^2 5p^3 6s$;
d - multiconfigurational Dirac-Fock calculation for Kr $4s4p^5 + 4s^2 4p^3 4d + 4s^2 4p^3 5s$ and Xe $5s5p^5 + 5s^2 5p^3 5d + 5s^2 5p^3 6s$, then taking into account the configurations with the higher d and s orbitals in the CI approximation for transition probabilities.

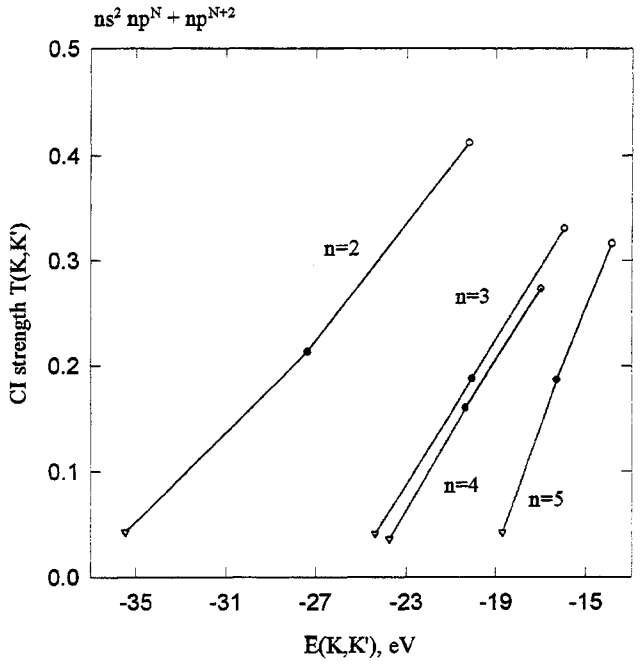


Fig. 5. Correlation between the CI strength $T(K, K')$ and the average distance between the interacting levels $\bar{E}(K, K')$ of the $ns^2 np^N + ns^0 np^{N+2}$ configurations for $N = 2$ ($\circ$), 3 ($\bullet$) and 4 (∇). The principal quantum number n is indicated near the curve.

for the $ns^2 np^N + ns^0 np^{N+2}$ complex is shown in Fig. 5. The dependence is approximately linear and is described for various N by almost parallel lines. The similarity of this dependence for $n = 3$ and 4 is caused by the slow variation of the sum $M(K, K')$ as well as of $\sigma(K, K')$ (15) on going from $n = 3$ to $n = 4$ (Fig. 6). These quantities depend on n and N rather nonmonotonically.

The intersection of configurations in the isoelectronic series also manifests by the anomalies in variation of global characteristics for the corresponding emission spectra. Figure 7 shows the change of σ , κ_1 and κ_2 for the characteristic emission spectrum corresponding to the transitions



According to Fig. 3, the intersection of the initial configurations takes place at $J = 10$. Namely, for Br X the mean deviation obtains its minimum value, the skewness and excess also varies nonmonotonically (Fig. 7). For this and neighboring values of J the κ_1 and κ_2 essentially differ in the single-configuration and the CI approximations. The CI effect is more pronounced for the emission spectrum than for the corresponding energy level spectrum.

In the CI approximation like in the single-configuration approximation [21, 9] the transition zones of the emission spectrum can be introduced. They characterize the participation of various initial or final levels in the considered transitions. As it is demonstrated in Fig. 8 the CI can essentially change the position and width of the emissive zone.

The CI between configurations with symmetric exchange of symmetry can play very important role in the formation of Auger spectra. For example, the strong satellite structure due to CI appears in the $M_{4,5}N_1N_{2,3}$ spectrum of Kr and the $N_{4,5}O_1O_{2,3}$ spectrum of Xe. The values of the mean deviation, skewness and excess for these spectra, calculated in the single-configuration approximation, differs considerably from the corresponding values of the experimental

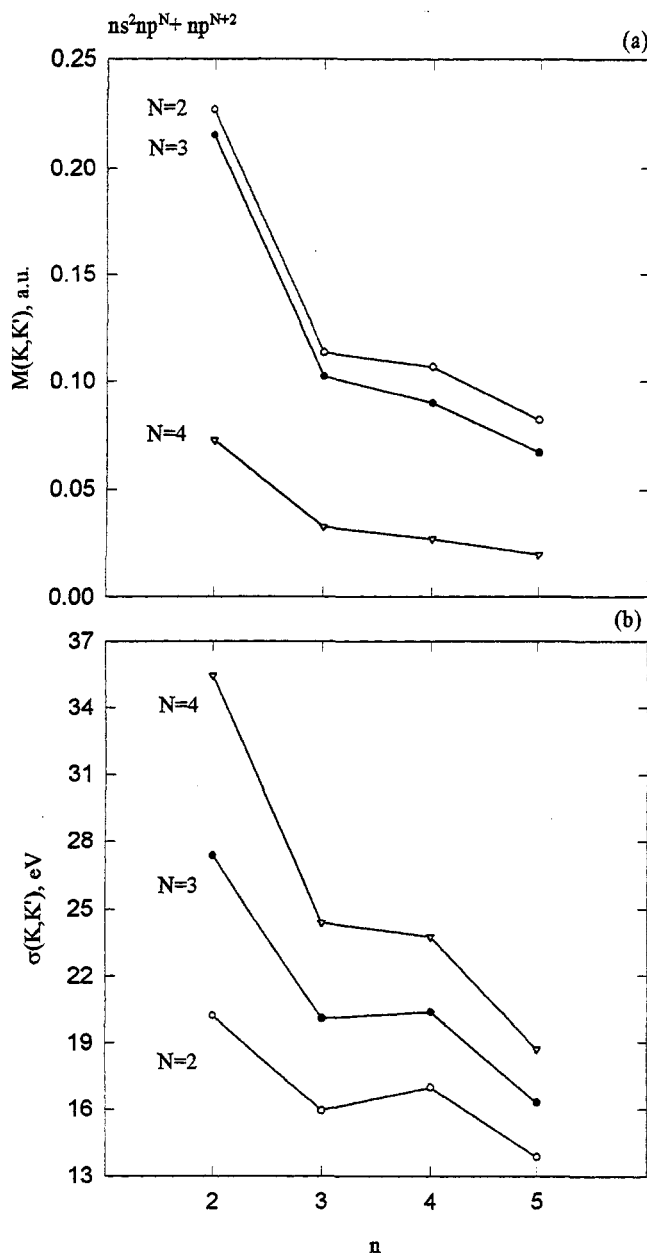


Fig. 6. Dependence of the sum $M(K, K')$ (a) and the mean deviation $\sigma(K, K')$ (b) on the principal quantum number n for the configurations $K = ns^2 np^N$, $K' = np^{N+2}$. The number of electrons N in the np^N shell is indicated near the curve.

spectra (Table I). The theoretical values are essentially improved, taking into account the interaction of the final configuration $nsnp^5$ with the $ns^2 np^3 nd$, which gives a rise to the strongest satellite lines. The addition of the $ns^2 np^3 (n+1)s$ configuration to the final complex of configurations in the CI approximation almost does not change the values of global characteristics. On the other hand the multiconfiguration calculation of these three configurations and the account of configurations with higher d and s orbitals for the obtaining of transition probabilities in the CI approximation [22] gives more accurate values of σ and κ_1 , though some discrepancies for κ_1 , κ_2 still remain.

5. Conclusions

The global characteristics of CI effects in atoms give the possibility to estimate and investigate CI and its influence on various spectra without performing the detailed calcu-

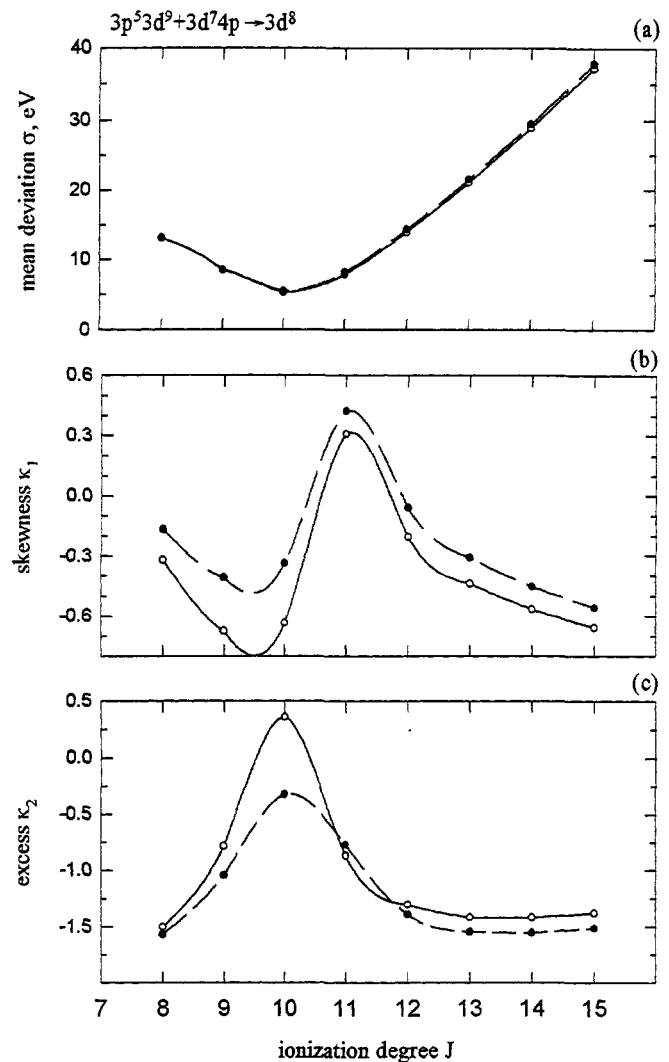


Fig. 7. Mean deviation σ (a), skewness κ_1 (b) and excess κ_2 (c) for the emission spectra, corresponding to the $3p^5 3d^9 + 3d^7 4p \rightarrow 3d^8$ in the Fe isoelectronic series. The solid line represents values in the single-configuration approximation and the dashed line in the CI approximation.

lation of spectra. At the ionization degrees for which the configurations interchange their mutual positions, the variance, skewness and excess show the nonmonotonical variation. Such variation is more sudden for simpler spectra with smaller number of levels. The CI strength mainly depends on the energetic distance between interacting configurations; in the isoelectronic sequence it obtains a sharp maximum for the intersecting configurations, but monotonically approaches to some rather large asymptotic value for the configurations, for which all electrons maintain their principal quantum numbers.

The global characteristics of the considered emission and Auger spectra are more sensitive to the CI effects than the characteristics of the energy level spectra: the two- or three-configuration CI approximation does not always ensure even the qualitative agreement between the global characteristics of calculated and experimental spectra.

The values of skewness and especially excess depend more on the accuracy of the used approximation, than the value of variance.

Acknowledgement

This work is partially supported by EC under Contract No ERB CIPD CT94-0025.

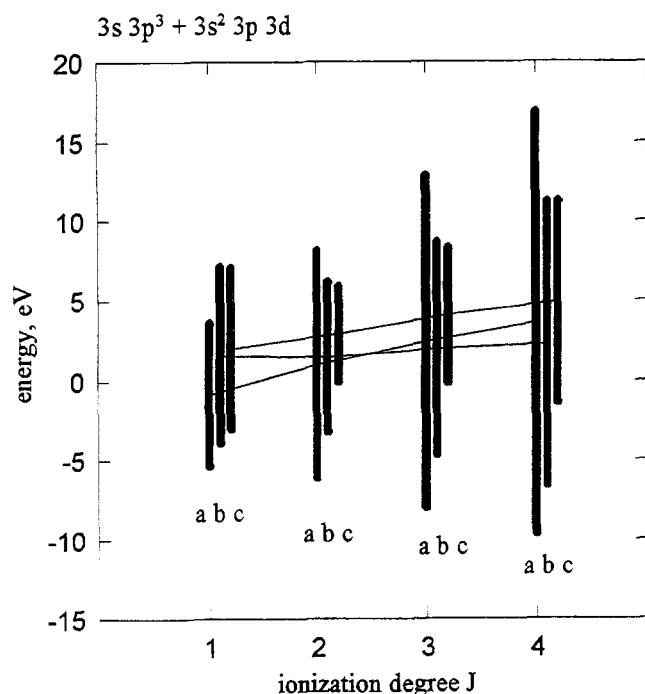


Fig. 8. The energy intervals of the complex of $3s3p^3 + 3s^23p3d$ configurations (a) and of the emissive zones of this complex for the transitions to the $3s^23p^2$ configuration in the single-configuration (b) and the CI (c) approximations for various ionization degrees J in the Si isoelectronic series. The energies are given with respect to $\bar{E}(3s3p^3)$, which has been taken equal to 0.

Appendix I.

Expressions for the sums of the squares of interconfiguration matrix elements

When the interacting configurations differ by the quantum numbers of two electrons, the sum of the squares of matrix elements over all many-electron states of both configurations for the operator of Coulomb interaction is expressed:

$$\sum_{\gamma\gamma'} \langle K_0 l_1^{N_1} l_2^{N_2} \gamma | H^e | K_0 l_1^{N_1-2} l_2^{N_2+2} \gamma' \rangle^2 = g(K_0) \binom{4l_1}{N_1-2} \binom{4l_2}{N_2} M(l_1 l_1, l_2 l_2). \quad (\text{A.1})$$

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

In (A.1), (A.2) $g(K_0)$ is the statistical weight of the electronic shells, which have the same number of electrons in both configurations, and $M(l_1 l_1, l_2 l_2)$, $M(l_1 l_1, l_2 l_3)$ are the particular cases of the sum of two electron matrix elements:

$$\begin{aligned} M(l_1 l_2, l_3 l_4) &= \sum_{LS} [L, S] \langle l_1 l_2 L S | h^e | l_3 l_4 L S \rangle^2 \\ &= 16 N_{l_1, l_2}^2 N_{l_3, l_4}^2 \\ &\times \sum_{kk'} \left\{ \frac{\delta(k, k')}{2k+1} \right. \\ &\times [\mathcal{R}^k(l_1 l_2, l_3 l_4)^2 + \mathcal{R}^k(l_1 l_2, l_4 l_3)^2] \\ &\left. - (-1)^{k+k'} \begin{pmatrix} l_1 & l_3 & k \\ l_2 & l_4 & k' \end{pmatrix} \right\} \end{aligned}$$

$$\times \mathcal{R}^k(l_1 l_2, l_3 l_4) \mathcal{R}^k(l_1 l_2, l_4 l_3) \}, \quad (\text{A.3})$$

where h^e is the two electron Coulomb interaction operator, N_{l_1, l_2} is the normalization constant

$$\begin{aligned} N_{l_1, l_2} &\equiv N_{n_1 l_1, n_2 l_2} \\ &= \begin{cases} 1/2 & \text{for the equivalent electrons } (n_1 = n_2, l_1 = l_2); \\ 1/\sqrt{2} & \text{for the nonequivalent electrons;} \end{cases} \end{aligned} \quad (\text{A.4})$$

and $\mathcal{R}^k$ is the radial integral R^k for Coulomb interaction, multiplied by the single electron reduced matrix elements of spherical harmonic $C^{(k)}$

$$\begin{aligned} \mathcal{R}^k(l_1 l_2, l_3 l_4) &\equiv \mathcal{R}^k(n_1 l_1 n_2 l_2, n_3 l_3 n_4 l_4) \\ &= R^k(n_1 l_1 n_2 l_2, n_3 l_3 n_4 l_4) \\ &\times \langle l_1 || C^{(k)} || l_3 \rangle \langle l_2 || C^{(k)} || l_4 \rangle. \end{aligned} \quad (\text{A.5})$$

When the interacting configurations differ by the orbital quantum number of one electron, the interconfiguration matrix elements of one-electron operator of potential and kinetic energy as well as of the spin-orbit operator vanish. The sum of the squares of matrix elements of the Coulomb interaction operator becomes equal to

$$\begin{aligned} \sum_{\gamma\gamma'} \langle K_0 l_1^{N_1} l_2^{N_2} \gamma | H^e | K_0 l_1^{N_1-1} l_2^{N_2+1} \gamma' \rangle^2 &= g(K_0) \left[\binom{4l_1-1}{N_1-2} \binom{4l_2+1}{N_2} \right. \\ &\times M(l_1 l_1, l_1 l_2) + \binom{4l_1+1}{N_1-1} \binom{4l_2-1}{N_2-1} M(l_1 l_2, l_2 l_2) \left. \right] \\ &+ \sum_i \frac{g(K_0)}{g(l_i^{N_i})} \binom{4l_i}{N_i-1} \binom{4l_i+1}{N_i-1} \\ &\times \binom{4l_2+1}{N_2} M(l_i l_1, l_i l_2), \quad l_1 \neq l_2, \end{aligned} \quad (\text{A.6})$$

where the summation i is carried out over all shells of K_0 , having the same electron numbers in both configurations.

In the case of one electron excitation without the change of its orbital quantum number the considered sum for the nonrelativistic Hamiltonian obtains the following expression:

$$\begin{aligned} \sum_{\gamma\gamma'} \langle n_1 l_1^{N_1} n_2 l_2^{N_2} \gamma | H | n_1 l_1^{N_1-1} n_2 l_2^{N_2+1} \gamma' \rangle^2 &= \binom{4l+1}{N_1-1} \binom{4l-1}{N_2-1} M(n_2 l n_2 l, n_1 l n_2 l) \\ &+ \binom{4l-1}{N_1-2} \binom{4l+1}{N_2} M(n_1 l n_1 l, n_1 l n_2 l) + [l]^{-1} \\ &\times \left[\binom{4l+1}{N_1-1} \binom{4l-1}{N_2-2} M'(n_2 l n_2 l, n_2 l n_1 l)^2 \right. \\ &+ \binom{4l-1}{N_1-3} \binom{4l+1}{N_2} M'(n_1 l n_1 l, n_1 l n_2 l)^2 \\ &+ 2 \binom{4l}{N_1-2} \binom{4l}{N_2-1} \\ &\times M'(n_1 l n_1 l, n_1 l n_2 l) M'(n_2 l n_2 l, n_2 l n_1 l) \left. \right] \\ &+ 2\sqrt{2} I(n_1 l, n_2 l) \left[\binom{4l}{N_1-2} \binom{4l+1}{N_2} \right. \end{aligned}$$

$$\begin{aligned}
& \times M'(n_1 l n_1 l, n_1 l n_2 l) + \binom{4l+1}{N_1-1} \\
& \times \binom{4l}{N_2-1} M'(n_2 l n_2 l, n_2 l n_1 l) \Big] \\
& + (4l+2) \binom{4l+1}{N_1-1} \binom{4l+1}{N_2} I(n_1 l, n_2 l)^2 \\
& + \binom{4l+1}{N_1-1} \binom{4l+1}{N_2} \frac{1}{2} l(l+1)(2l+1) \zeta_{n_1 l, n_2 l}^2. \quad (\text{A.7})
\end{aligned}$$

Here not only the minimal sum (A.3) but also the sum of other type appears:

$$\begin{aligned}
& M'(n_1 l_1 n_2 l_2, n'_1 l_1 n'_2 l_2) \\
& = \sum_{LS} [L, S] \langle n_1 l_1 n_2 l_2 L S | h^e | n'_1 l_1 n'_2 l_2 L S \rangle \\
& = 4N_{n_1 l_1, n_2 l_2} N_{n'_1 l_1, n'_2 l_2} \left[2[l_1, l_2] R^0(n_1 l_1 n_2 l_2, n'_1 l_1 n'_2 l_2) \right. \\
& \quad \left. - \sum_k (-1)^k \mathcal{R}^k(n_1 l_1 n_2 l_2, n'_2 l_2 n'_1 l_1) \right] \quad (\text{A.8})
\end{aligned}$$

In (A.7) $\zeta_{n_1 l, n_2 l}$ is the spin-orbit parameter for the nondiagonal with respect to configurations matrix element and $I(n_1 l, n_2 l)$ is the integral:

$$I(n_1 l, n_2 l) = -\frac{1}{2} \int_0^\infty P_{n_1 l}(r) \left[\frac{d^2}{dr^2} + \frac{2Z}{r} - \frac{l(l+1)}{r^2} \right] P_{n_2 l}(r) dr, \quad (\text{A.9})$$

where $P_{n_1 l}(r)$ is the radial orbital.

When the third passive shell is contained besides the shells involved in the excitation, some additional terms appear:

$$\begin{aligned}
& \sum_{\gamma\gamma'} \langle n_1 l^{N_1} n_2 l^{N_2} n_3 l^{N_3} \gamma | H | n_1 l^{N_1-1} n_2 l^{N_2+1} n_3 l^{N_3} \gamma' \rangle^2 \\
& = \binom{4l_3+2}{N_3} \sum_{\gamma\gamma'} \langle n_1 l^{N_1} n_2 l^{N_2} \gamma | H | n_1 l^{N_1-1} n_2 l^{N_2+1} \gamma' \rangle^2 \\
& \quad + \binom{4l+1}{N_1-1} \binom{4l+1}{N_2} \binom{4l_3}{N_3-1} M(n_1 l n_3 l_3, n_2 l n_3 l_3) \\
& \quad + \frac{1}{4l+2} \binom{4l+1}{N_1-1} \binom{4l+1}{N_2} \\
& \quad \times \binom{4l_3}{N_3-2} M'(n_1 l n_3 l_3, n_2 l n_3 l_3)^2
\end{aligned}$$

$$\begin{aligned}
& + \frac{\sqrt{2}}{2l+1} \binom{4l_3+1}{N_3-1} M'(n_1 l n_3 l_3, n_2 l n_3 l_3) \\
& \times \left[\binom{4l+1}{N_1-1} \binom{4l}{N_2-1} M'(n_2 l n_2 l, n_2 l n_1 l) \right. \\
& \quad \left. + \binom{4l}{N_1-2} \binom{4l+1}{N_2} M'(n_1 l n_1 l, n_1 l n_2 l) \right] \\
& + 2 \binom{4l+1}{N_1-1} \binom{4l+1}{N_2} \binom{4l_3+1}{N_3-1} \\
& \times I(n_1 l, n_2 l) M'(n_1 l n_3 l_3, n_2 l n_3 l_3). \quad (\text{A.10})
\end{aligned}$$

This formula can be easily generalized for the larger number of the passive shells.

References

1. Bauche, J., Bauche-Arnoult, C., Klapisch, M., Mandelbaum P. and Schwob, J.-L., *J. Phys. B. At. Mol. Phys.* **20**, 1443 (1987).
2. Kučas, S. and Karazija, R., *Liet. Fiz. Rink.* **29**, 275 (1989).
3. Bauche, J. and Bauche-Arnoult, C., *J. Phys. B. At. Mol. Opt. Phys.* **22**, 2503 (1989).
4. Karazija, R., "Sums of Atomic Quantities and Mean Characteristics of Spectra" (Mokslas, Vilnius 1991) (in Russian).
5. Kučas, S., Karazija, R. and Tutlys, V., *Liet. Fiz. Rink.* **24**, 16 (1984).
6. Oreg, J., Goldstein, W. H., Bar-Shalom, A. and Klapisch, B., *Phys. Rev. A. Gen. Phys.* **39**, 4599 (1989).
7. Karazija, R. and Kučas, S., *Lithuan. J. Phys.* **35**, 155 (1995).
8. Kučas, S. and Karazija, R., *Physica Scripta* **47**, 754 (1993).
9. Kučas, S., Jonauskas, V., Karazija, R. and Martinson, I., *Physica Scripta* **51**, 566 (1995).
10. Kučas, S., Karazija, R., Jonauskas, V. and Aksela, S., *Physica Scripta* **52**, 639 (1995).
11. Cowan, R. D., "The Theory of Atomic Structure and Spectra" (University of California, Berkeley, 1981).
12. Karazija, R. and Rudzikaitė, L., *Liet. Fiz. Rink.* **27**, 144 (1987).
13. Ginocchio, J. N., *Phys. Rev.* **C8**, 135 (1973).
14. Bauche, J., Bauche-Arnoult, C. and Klapisch, M., *Adv. Atom. Mol. Phys.*, **23**, 131 (1987).
15. Judd, B. R. "Second Quantization and Atomic Spectroscopy" (John Hopkins University Press, Baltimore, 1967).
16. Bogdanovich, P. O. and Žukauskas, G. L., *Liet. Fiz. Rink.* **23**, 18 (1983).
17. Beck, D. R. and Nicolaides, C. A., *Phys. Rev.* **A26**, 857 (1982).
18. Hirata, R. and Haraguchi, T., "Atomic Spectral Line List", *Electronic Data Basis* (1994).
19. Kelly, R. L., *J. Phys. Chem. Ref. Data* **16**, Supl. No 1, 418 (1987).
20. Beckman, A., "Bidrag till kännedomen om skandiums spektrum i yttersta ultraviolett" (Almqvist och Wiksells Boktryckeri, Uppsala, 1937).
21. Bauche, J., Bauche-Arnoult, C., Luc-Koenig, E. and Wyart, J.-F., *Phys. Rev.* **A28**, 829 (1983).
22. Jauhiainen, J., *et al.*, *J. Phys. B. At. Mol. Opt. Phys.* **28**, 3831 (1995).