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Additional symmetry for the electronic shell in its ground state and many-electron effects

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Abstract. The additional symmetry for the properties related to the ground state of the atom is considered taking into account many-electron effects. Calculations of the $I_{4f}, I_{3d}, I_{2p}, I_{3p}$ binding energies, $4f^{N-1}5d - 4f^N$ system differences and $2p, 3p$ electron affinities in the second order of perturbation theory and in the configuration interaction approximation have been performed for the ground configurations with one open shell. The analysis of separate many-electron corrections for these quantities and their variation along the sequences of atoms and ions shows that the main corrections maintain the considered symmetry.

PACS. 31.10.+z Theory of electronic structure, electronic transitions, and chemical binding

1 Introduction

Some characteristics and properties of the ground state of atoms and ions (binding energies, differences between the energies of the lowest levels of two configurations $l^{N-1}l'$ and l^N [1–3] as well as some other physical and chemical quantities [4–7]) show additional symmetry properties. Variation of the experimental data for such quantities along the isoionic sequences, when f^N or d^N shell is filled, demonstrates regularities with respect to a quarter of the shell. Their theoretical explanation was given in single-configuration pure ground state approximation [1–8]. Usually it is related to the properties of the energy expression for the ground level of an atom [1–5,8]. The spin-polarized model in the LL-coupling scheme developed in [9] and applied for the consideration of the maximum multiplicity and ground states in [10] allows the simpler interpretation of the additional symmetry [6,7]. Such interpretation is outlined and generalized in Section 2 of this work.

The main aim of our work is to show that the dominant many-electron effects maintain the considered symmetry. Till now only the symmetry of the empirical corrections to the ground state energy was investigated [7]. In Section 3 we analyze for the first time the symmetry of various many-electron corrections to the ground state energies and their differences. For this purpose the results of systematic calculations for atoms and ions with one open shell by second order perturbation theory and configuration interaction method are used. These calculations have been performed with transformed radial orbitals [11], they are obtained from the orbitals of the considered configuration and approximate fairly well the multiconfiguration orbitals for the admixed configurations [12].

2 Symmetry with respect to a quarter of the shell in the single-configuration approximation

In the single-configuration central field model the well-known approximate symmetry between the electrons and vacancies takes place. The partially (l^N) and almost (l^{4l+2-N}) filled shells have the same many-electron terms and there exist some simple relations between spin-angular parts of matrix elements of operators for these complementary shells [12].

The electronic shell in its highest spin-multiplicity state (in the following shortly highest multiplicity state) can be separated in a unique way into two subshells with spins of electrons directed up and down [9]:

$$l^N \to \begin{cases} l_{\downarrow}^{N} & \text{for} \quad N \le 2l+1, \\ l_{\downarrow}^{2l+1} l_{\uparrow}^{N-2l-1} & \text{for} \quad N > 2l+1. \end{cases} \tag{1}$$

The electron-vacancy symmetry for the subshell having only $2l+1$ single-electron states manifests as the symmetry with respect to a quarter of the shell:

$$\begin{aligned} l^N &\to l^{2l+1-N} \quad && \text{for} \quad N \le 2l+1, \\ l^N &\to l^{6l+3-N} \quad && \text{for} \quad N > 2l+1. \end{aligned} \tag{2}$$

It takes place in the orbital space, but like the symmetry with respect to a half of the shell it is distorted in the radial space. Thus the coefficients at the radial integrals in the matrix elements of operators, whose mean value is equal to zero, differ for the highest multiplicity states of complementary shells (2) only by a phase factor. For example, the matrix element of the standard unit operator

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$U^{(k)}$ $(k \neq 0)$ fulfils the relations [9]:

$$\left\langle l^N\gamma_{\rm h}\middle|U^{(k)}\middle|l^N\gamma_{\rm h}\right\rangle = (-1)^{k+1}\left\langle l^{2l+1-N}\gamma'_{\rm h}\middle|U^{(k)}\middle|l^{2l+1-N}\gamma'_{\rm h}\right\rangle \quad \text{for} \quad N \le 2l+1, \tag{3}$$

$$\left\langle l^N\gamma_{\rm h}\middle|U^{(k)}\middle|l^N\gamma_{\rm h}\right\rangle = (-1)^{k+1}\left\langle l^{6l+3-N}\gamma'_{\rm h}\middle|U^{(k)}\middle|l^{6l+3-N}\gamma'_{\rm h}\right\rangle \quad \text{for} \quad N > 2l+1, \tag{4}$$

where $\gamma_{\rm h}$, $\gamma'_{\rm h}$ are the states of highest multiplicity (they have the same quantum numbers defined in the orbital space, but differ by the spin and seniority values).

The corresponding symmetry for the matrix elements of the Coulomb interaction within the l^N shell follows from (3, 4). The contribution of one-electron spin-orbit interaction to the ground state energy may be expressed in terms of the orbital quantum number of the shell, thus the matrix element of this interaction also obeys the considered symmetry. The other more important relativistic orbit-orbit correction has the same symmetry properties as the Coulomb interaction between electrons. Consequently, in the case of LS coupling within an electronic shell the main term-dependent relativistic corrections also obey the symmetry with respect to a quarter of the shell. However, when JJ-coupling within a shell takes place, it is split into nlj^N subshells with different number of one-electron states and the considered symmetry disappears. In actinides within $5f^N$ shell the scheme of coupling is closer to LS-coupling, thus the symmetry with respect to a quarter of the shell is characteristic not only of $4f^N$ shell in lanthanides, but also of $5f^N$ shell in actinides [5].

The binding energy of nl electron in the nl^N shell equals to the energy difference for the ground states of nl^{N-1} and nl^N configurations. The variation of this quantity in the series of atoms or ions with the filling nl^N shell mainly depends on the angular parts of matrix elements. Thus, taking the radial integrals equal for both configurations, I_{nl} is expressed in terms of the differences of coefficients at the integrals. These differences for the Coulomb and spin-orbit interaction show the "shifted" symmetry with respect to the numbers of electrons $N_0 = l+1$ and $3l+2$:

$$\begin{aligned} l^N &\to l^{2l+2-N} && \text{for} \quad N \le 2l+1, \\ l^N &\to l^{6l+4-N} && \text{for} \quad N > 2l+1. \end{aligned} \tag{5}$$

The most interesting is the case of f^N shell with a rather large number of single-electron states. Then the differences of coefficients are used:

$$\Delta e_i\left(f^N\right) = e_i\left(f^{N-1}\gamma_{\rm g}\right) - e_i\left(f^N\gamma'_{\rm g}\right), \quad i = 1, 3, \tag{6}$$

$$\Delta\chi_f\left(f^N\right) = \chi_f\left(f^{N-1}\gamma_{\rm g}\right) - \chi_f\left(f^N\gamma'_{\rm g}\right), \tag{7}$$

where e_i are the coefficients at Racah integrals E^i and χ_f is the coefficient at the spin-orbit constant; $\Delta e_2 = 0$ for the highest multiplicity states (the energies of levels are taken with respect to the average energy), $\gamma_{\rm g}$, $\gamma'_{\rm g}$ are the ground states of configurations l^{N-1} and l^N.

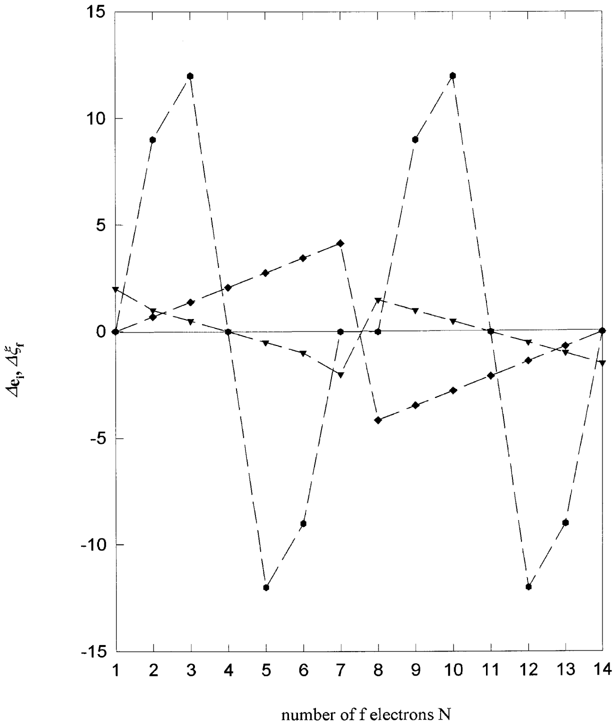

Fig. 1. Dependence of the differences of coefficients $\Delta e_1\left(f^N\right)$ (♦), $\Delta e_3\left(f^N\right)$ (●) (6) and $\Delta\chi_f\left(f^N\right)$ (7) (▾) on the number of electrons N.

The quantities $\Delta e_i, \Delta\chi_f$ fulfil the following symmetry relations [7]:

$$\begin{aligned} \Delta e_1\left(f^{N_0-q}\right) - \Delta e_1\left(f^{N_0}\right) &= -\left[\Delta e_1\left(f^{N_0+q}\right) - \Delta e_1\left(f^{N_0}\right)\right]; \\ \Delta e_3\left(f^{N_0-q}\right) &= -\Delta e_3\left(f^{N_0+q}\right); \\ \Delta\chi\left(f^{N_0-q}\right) &= -\Delta\chi\left(f^{N_0+q}\right), \\ N_0 &= 4,\ 11;\ q = 1,\ 2,\ 3. \end{aligned} \tag{8}$$

Thus Δe_i, $\Delta\chi_f$ as the functions of N consist of two similar segments (symmetry with respect to a half of the shell) and each segment can be coincided with itself performing the rotation by the angle 180° around the points corresponding to $N_0 = 4$ or 11 (symmetry with respect to a quarter of the f^N shell) (Fig. 1). The differences of the coefficients for p^N and d^N shells fulfil the similar relations, but then the dependence on N is more simple. The trivial case of the symmetry with respect to a quarter of the shell is the linear dependence of the quantity on N (the segment of the straight line is coincided with itself rotating it by the angle 180° around a mean point of the segment).

The dependence of the binding energy on N in single-configuration approximation is mainly determined by the difference of the principal coefficient (for $4f$ and even $5f$ electrons by Δe_1 having simple zigzag form), but obtains more complex character due to the contributions of other coefficients (Fig. 2). The results are given for the triple ions of lanthanides with the ground configuration containing no other open shells except $4f^N$. The calculations have

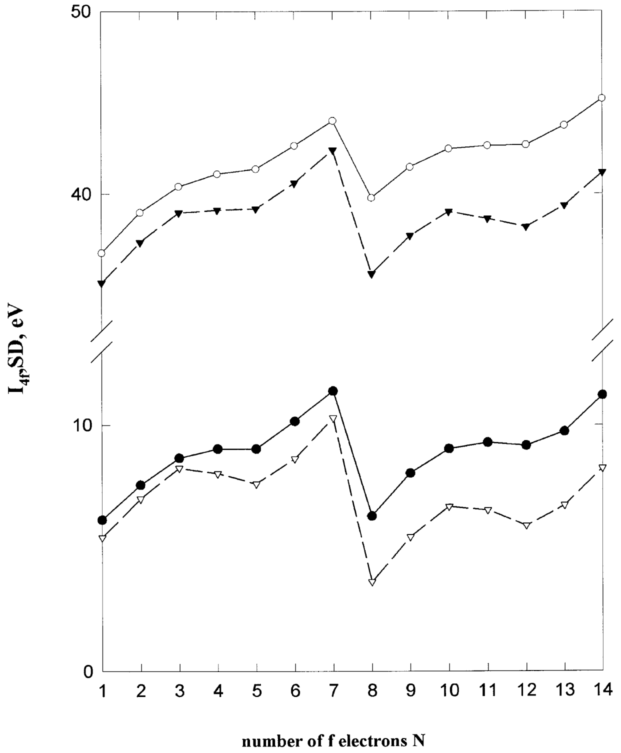

Fig. 2. I_{4f} binding energy (○, experiment [13,14], ▼ HFP pure coupling calculation) and the system difference (SD) (●, experiment compiled in [12]; ▽, HFP calculation) in the sequence of triply ionized lanthanides Ln^{3+}.

been performed in a single-configuration pure ground state approximation with Hartree-Fock wave functions taking into account the relativistic corrections in the Breit-Pauli form [15] (Hartree-Fock-Pauli (HFP) method). The same though more approximate symmetry with respect to a quarter of the nl^N shell takes place for the difference of the ground state energies of two configurations $nl^{N-1}n'l'$ and nl^N [1,2], if the interaction within nl^{N-1} shell is considerably stronger than its interaction with the excited $n'l'$ electron. The characteristic example is given by the configurations $nf^{N-1}(n+1)d - nf^N$, then this quantity has the special name "system difference" (SD).

3 Configuration-mixing corrections and their symmetry

The regularities briefly described in the previous section follow from the single-configuration pure ground state approximation. However, this symmetry is usually not distorted by term and configuration mixing effects: for example, the experimental values of I_{4f} and system difference in the sequence of triply ionized lanthanides differ significantly from the values calculated in the one-term HFP approximation (see Fig. 2), but characteristic symmetry properties with respect to a half and a quarter of the shell remain. What are the reasons of such invariance?

Of course, the ground state is usually separated energetically from other states, especially in the case of one open shell, thus the pure coupling approximation is the best namely for the ground state. On the other hand, the terms of the highest multiplicity tend to lay lower in the spectrum and the ground term is mixed more strongly with them. Such mixing does not violate the considered symmetry which takes place for all terms of the highest multiplicity.

The mixing with distant configurations can be taken into account in the second order of perturbation theory. Then the difference between the energies of the γ_g ground level of configuration K and γ perturbing levels of configuration K' can be averaged ($E(K\gamma_g) - E(K'\gamma)$ is replaced by $E(K\gamma_g) - E^{av}(K')$) and the correction to the ground state energy $\Delta E(K\gamma_g)$ is expressed in terms of the matrix element of some effective operator acting on the ground state [16].

In the case of one open l^N shell there exist only four basic types of admixing configurations K', which differ from the considered configuration K with one open nl^N shell by the quantum numbers of two electrons:

(a) $nl^{N-2}l'l''$ and $nl^{N-2}l'^2$;

(b) $l'^{4l'+1}l''^{4l''+1}l^{N+2}$ and $l'^{4l'}l^{N+2}$;

(c) $l_1^{4l_1}l^{N+1}l'$ and $l_1^{4l_1+1}l_2^{4l_2+1}l^{N+1}l'$;

(d) $l_1^{4l_1}l^Nl'l''$, $l_1^{4l_1}l^Nl'^2$, $l_1^{4l_1+1}l_2^{4l_2+1}l^Nl'l''$ and $l_1^{4l_1+1}l_2^{4l_2+1}l^Nl'^2$.

It is convenient to separate $\Delta E(K\gamma_g)$ into term-dependent (ΔE_t) and term-independent (ΔE_0) parts in the following way (the expression is given for the first configuration of every type, the contributions of other configurations have the similar form and the same dependence on N):

(a, b)

$$\Delta E_t = -\left[E(K\gamma_g) - E^{av}(K')\right]^{-1} \sum_{kk'} \mathfrak{R}^k \mathfrak{R}^{k'} \times \sum_{t>0} (-1)^t (2t+1) \begin{Bmatrix} k & k' & t \\ l & l & l' \end{Bmatrix} \begin{Bmatrix} k & k' & t \\ l & l & l'' \end{Bmatrix} \times \langle l^N\gamma_g | (U^{(t)}U^{(t)}) | l^N\gamma_g \rangle; \quad (9)$$

(a)

$$\Delta E_0 = \frac{N}{2l+1}\left[E(K\gamma_g) - E^{av}(K')\right]^{-1} \sum_{kk'} \mathfrak{R}^k \mathfrak{R}^{k'} \times \left[\begin{Bmatrix} k & l & l' \\ k' & l & l'' \end{Bmatrix} - \frac{\delta(k,k')}{2k+1}\frac{N}{2l+1}\right]; \quad (10)$$

(b)

$$\Delta E_0 = \frac{4l+2-N}{2l+1}\left[E(K\gamma_g) - E^{av}(K')\right]^{-1} \sum_{kk'} \mathfrak{R}^k \mathfrak{R}^{k'} \times \left[\begin{Bmatrix} k & l & l' \\ k' & l & l'' \end{Bmatrix} - \frac{\delta(k,k')}{2k+1}\frac{4l+2-N}{2l+1}\right]; \quad (11)$$

(c, d)

$$\Delta E_{\mathrm{t}} = 0; \tag{12}$$

(c)

$$\Delta E_0 = \frac{4l+2-N}{2l+1}\Big[E\big(K\gamma_{\mathrm{g}}\big) - E^{\mathrm{av}}(K')\Big]^{-1} \sum_{kk'} \mathfrak{R}^k \mathfrak{R}^{k'} \times \left[\begin{Bmatrix} k & l_1 & l \\ k' & l_1 & l' \end{Bmatrix} - 2\frac{\delta(k,k')}{2k+1}\right]; \tag{13}$$

(d)

$$\Delta E_0 = 2\Big[E\big(K\gamma_{\mathrm{g}}\big) - E^{\mathrm{av}}(K')\Big]^{-1} \sum_{kk'} \mathfrak{R}^k \mathfrak{R}^{k'} \times \left[\begin{Bmatrix} k & l_1 & l' \\ k' & l_1 & l'' \end{Bmatrix} - 2\frac{\delta(k,k')}{2k+1}\right]. \tag{14}$$

Here $\mathfrak{R}^k$, $\mathfrak{R}^{k'}$ are the Coulomb radial integrals multiplied by the corresponding one-electron submatrix elements of spherical harmonics. It follows from (3, 4) that the coefficients at the radial integrals $\mathfrak{R}^k$, $\mathfrak{R}^{k'}$, for the term-dependent part of the correction (9) are symmetric with respect to a quarter of the shell (ΔE_{t} disappears in the (c) and (d) cases). On the other hand, the quantity ΔE_0 contains a term quadratic on N which does not obey the considered symmetry.

The correction due to mixing with a distant configuration corresponding to one-electron excitation can also be separated into term-dependent and term-independent parts, however, the first one contains the matrix element of a three-electron operator, which is not symmetric for complementary configurations (2). On the other hand, there are rather large matrix elements between the admixed configurations of the Brillouin's type while using the approximate wave functions and the calculation of many-electron effects in the second order of the perturbation theory becomes inaccurate. For this reason the influence of such configurations have been calculated by the configuration interaction method.

Calculation in the second order perturbation theory becomes rather effective using the transformed radial orbitals [11,17]. In contrast to previous works with their use [17–19], in this work we applied more complex transformations with a variable parameter [20]. The transformed radial orbital $P_{\mathrm{tr}}\big(n'l'\big|r\big)$ is obtained from the Hartree-Fock radial orbital $P_{\mathrm{HF}}\big(nl\big|r\big)$ of the configuration under adjustment multiplying it by the transforming function $f(r)$

$$P_{\mathrm{tr}}\big(n'l'\big|r\big) = Nf(r)\,P_{\mathrm{HF}}\big(nl\big|r\big), \tag{15}$$

where N is the normalization factor. The two forms (algebraic and exponential) of the $f(r)$ function have been used:

$$f_{\mathrm{a}}(r) = \frac{r^k}{\alpha + r^m}, \quad f_{\mathrm{e}}(r) = r^k \exp\big(-\alpha r^m\big). \tag{16}$$

The parameters k and m are positive and integer numbers, they could be deduced in some way from a physical consideration [20]. The parameter α as well as the form of $f(r)$ function are determined from the condition of the maximum of the averaged (over all terms of the considered configuration) energy correction in the second order of perturbation theory.

For the atoms and ions with a filling $2p^N$ shell the basis of the transformed radial orbitals with the principle quantum number n from 3 up to 5 and orbital quantum number $l \leq 4$ was set. Such basis takes into account about 30 admixed configurations. In the case of $3p^N$ shell the orbitals with $4 \leq n \leq 6$ and $l \leq 5$ were used and the number of admixed configurations was about 140. The consideration of configurations with the open $3d^N$ shell included the transformed radial orbitals with $4 \leq n \leq 7$ and $l \leq 5$, thus the number of admixed configurations reached 170. The largest number of such configurations (1400–2100) was taken into account for the lanthanide ions, then all possible admixed configurations corresponding to two-electron excitations with $6 \leq n \leq 10,\ 0 \leq l \leq 6$ were calculated in the second order of perturbation theory. The spin-angular parts of the matrix elements were calculated using the tables of reduced coefficients of fractional parentage [21].

The systematic investigation of the many-electron corrections for the energies of the ground state and the binding energies of $4f^N$ electrons has been performed for the triple lanthanide ions (Ln^{3+}) with $4f^N$ open shell.

The corrections for the binding energy I_{4f} in various approximations are shown in Figure 3. In the case of f^N shell, the symmetry of the considered quantity with respect to a half of the shell manifests itself by similarity of two segments of the curve corresponding to the intervals $N = 1{-}7$ and $8{-}14$ and the symmetry with respect to a quarter of the shell manifests by the coincidence of the segment with itself performing the rotation by the angle 180° around the points corresponding to $N_0 = 4$ and 11. Such symmetry is characteristic of the corrections $\Delta I_{4f}^{(2)}$ and $\Delta I_{4f}^{(1)}$ corresponding to two-electron and single-electron excitations as well as for the total correction, which account for about 70–90% of difference between the HFP results and experiment. Of course, two-electron excitations play a more important role than single-electron excitations; in the second half of the group they even give negative contribution. The difference $I_{4f}^{\mathrm{exp}} - I_{4f}^{\mathrm{HFP}}$ between the experimental and calculated by single-configuration method values of I_{4f} binding energy shows that all other many-electron corrections also obey the considered symmetry.

The correction $\Delta I_{4f}^{(2)}$ is mainly determined by its term-independent part following from (10, 11, 13, 14); the term-dependent part gives only a small contribution (Fig. 4). The variation of this last quantity as well as its parts (corrections to the energies of Ln^{3+} and Ln^{4+} ground states) has symmetric but rather complicated character.

Four types of term-independent corrections (10, 11, 13, 14) have different dependence on N. As the term with $\delta(k,k')$ exceeds as a rule the $6j$ coefficient value, the correction (10) increases quadratically, (11) decreases quadratically with N, (13) decreases linearly with N and (14) does not depend on N. Taking the differences of

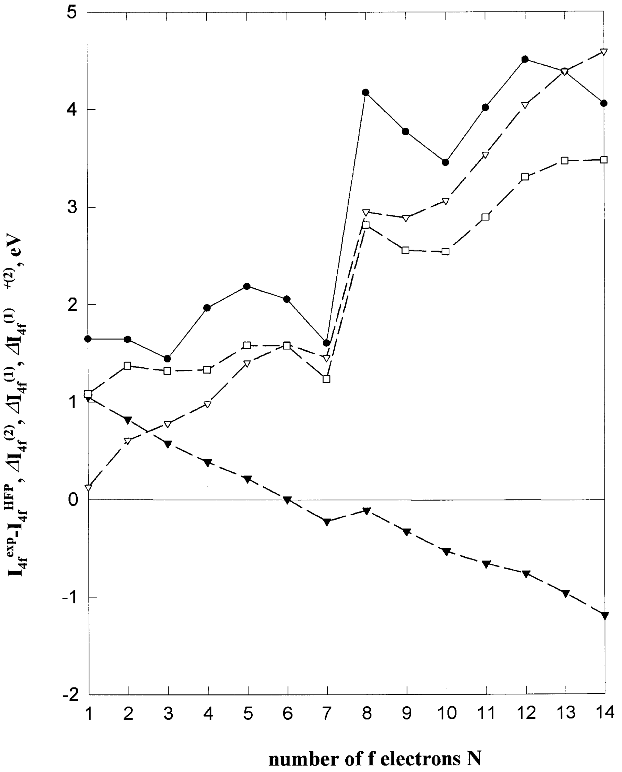

Fig. 3. Dependence of the difference $I_{4f}^{\mathrm{exp}} - I_{4f}^{\mathrm{HFP}}$ (●) as well as of configuration mixing corrections $\Delta I_{4f}^{(2)}$ (▽) (corresponding to two-electron excitation in the second order of perturbation theory), $\Delta I_{4f}^{(1)}$ (▼) (corresponding to the single-electron excitations calculated by the configuration interaction method) and the total configuration mixing correction $\Delta I_{4f}^{(1)+(2)}$ (□) (single- and two-electron excitations calculated together) on the number of $4f$ electrons in the Ln^{3+} $4f^N$ sequence.

these corrections for f^N and f^{N-1} shells, the quadratic dependence turns into linear and the linear dependence turns into the constant contribution. The linear increase of the term-independent part of $\Delta I_{4f}^{(2)}$ with N shows that it is mainly determined by two-electron excitations from $4f^N$ shell (case (a)). Some deviations from linearity, especially in the middle of the group, are caused by the dependence of the wave functions and energy denominator $\left[E(K\gamma_{\mathrm{h}}) - E^{\mathrm{av}}(K')\right]^{-1}$ on the energy of the ground state.

The correction $\Delta I_{4f}^{(1)}$ is obtained as the difference of two corrections for the energies of ground states of Ln^{4+} and Ln^{3+} (Fig. 5). They have the quadratic dependence on N and are shifted one with respect to another by $\Delta N = 1$. This explains why $\Delta I_{4f}^{(1)}$ changes the sign and becomes negative in the second part of the group. The jump between Gd^{3+} $4f^7$ and Tb^{3+} $4f^8$ is mainly caused by the dependence of the radial integrals on the ground state energy: the main term-dependent coefficient is changed in a largest extent at the middle of the group. The monotonic character of $\Delta I_{4f}^{(1)}$ and of its contributions demonstrates that as the two-electron corrections, they are mainly

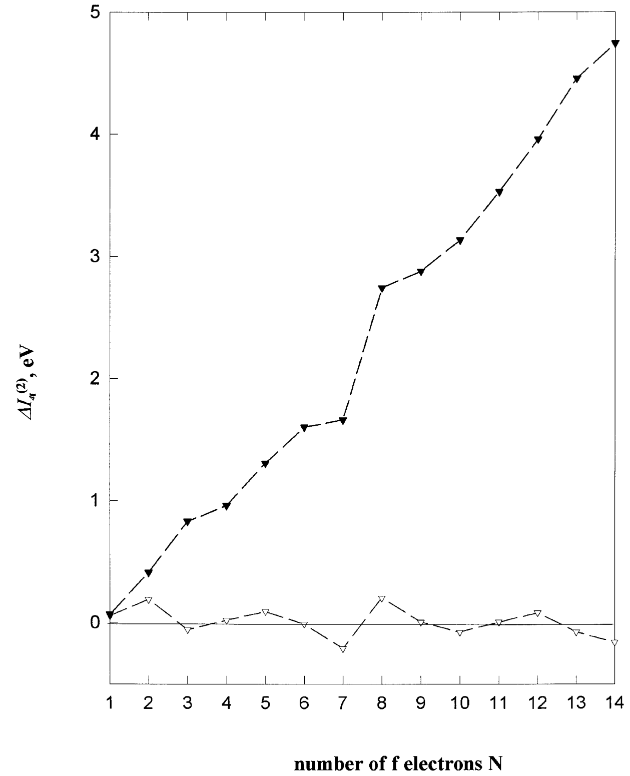

Fig. 4. Term-independent (▼) and term-dependent (▽) parts of the $\Delta I_{4f}^{(2)}$ correction for Ln^{3+}.

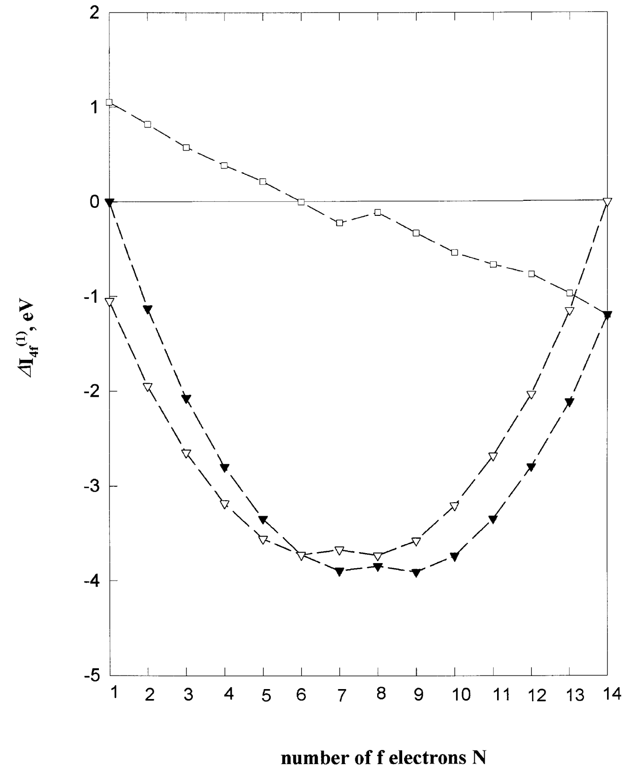

Fig. 5. Dependence of the correction $\Delta I_{4f}^{(1)}$ (□) and its separate parts for Ln^{3+} $4f^N$ (▽) and Ln^{4+} $4f^{N-1}$ (▼) ions on the number of electrons N.

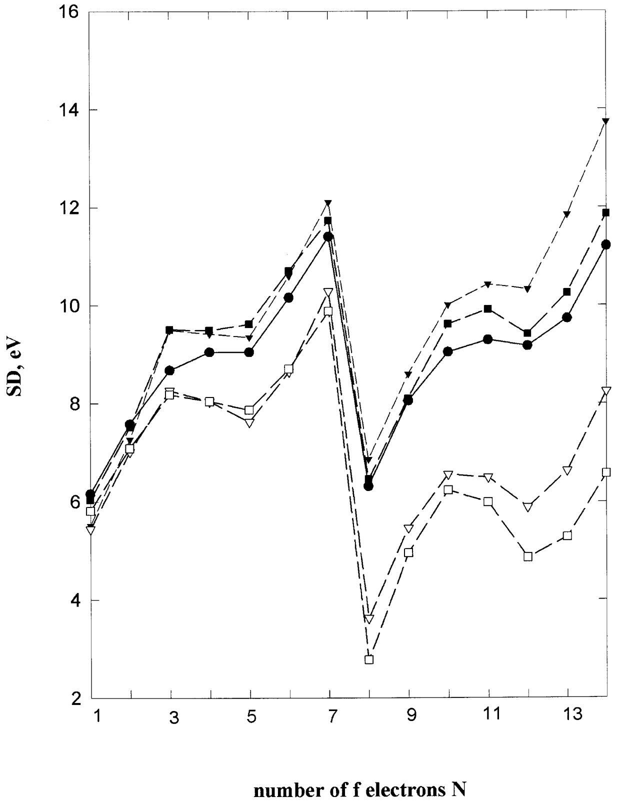

Fig. 6. System difference values for the $4f^{N-1}5d$–$4f^N$ configurations of Ln^{3+}: (●) experiment [14]; (▽) HFP calculation; (▼) $SD^{\mathrm{HFP}} + \Delta SD^{(2)}$; (□) $SD^{\mathrm{HFP}} + \Delta SD^{(1)}$; (■) $SD^{\mathrm{HFP}} + \Delta SD^{(1)+(2)}$.

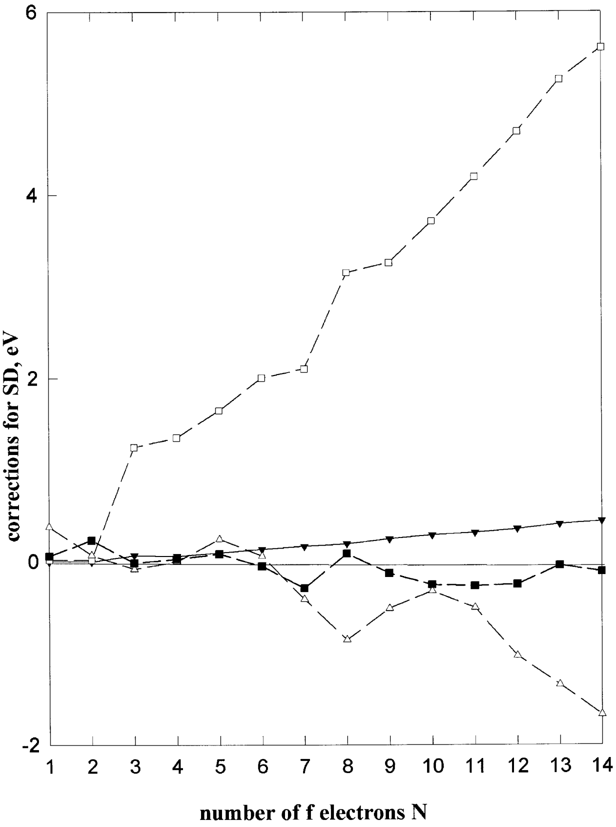

Fig. 7. Various configuration mixing corrections for the system difference in the Ln^{3+} $4f^N$ sequence: (□) term-independent part of $\Delta SD^{(2)}$; (■) term-dependent part of $\Delta SD^{(2)}$; (△) the $\Delta SD^{(1)}$ correction and (▾) $\Delta SD^{(3)+(4)}$ contribution of the three- and four-electron operators.

determined by the term-independent part. Thus $\Delta I_{4f}^{(1)}$ becomes symmetric with respect to a quarter of the shell, though its parts do not possess this property.

The values of the system difference for configurations $4f^{N-1}5d$ and $4f^N$ calculated in various approximations (Fig. 6) show more approximate symmetry than for I_{4f}. The symmetry of SD^{HFP} is distorted by Coulomb exchange interaction between $4f^{N-1}$ and $5d$ electrons as well as by mixing with the terms of lower multiplicity. The configuration-mixing corrections in the second order of perturbation theory also contain the additional part, corresponding to the three- and four-electron effective operators. It is interesting to note that the experimental values show better symmetry than the calculated values. This indicates partial compensation of non-symmetric contributions.

Configuration-mixing corrections for the system difference show the similar regularities as for I_{4f}: the term-independent part of $\Delta SD^{(2)}$ considerably exceeds its term-dependent part and increases with N, the $\Delta SD^{(1)}$ correction decreases and becomes negative (however, its linear dependence on N is distorted by the stronger dependence on the term) (Fig. 7). At the numbers of electrons $N = 0$, 1 and 13, 14 some types of excitations become impossible; it is the reason of deviations of the term-independent part of $\Delta SD^{(2)}$ from linearity as well as of the distortion of symmetry for the term-dependent part of $\Delta SD^{(2)}$ at small and large numbers of electrons. The contribution of the additional three- and four-electron terms of the effective operator $\left(\Delta SD_{4f}^{(3)+(4)}\right)$ obtains relatively small values and varies almost linearly.

In order to investigate whether the symmetry properties of the mixing corrections for I_{4f} hold for other configurations with one open shell, the calculations of I_{3d} for triple ions of the iron group have been performed. Such ionization degree was chosen to obtain the $3d^N$ ground configuration for all elements and to avoid strong $(s+d)^N$ mixing. In triple ions the configuration $3d^{N-2}4s^2$ has been treated as distant with respect to $3d^N$ configuration, its contribution calculated in the second order of perturbation theory and included into the correction $\Delta I_{3d}^{(2)}$. The configuration $3d^{N-1}4s$ has been taken into account by the configuration interaction method.

The dependence of I_{3d} on N has simpler character than for I_{4f} and is almost linear within the first and second half of the shell (Fig. 8) (as it was already mentioned, the linearity is the trivial case of the symmetry with respect to a quarter of the shell). The corrections $\Delta I_{3d}^{(2)}$ and $\Delta I_{3d}^{(1)}$ show the same regularities as for $4f$ electrons

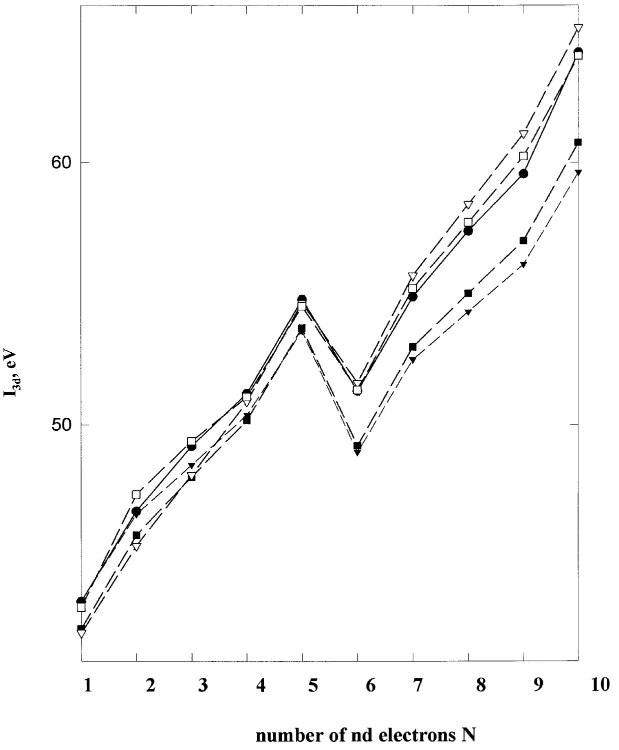

Fig. 8. I_{3d} binding energy for the triple ions of the iron group: (●) I_{3d}^{exp} [22]; (■) I_{3d}^{HFP}; (▽) $I_{3d}^{\mathrm{HFP}} + \Delta I_{3d}^{(2)}$; (▼) $I_{3d}^{\mathrm{HFP}} + \Delta I_{3d}^{(1)}$; (□) $I_{3d}^{\mathrm{HFP}} + \Delta I_{3d}^{(1)+(2)}$.

(Fig. 9): they vary almost linearly with N, though their contributions from separate configurations have quadratic character; $\Delta I_{3d}^{(2)}$ increases and, *vice versa*, $\Delta I_{3d}^{(1)}$ decreases and becomes negative in the second part of the group; the increase of the main correction $\Delta I_{3d}^{(2)}$ worsens the correspondence between the single-configuration and experimental values for the second half of the group; the term-dependent part of $\Delta I_{3d}^{(2)}$ obtains rather small values. The discrepancy of the term-independent part of $\Delta I_{3d}^{(2)}$ from linearity at small numbers of electrons is caused by the above-mentioned interdiction of some excitations from the shell with $N = 0$, 1.

It is necessary to note that not only the distant configurations but also some neighboring configurations can give the shift approximately symmetric with respect to a quarter of the shell. For example, mixing of the ground state of d^N shell with the exited state of configuration $d^{N-2}s^2$ is determined by the matrix element whose square is linear on N:

$$\left\langle d^N\gamma_{\mathrm{g}}|H^e|d^{N-2}\gamma_{\mathrm{g}}s^2\ {}^1\mathrm{S}\right\rangle^2 = \frac{1}{50}G^2(d,s)^2 \times \begin{cases} 0 & \text{if } N \le 5, \\ 2(N-5) & \text{if } N > 5, \end{cases} \tag{17}$$

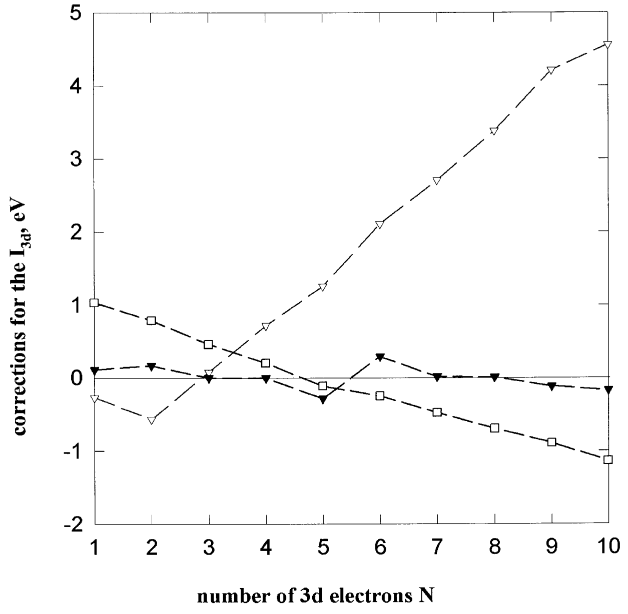

Fig. 9. Various configuration mixing corrections for the I_{3d} binding energy in the sequence of the triple ions with $3d^N$ open shell of the iron group: (▽) term-independent part of the $\Delta I_{3d}^{(2)}$ correction; (▼) term-dependent part of the $\Delta I_{3d}^{(2)}$ and (□) $\Delta I_{3d}^{(1)}$ correction.

where H^e is the Coulomb interaction operator and $G^2(d,s)$ is the Slater exchange integral. This expression is obtained by the formal summation over the states of $d^{N-2}s^2$ configuration and using of the explicit expression for the matrix element of the effective operator in the case of the highest multiplicity state.

The half of p^N shell contains only 3 electrons. The dependence of I_{np} on N is usually rather regular and linear within two halves of the shell. This is characteristic of the experimental as well as of Hartree-Fock and configuration mixing values (Fig. 10, Tab. 1). The last ones have been calculated by the configuration interaction method, because the second order of perturbation theory is not suitable for the mixing of quasidegenerate configurations (one such configuration $2s^0 2p^{N+2}$ for $2p^N$ exists even at $n = 2$). The common feature of I_{np} with I_{4f} and I_{3d} is the increase of the total correction $\Delta I^{\mathrm{exp}} - \Delta I^{\mathrm{HFP}}$ with N, especially for the second half of the group; as shown, it is caused by the main term-independent correction corresponding to the two-electron excitations from the considered shell.

The symmetry with respect to a half of the shell takes place even for the electron affinities, which strongly depend on the configuration mixing effects (Figs. 11 and 12). The linear dependence of this quantity as well as of the configuration mixing correction for it with N within the two half of the group enables their interpolation. This symmetry is approximately manifested for the ground states of negative ions with $3d^N$ open shell too [23].

Table 1. Binding energies, system differences and electron affinities calculated by configuration interaction method (CI) or combining CI with second-order perturbation method for two-electron excitations (CI+PT), in eV.

Quantity	Ionization degree	Method N	1	2	3	4	5	6	7	8	9	10	11	12	13	14
I_{4f}	4	CI+PT	36.19	38.71	40.28	40.45	40.76	42.17	43.64	38.43	40.25	41.57	41.53	41.48	42.82	44.61
SD	4	CI+PT	6.03	7.52	9.51	9.49	9.62	10.72	11.73	6.46	8.10	9.62	9.92	9.42	10.25	11.86
I_{3d}	4	CI+PT	43.05	47.35	49.39	51.07	54.55	51.33	55.21	57.72	60.24	64.06	–	–	–	–
I_{2p}	1	CI	8.24	11.13	14.40	13.33	17.16	22.10	–	–	–	–	–	–	–	–
I_{2p}	2	CI	24.27	29.49	34.98	34.74	40.77	47.08	–	–	–	–	–	–	–	–
I_{3p}	1	CI	5.92	8.03	10.29	9.87	12.36	15.15	–	–	–	–	–	–	–	–
I_{3p}	2	CI	16.23	19.67	23.26	23.49	27.37	–	–	–	–	–	–	–	–	–
$EA(2p)$	0	CI	–	0.17	1.12	−0.67	0.99	2.91	–	–	–	–	–	–	–	–
$EA(3p)$	0	CI	–	−2.51	0.85	0.99	0.94	3.42	–	–	–	–	–	–	–	–

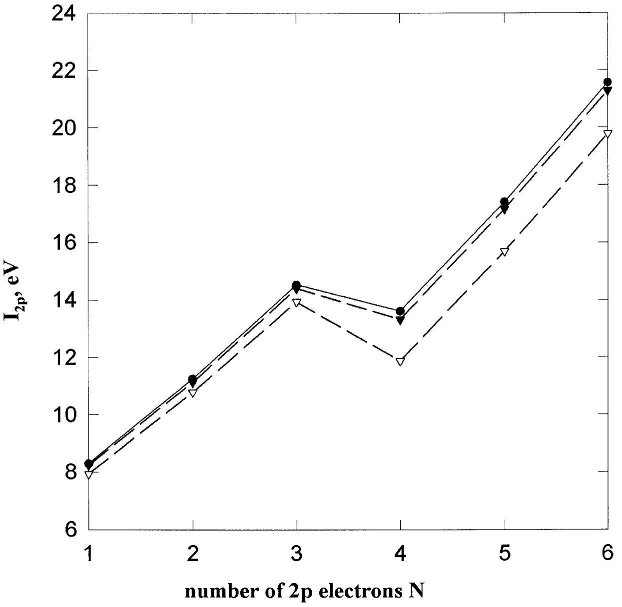

Fig. 10. I_{2p} binding energies for the neutral atoms with $2p^N$ open shell: (●) experiment [22]; (▽) HFP calculation and (▼) calculation by the configuration interaction method.

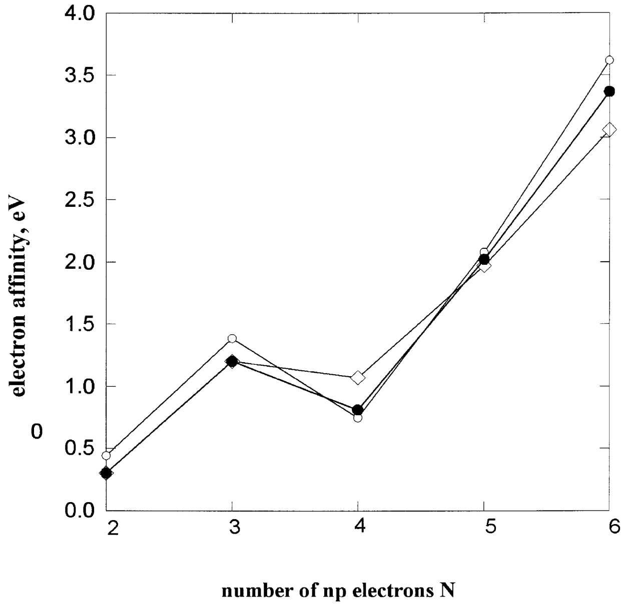

Fig. 11. Electron affinity for the negative ions with the np^N open shell as a function of the number of electrons N: experimental data [22] for $n = 3$ (○), 4 (●) and 5 (◇).

4 Conclusion

Some important atomic quantities related to the ground state of atoms show the additional symmetry with respect to a quarter of the electronic shell, but this symmetry was interpreted theoretically using only single configuration pure LS-coupling approximation. In this work it is shown, that the additional symmetry is maintained by some important many-electron effects.

The systematic investigation of the configuration mixing corrections for the $I_{4f}, I_{3d}, I_{2p}, I_{3p}$ binding energies, $4f^{N-1}5d - 4f^N$ system differences as well as for $2p$ and $3p$ electron affinities shows that the main corrections weakly depend on the quantum numbers of the ground term. Though the main corrections for the ground state energy depend quadratically on the number of electrons N, their difference for the binding energy or system difference obtains linear character (except of a discontinuity at middle of the group due to the strong dependence of the radial integrals on the term of the ground state). Consequently, the mixing with distant configurations maintains the symmetry with respect to a quarter of the shell.

Taking into account such mixing effects for binding energies usually only term-independent part (having simple expression) can be calculated. On the other hand, the additional symmetry properties give the possibility to interpolate and extrapolate the experimental values more accurately.

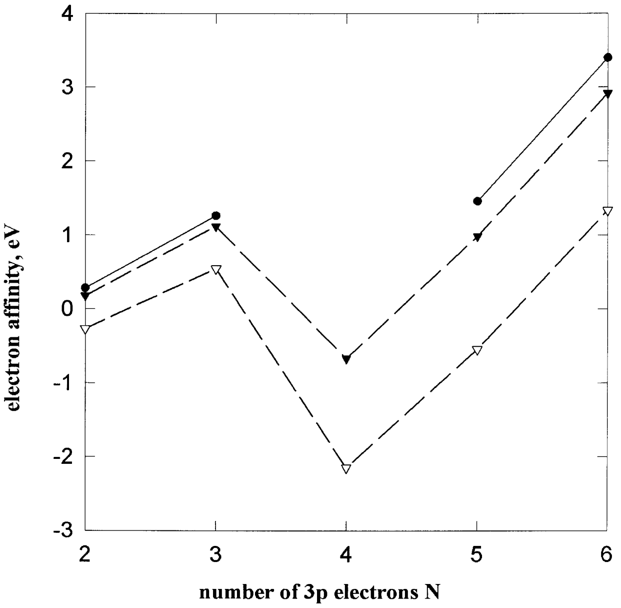

Fig. 12. Electron affinity for the negative ions with the $3p^N$ open shell as a function of the number of electrons N: (●) experimental data [22] and the values calculated by the Hartree-Fock-Pauli (▽) and configuration interaction (▼) methods.

The obtained fairly close correspondence of the calculated values to experimental data for binding energies and system differences shows that the second order perturbation approach using transformed radial orbitals allows one to take effectively into account the configuration mixing effects for these quantities.

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