

# ADDITIONAL SYMMETRY PROPERTIES OF ATOMIC STATES WITH ONE AND TWO OPEN SHELLS

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Additional symmetry properties of the ground state of an atom and quantities related with it, of the configuration with two open shells with the same orbital quantum number, and of the maximal Auger amplitudes are considered. Algebraic energy expressions for terms of the highest multiplicity and terms related with them as well as for the ground and highest levels are presented. Classification of states for the  $n_1 l^{N_1} n_2 l^{N_2}$  configuration according to their parentage in the isoelectronic sequence of configurations and the properties of such a basis are considered. Reformulation of this basis using the isospin formalism is discussed. Existence of selection rules for the maximal Auger amplitudes is indicated.

**Keywords:** ground state of atom, symmetry with respect to a quarter of shell, binding energy, interval rule, isospin basis

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## 1. Introduction

Symmetry properties play a very important role in the atomic theory, they point to the essential features of the many-electron system. The basic symmetries intrinsic to an atom were noticed already at the formulation of quantum mechanics: the antisymmetric property of wavefunction, the central symmetry of the field within an atom, and the electron-vacancy symmetry. Conservation of the angular momentum, not only of the total momentum of an atom but also approximately of the moments of separate electrons and their groups, follows from the central symmetric model of a free atom. For this reason the concept of angular momentum is of the main importance to atomic physics [1]. Various symmetric properties for the matrix elements of Hamiltonian and other physical operators were determined by the general theory of quantum angular momentum [2, 3], especially by the mathematical formalism of irreducible tensorial operators (Wigner-Ecart theorem, selection rules, quasispin concept, etc.) [4–7]. The second quantization method enables one to transfer the antisymmetry properties from the wavefunctions to the operators, introduces the conjugation operation and useful additional relations [8]. The theory of groups reveals the hidden symmetries, for example,

the degeneracy of a hydrogen atom [9], applicability of a quark model for the  $f^N$  shell [10], unexpected vanishing of some matrix elements of operators [10, 11].

The aim of this paper is a review of additional symmetries characteristic of some states of configurations with one and two open shells. These results were mainly published in papers [12–18]; in this work some expressions are corrected or presented in a more useful form as well as the comparison of theoretical results with new experimental data is presented.

## 2. Algebraic expressions for the energy of the highest multiplicity terms and of the ground and highest levels

### 2.1. Space of states with the fixed spin projection and the expressions for operators in such a space

According to the spin-polarised model, the shell of electrons can be treated as consisting of two subshells with spins of electrons directed up and down [19, 20]. However, such a model usually does not give any advantage, because this partition between subshells may be accomplished in various ways. It becomes unambiguous only for terms of the highest multiplicity. Then only one open subshell appears:

$$l^N \rightarrow \begin{cases} l_{\uparrow}^N, & \text{for } N < 2l + 1; \\ l_{\downarrow}^{2l+1} l_{\uparrow}^{N-2l-1}, & \text{for } N \geq 2l + 1. \end{cases} \quad (1)$$

Attribution of the spin projection in this open subshell is conventional; it is accepted that the spins of all its electrons are directed up.

Such additional constraint for the distribution of electrons in the subshells and the application of electron-vacancy symmetry for the open subshell enables one to obtain the explicit expressions for energy of the highest multiplicity state and its quantum numbers.

In the second quantization representation, let us introduce the following operator having the form of the tensorial product of rank  $k$ :

$$A_q^{(k)} = [a^{(l)\dagger} \times \tilde{a}^{(l)}]_q^{(k)}, \quad (2)$$

where  $a_m^{(l)\dagger}$  is the electron creation operator in the state  $nlm$  and the spin directed up, and  $\tilde{a}_q^{(l)} = (-1)^{l-m} a_m^{(l)}$  is related with the electron annihilation operator  $a_m^{(l)}$  in the same state. Using the known anticommutation rules for the operators  $a_m^{(l)}$  and  $a_m^{(l)\dagger}$ , the following relations for operator (2) and for the other similar tensorial product can be obtained [13]:

$$\begin{aligned} [A^{(k)} \times A^{(k)}]^{(0)} = & \\ - \sum_{k'} [(2k+1)(2k'+1)]^{\frac{1}{2}} \left\{ \begin{matrix} l & l & k \\ l & l & k' \end{matrix} \right\} [A^{(k')} \times A^{(k)}]^{(0)} & \\ + \left[ (-1)^k \frac{\sqrt{2k+1}}{2l+1} + \delta(k,0) \right] N; & \end{aligned} \quad (3)$$

$$\begin{aligned} [[a^{(l)\dagger} \times a^{(l)\dagger}]^{(k)} \times [\tilde{a}^{(l)} \times \tilde{a}^{(l)}]^{(k)}]^{(0)} = & \\ (-1)^k \frac{\sqrt{2k+1}}{2l+1} N & \\ + \sum_{k'} [k'(2k+1)(2k'+1)]^{\frac{1}{2}} (-1)^{k+k'} & \\ \times \left\{ \begin{matrix} l & l & k \\ l & l & k' \end{matrix} \right\} [A^{(k')} \times A^{(k)}]^{(0)}. & \end{aligned} \quad (4)$$

Here the quantity in the braces is 6j coefficient.

Equations (3) and (4) at various values of rank  $k$  present the system of equations for operator (2). Taking into account that in particular cases this operator or some its combinations are expressed via the operators with the known eigenvalues, the explicit formulae for operator (2) are obtained. They can be applied for the derivation of expression for the Coulomb interaction energy of the highest multiplicity state  $\gamma_m$ . The coefficient  $f_k$  at the radial integral  $F^k(nl, nl)$  is expressed in terms of the matrix element of operator (2):

$$\begin{aligned} f_k(l^N \gamma_m) = \langle l \| C^{(k)} \| l \rangle^2 & \\ \times [(-1)^{k+1} \frac{1}{2\sqrt{2k+1}} \langle l^N \gamma_m | [A^{(k)} \times A^{(k)}]^{(0)} | l^N \gamma_m \rangle & \\ - \frac{N}{4l+2} ]. & \end{aligned} \quad (5)$$

Here  $\langle \| C^{(k)} \| l \rangle$  is the single electron submatrix element of the spherical function of rank  $k$ .

Only one solution of Eqs. (3) and (4) is sufficient for the consideration of the  $p^N$  shell:

$$\begin{aligned} \sum_{k \text{ even}}^{2l} \sqrt{2k+1} [A^{(k)} \times A^{(k)}]^{(0)} = & \\ \frac{2l+3}{4l+2} N(2l+1-N). & \end{aligned} \quad (6)$$

In the case of d electrons the second relation must be added:

$$\begin{aligned} [A^{(k)} \times A^{(k)}]^{(0)} = & \\ \frac{\sqrt{2k+1}}{5} \left[ \frac{k(k+1)}{3 \cdot 4 \cdot 5} - \frac{1}{5} - \left\{ \begin{matrix} 2 & 2 & k \\ 2 & 2 & 3 \end{matrix} \right\} \right] (L^{(1)} \cdot L^{(1)}) & \\ + \sqrt{2k+1} \left\{ \begin{matrix} 2 & 2 & k \\ 2 & 2 & 3 \end{matrix} \right\} N(5-N) \quad (k \text{ is even}). & \end{aligned} \quad (7)$$

It is replaced by the following equation for f electrons:

$$\begin{aligned} [A^{(k)} \times A^{(k)}]^{(0)} = & \\ -2\sqrt{2k+1} \left[ \frac{1}{4 \cdot 7} \left\{ \begin{matrix} 3 & 3 & k \\ 3 & 3 & 5 \end{matrix} \right\} + \frac{24-k(k+1)}{4 \cdot 6 \cdot 7} \right] & \\ \times (L^{(1)} \cdot L^{(1)}) + \frac{1}{3 \cdot 4 \cdot 7} N(N-7) & \\ - \left[ \left\{ \begin{matrix} 3 & 3 & k \\ 3 & 3 & 5 \end{matrix} \right\} - \frac{1}{2 \cdot 3 \cdot 7} \right] \mathcal{G}(G_2) \quad (k \text{ is even}). & \end{aligned} \quad (8)$$

However, yet one additional equation is necessary for the  $f^N$  shell. It follows from the formula for the Casimir operator of the  $G_2$  group in the spin-up space:

$$\mathcal{G}(G_2) = \frac{1}{4 \cdot 7} (L^{(1)} \cdot L^{(1)}) - \sqrt{11} [A^{(5)} \times A^{(5)}]^{(0)}. \quad (9)$$

## 2.2. Coulomb and spin-orbit energy for the terms of the highest multiplicity and the terms related with them

Expressions of the coefficients  $f_k$  for terms of the highest multiplicity can be obtained using Eqs. (6)–(9) and relation (5). In order to take into account the electron-vacancy symmetry, the coefficients  $f'_k$  with the excluded average value  $\bar{f}_k$  must be considered:

$$f'_k(l^N \gamma_m) = f_k(l^N \gamma_m) - \bar{f}'_k(l^N) = f_k(l^N \gamma_m) + \frac{N(N-1)}{(4l+2)(4l+1)} \langle l \| C^{(k)} \| l \rangle^2 \quad (k > 0). \quad (10)$$

It is convenient to introduce also the quantity  $\mathcal{N}$  which is equal to the number of electrons  $N$  for a partially-filled shell ( $N < 2l + 1$ ) and to the number of vacancies  $4l + 2 - N$  for a half-filled and almost-filled shell ( $N \geq 2l + 1$ ):

$$\mathcal{N} = \begin{cases} N, & \text{if } N < 2l + 1, \\ 4l + 2 - N, & \text{if } N \geq 2l + 1. \end{cases} \quad (11)$$

Evaluation of Eqs. (5)–(8) for the particular values of  $l$  and  $k$  gives the following expressions for the spin-angular part of Coulomb interaction energy in the case of the highest multiplicity states [13]:

$$f'_2(p^N \gamma_m) = -\frac{3}{2 \cdot 5^2} [L(L+1) + 2\mathcal{N}(\mathcal{N}-2)], \quad (12)$$

$$f'_2(d^N \gamma_m) = -\frac{1}{2 \cdot 3^2 \cdot 7^2} [27L(L+1) + 2\mathcal{N}(29\mathcal{N}-110)], \quad (13)$$

$$f'_4(d^N \gamma_m) = \frac{5}{2 \cdot 3^2 \cdot 7^2} [3L(L+1) + \mathcal{N}(\mathcal{N}-19)], \quad (14)$$

$$f'_2(f^N \gamma_m) = -\frac{1}{2 \cdot 3^2 \cdot 5} [L(L+1) - 6g(G_2)] - \frac{7}{3^2 \cdot 5 \cdot 13} N(N-1), \quad (15)$$

$$f'_4(f^N \gamma_m) = -\frac{1}{3 \cdot 11^2} [L(L+1) - 6g(G_2)] - \frac{7}{2 \cdot 3 \cdot 11 \cdot 13} \mathcal{N}(\mathcal{N}-1); \quad (16)$$

$$f'_6(f^N \gamma_m) = -\frac{5^2 \cdot 7}{2 \cdot 3^2 \cdot 11^2 \cdot 13} [L(L+1) - 6g(G_2)] - \frac{5^2 \cdot 7}{3^2 \cdot 11 \cdot 13^2} \mathcal{N}(\mathcal{N}-1), \quad (17)$$

where  $g(G_2)$  is the eigenvalue of the operator  $\mathcal{G}(G_2)$ :

$$g(G_2) = (u_1^2 + u_2^2 + u_1 u_2 + 5u_1 + 4u_2)/3. \quad (18)$$

Algebraic formulae for all terms of the  $p^N$  shell were obtained in [4].

It is necessary to add to Eqs. (12)–(17) also the expression for the energy of spin-orbit interaction for the highest multiplicity state:

$$E_{\text{so}} \left( l^N LS = \frac{\mathcal{N}}{2} J \right) = \text{sign}(2l+1-N) \times \left[ J(J+1) - L(L+1) - \frac{\mathcal{N}}{2} \left( \frac{\mathcal{N}}{2} + 1 \right) \right] \frac{\xi(nl)}{2\mathcal{N}}, \quad (19)$$

where  $\xi(nl)$  is the spin-orbit constant.

All the terms of the highest multiplicity for the  $p^N$ ,  $d^N$  and  $f^N$  shells are given in the Table.

It is also possible to derive the algebraic expressions for the terms with the seniority number  $\nu = 2S$ . They can be obtained from the corresponding formulae for the terms of the highest multiplicity using the relation between the matrix elements for the  $l^N$  configuration at  $\nu = 2S$  and for the  $l^\nu$  configuration at  $S = \nu/2$  [21]:

$$\begin{aligned} & \langle l^N(\nu = 2S) LS | [A^{(k)} \times A^{(k)}]^{(0)} | l^N(\nu = 2S) LS \rangle = \\ & \frac{(2l+1-N)^2 - (2l+1-\nu)}{(2l+1-\nu)(2l-\nu)} \\ & \times \left\langle l^\nu L \left( S = \frac{\nu}{2} \right) | [A^{(k)} \times A^{(k)}]^{(0)} | l^\nu L \left( S = \frac{\nu}{2} \right) \right\rangle \\ & + (-1)^{k+1} \sqrt{2k+1} \frac{(N-\nu)(4l+2-N-\nu)}{(2l-\nu)(2l+1)}. \quad (20) \end{aligned}$$

Such terms are also given in the Table.

### 3. Electrostatic and spin-orbit energy for the ground and highest levels

Except the heaviest atoms, the coupling scheme within an electronic shell is usually close to the  $LS$  coupling. Then, according to the Hund's rule, the ground level is of the highest multiplicity. It easily follows that the many-electron quantum numbers for such a level can be expressed in terms of the  $\mathcal{N}$  number:

$$S = \frac{\mathcal{N}}{2}; \quad \nu = N; \quad L = \frac{1}{2} \mathcal{N}(2l+1-\mathcal{N}), \quad (21)$$

$$Q = \frac{2l+1-\mathcal{N}}{2}, \quad (22)$$

$$J = \begin{cases} \frac{N(2l-N)}{2}, & \text{if } N < 2l+1, \\ \frac{(4l+2-N)(N-2l)}{2}, & \text{if } N \geq 2l+1. \end{cases} \quad (23)$$

Table. Terms of the  $1^N$  shell: ground term, other terms of the highest multiplicity and related with them. For all these terms the matrix elements of Coulomb and spin-orbit interaction operators have the algebraic expressions.

Shell	Terms		
	Ground	Other terms of maximal multiplicity	Related with the terms of maximal multiplicity
$p^2$	${}^3_2P$		${}^1_0S$
$p^3$	${}^4_2S$		${}^2_1P$
$d^2$	${}^3_2F$	${}^3_2P$	${}^1_0S, {}^1_2D, {}^1_2G$
$d^3$	${}^4_3F$	${}^4_3P$	${}^2_1D$
$d^4$	${}^5_4D$		${}^1_0S, {}^3_2P, {}^3_2F, {}^1_4S, {}^1_4D, {}^1_4F, {}^1_4G, {}^1_4I$
$d^5$	${}^6_5S$		${}^2_1D, {}^4_3P, {}^4_3F, {}^2_5S, {}^2_5D, {}^2_5F, {}^2_5G, {}^2_5I$
$f^2$	$\binom{11}{110} {}^3_2H$	$\binom{11}{110} {}^3_2P, \binom{10}{110} {}^3_2F$	$\binom{00}{000} {}^1_0S$
$f^3$	$\binom{20}{111} {}^4_3I$	$\binom{00}{111} {}^4_3S, \binom{20}{111} {}^4_3D, \binom{10}{111} {}^4_3F, \binom{20}{111} {}^4_3G$	$\binom{10}{100} {}^2_1F$
$f^4$	$\binom{20}{111} {}^5_4I$	$\binom{00}{111} {}^5_4S, \binom{20}{111} {}^5_4D, \binom{10}{111} {}^5_4F, \binom{20}{111} {}^5_4G$	$\binom{00}{000} {}^1_0S, \binom{11}{110} {}^3_2P, \binom{10}{110} {}^3_2F, \binom{11}{110} {}^3_2H$
$f^5$	$\binom{11}{110} {}^6_5H$	$\binom{11}{110} {}^6_5P, \binom{10}{110} {}^6_5F$	$\binom{10}{100} {}^2_1F, \binom{00}{111} {}^4_3S, \binom{20}{111} {}^4_3D, \binom{10}{111} {}^4_3F, \binom{20}{111} {}^4_3G, \binom{20}{111} {}^4_3I$
$f^6$	$\binom{10}{100} {}^7_6F$		$\binom{00}{000} {}^1_0S, \binom{11}{110} {}^3_2P, \binom{10}{110} {}^3_2F, \binom{11}{110} {}^3_2H, \binom{00}{111} {}^4_3S, \binom{20}{111} {}^4_3D, \binom{10}{111} {}^4_3F, \binom{20}{111} {}^4_3G, \binom{20}{111} {}^4_3I$
$f^7$	$\binom{00}{000} {}^8_7S$		$\binom{10}{100} {}^2_1F, \binom{00}{111} {}^4_3S, \binom{20}{111} {}^4_3D, \binom{10}{111} {}^4_3F, \binom{20}{111} {}^4_3G, \binom{20}{111} {}^4_3I, \binom{11}{110} {}^6_5P, \binom{10}{110} {}^6_5F$

Here  $\nu$  is a seniority and  $Q$  is quasispin quantum numbers.

Eigenvalue of the Casimir operator for the  $G_2$  group can be also presented in such a form [13]:

$$g(G_2) = \frac{\mathcal{N}(\mathcal{N}-1)}{2^2 \cdot 3^3 \cdot 5} [6 + 41\mathcal{N}(7-\mathcal{N}) - 2\mathcal{N}^2(7-\mathcal{N})^2]. \tag{24}$$

While using expressions (21) and (24) in Eqs. (12)–(17), the spin-angular coefficients  $f'_k$  for the ground state  $\gamma_g$  are presented in a form of the  $\mathcal{N}$  degree polynomial [13]:

$$f'_2(p^N \gamma_g) = -\frac{3}{2^3 \cdot 5^2} \mathcal{N}(\mathcal{N}-1)(\mathcal{N}^2 - 5\mathcal{N} + 10), \tag{25}$$

$$f'_2(d^N \gamma_g) = \frac{\mathcal{N}(\mathcal{N}-1)}{2^3 \cdot 3^2 \cdot 7^2} [27\mathcal{N}^2 - 243\mathcal{N} + 610], \tag{26}$$

$$f'_4(d^N \gamma_g) = \frac{5\mathcal{N}(\mathcal{N}-1)}{2^3 \cdot 3^2 \cdot 7^2} [3\mathcal{N}^2 - 27\mathcal{N} + 46], \tag{27}$$

$$f'_2(f^N \gamma_g) = -\frac{\mathcal{N}(\mathcal{N}-1)}{2^3 \cdot 3^4 \cdot 5^2 \cdot 13} [A(\mathcal{N}) + 4578], \tag{28}$$

$$f'_4(f^N \gamma_g) = \frac{\mathcal{N}(\mathcal{N}-1)}{2^2 \cdot 3^3 \cdot 5 \cdot 11^2 \cdot 13} [A(\mathcal{N}) + 168], \tag{29}$$

$$f'_6(f^N \gamma_g) = \frac{5 \cdot 7\mathcal{N}(\mathcal{N}-1)}{2^3 \cdot 3^4 \cdot 11^2 \cdot 13^2} [A(\mathcal{N}) + 11058], \tag{30}$$

where  $A(\mathcal{N})$  denotes the following:

$$A(\mathcal{N}) = 13\mathcal{N}(4\mathcal{N}^3 - 80\mathcal{N}^2 + 545\mathcal{N} - 1345). \tag{31}$$

Expression for the ground state spin-orbit energy is obtained from Eq. (19) on substituting the formulae for  $L$  (21) and  $J$  (23):

$$E_{so}(1^N \gamma_g) = \begin{cases} -[N(2l+1-N)+2] \frac{\xi(nl)}{4}, & \text{if } N < 2l+1; \\ -[(N-2l-1)(4l+2-N)] \frac{\xi(nl)}{4}, & \text{if } N \geq 2l+1. \end{cases} \tag{32}$$

The other important energy level is the highest one. Consideration of experimental data for the atoms with the  $f^N$  open shell obeying the  $LS$  coupling scheme shows that such a level is  ${}^1S_0$  at an even number of electrons  $N$  and  ${}^2I_{1/2}$  (if  $N < 2l + 1$ ) or  ${}^2I_{1-1/2}$  (if  $N \geq 2l + 1$ ) at the odd number  $N$ . Thus, contrary to the ground level, the highest level is of the lowest possible multiplicity. However, according to Eq. (20), its matrix element is related with a simple or vanishing one for the shells  $l^I$  or  $l^0$ . This gives finally for  $f'_k$  [13]:

$$f'_k(l^N 1S) = \frac{N(4l+2-N)}{4l(4l+1)} \langle l \| C^{(k)} \| l \rangle^2, \quad (33)$$

$$f'_k(l^N 1I) = \frac{(N-1)(4l+1-N)}{4l(4l+1)} \langle l \| C^{(k)} \| l \rangle^2. \quad (34)$$

The corresponding expressions for the spin-orbit energy of the highest level follow from Eq. (19) taking into account the relation analogical to Eq. (20):

$$\begin{aligned} & \langle l^N(v=2S)LSJ | H_{so} | l^N(v=2S)LSJ \rangle \\ &= \frac{(2l+1-N)}{2l+1-\nu} \\ & \times \langle l^\nu \nu L(S=\nu/2)J | H_{so} | l^\nu \nu L(S=\nu/2)J \rangle, \end{aligned} \quad (35)$$

$$E_{so}(nl^N 1S) = 0, \quad (36)$$

$$E_{so}(nl^N 1I_{1/2}) = \frac{(2l+1-N)}{4} \xi(nl),$$

if  $N < 2l + 1$ , (37)

$$E_{so}(nl^N 1I_{1-1/2}) = \frac{(N-2l-1)(l+1)}{4l} \xi(nl),$$

if  $N \geq 2l + 1$ . (38)

#### 4. Symmetry with respect to a quarter of shell and the interval rules

Some important physical and chemical quantities show the symmetry with respect to a quarter of shell. They all are related with the ground state of an atom. Various explanations of such regularities were proposed: the Coulomb or spin-orbit interactions within the  $f^N$  shell, the extra stabilization in the crystal field, the nephelauxetic effect [22, 23]. This symmetry is mainly investigated for lanthanides and actinides because the  $f^N$  shell preserves the atomic properties in compounds and, moreover, such a property manifests

itself more distinctly for a shell with a larger number of electrons. Thus, we will restrict our consideration to the atoms with one open  $f^N$  shell. For the description of  $f$  electrons it is more convenient to introduce the linear combinations of radial integrals  $F^k$  and coefficients  $f'_k$  namely,  $E^k$  and  $e'_k$  which possess the well-defined group properties [5]:

$$E^1 = \frac{14}{405} F^2 + \frac{7}{297} F^4 + \frac{350}{1287} F^6, \quad (39)$$

$$E^2 = \frac{1}{2025} F^2 - \frac{1}{3267} F^4 + \frac{175}{1656369} F^6, \quad (40)$$

$$E^3 = \frac{1}{135} F^2 + \frac{2}{1089} F^4 - \frac{175}{42471} F^6, \quad (41)$$

$$e'_1 = \frac{225}{42} f'_2 + \frac{1089}{77} f'_4 + \frac{5577}{350} f'_6, \quad (42)$$

$$e'_2 = \frac{32175}{42} f'_2 - \frac{141570}{77} f'_4 + \frac{5577}{10} f'_6, \quad (43)$$

$$e'_3 = \frac{2475}{42} f'_2 + \frac{4356}{77} f'_4 - \frac{5577}{50} f'_6. \quad (44)$$

Spin-angular coefficient  $e'_k$  is also defined with the excluded average value. Then the energy of the ground state  $\gamma_g$  is expressed as follows:

$$E(nf^N \gamma_g) = E_{av}(nf^N) + \sum_i e'_i(f^N \gamma_g) E^i + \chi(f^N \gamma_g) \xi_{nr}. \quad (45)$$

One of the main atomic quantities, the binding energy of an electron in the shell (the ionization energy of shell), is defined as the energy difference of an ion with the vacancy in this shell and an atom in their ground states:

$$I_{nl} = E(nl^{N-1} \gamma'_g) - E(nl^N \gamma_g). \quad (46)$$

Dependence of this difference on  $N$  is mainly determined by the variation of coefficients  $e'_k$  and  $\Delta\chi$ , thus, the binding energy for the  $f$  electron can be approximated in the following way:

$$\begin{aligned} I_{nl}(nf^N) &\approx E_{av}(nf^{N-1}) - E_{av}(nf^N) + \sum_i \Delta e'_i(f^N) E^i \\ &+ \Delta\chi_f(f^N) \xi_{nr} \end{aligned} \quad (47)$$

where  $\Delta e'_i$  and  $\Delta\chi$  present the differences:

$$\Delta e'_i(f^N) = e'_i(f^{N-1}) - e'_i(f^N), \quad (48)$$

$$\Delta\chi_f(f^N) = \chi_f(f^{N-1}) - \chi_f(f^N). \quad (49)$$

The main advantage of coefficients  $e'_i$  is the vanishing of the difference for the second coefficient:

$$\Delta e'_2(f^N) = 0. \quad (50)$$

The other differences  $\Delta e'_k$  are expressed in terms of the number of electrons using Eqs. (42)–(44) as well as Eqs. (28)–(30):

$$\Delta e'_1(f^N) = \frac{9}{13} \begin{cases} N-1, & \text{if } N \leq 7, \\ N-14, & \text{if } N > 7, \end{cases} \quad (51)$$

$$\begin{aligned} \Delta e'_3(f^N) &= -\Delta e'_3(f^{15-N}) = \\ &= -\frac{1}{10}(2N^5 - 40N^4 + 285N^3 - 860N^2 + 1033N - 420). \end{aligned} \quad (52)$$

$\Delta e'_3$  equals 0 at  $N = 1, 7, 8$  and 14.

Expression for  $\Delta\chi_f$  follows from Eq. (32), but the more compact formula is obtained using the symmetry property for this quantity:

$$\begin{aligned} \Delta\chi_f(f^{N_0 \pm q}) &= \mp \left[ \frac{q}{2} + \frac{1}{2} \delta(q, 3) \right] \delta(N_0, 4) \\ (N_0 = 4, 11; q = 0, 1, 2, 3). \end{aligned} \quad (53)$$

All these explicit expressions enable one to investigate the dependence of quantities, obeying the symmetry with respect to a quarter of shell, on the number of electrons in this shell. According to the Koopman's theorem, the average energy part in Eq. (47) is approximately equal to the single-electron energy and depends almost linearly on the atomic number. Differences  $\Delta e'_1$  and  $\Delta e'_3$  as the functions of  $N$  consist of two similar segments (symmetry with respect to a half of shell) and each segment can be coincided with itself performing the rotation by the angle of  $180^\circ$  around the points corresponding to  $N_0 = 4$  or 11 (symmetry with respect to a quarter of shell) (Fig. 1). Difference  $\Delta\chi_f$  obeys the symmetry with respect to a quarter of shell, but only the distorted symmetry with respect to a half of shell.

In lanthanides and even in actinides, the structure of the  $f^N$  shell is mainly determined by the Coulomb interaction. Thus, the variation of  $I_{nl}(f^N)$  with  $N$  mostly depends on the difference of the first coefficient  $\Delta e'_1$  at the largest integral  $E^1$  (Fig. 2). This difference increases linearly up to the half of shell, suddenly jumps from 4.2 to  $-4.2$  on going from  $N = 7$  to 8 and then the second symmetric branch appears. This main regularity is slightly modified by smaller contributions of  $\Delta e'_3$  and  $\Delta\chi_f$  having more complex dependence on  $N$ . The experimental values of  $I_{nl}$  and results of calculation in the single-configuration approximation show

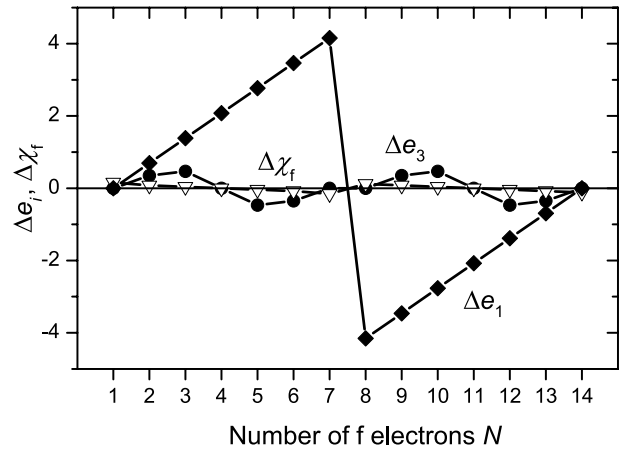


Fig. 1. Dependence of the differences of coefficients  $\Delta e'_1(f^N)$ ,  $\Delta e'_3(f^N)$  and  $\Delta\chi_f(f^N)$  on the number of electrons  $N$ . In order to compare the influence of these coefficients on the value of binding energy for triple lanthanide ions the coefficient  $\Delta e'_3$  is multiplied by  $E^3/E^1$  and  $\Delta\chi_f$  by the ratio  $\xi_{4f}/E^1$  ( $E^1$  and  $\xi_{4f}$  are calculated for  $Gd^{3+} 4f^7$  configuration).

a very similar dependence. It was explained in [17]: some significant configuration mixing effects also maintain this additional symmetry.

The other important quantity for the lanthanide atoms is the system difference (SD). It presents the difference between the energies of the lowest levels of  $4f^{N-1}5d6s^2$  and  $4f^N6s^2$  configurations [22]. Although the 4f electron is not removed but excited to the 5d shell, the SD is mainly determined by the change of the number of 4f electrons.

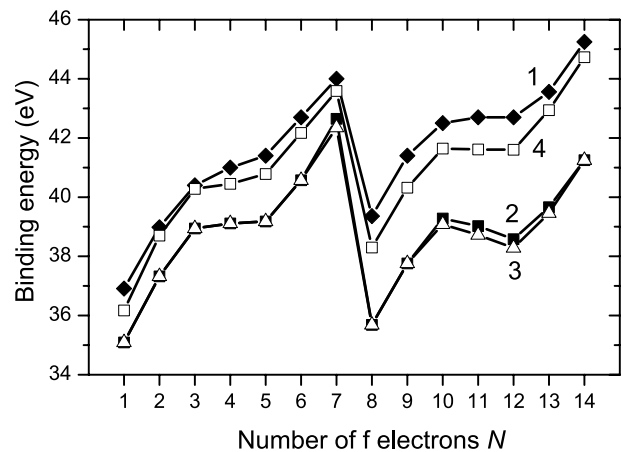


Fig. 2. Binding energy  $I_{4f}$  in the sequence of triply ionized lanthanides: (1) experiment [24]; (2) calculation using algebraic formulae for the ground level; (3) single-configuration quasirelativistic calculation; (4) calculation taking into account 1400–2100 admixed configurations corresponding to two-electron and single-electron excitations [17].

Such a symmetry can manifest itself also for the other quantities related with  $I_{nl}$  or SD. Namely, it was discovered for the ratio of intensities for the strongest lines of transitions [25]

$$4f^N 6s6p - 4f^N 6s^2 \cdot (I_1),$$

$$4f^{N-1} 5d6s6p - 4f^{N-1} 5d6s^2 (I_2) \quad (54)$$

emitted by lanthanide elements in the calibrated arcs (Fig. 3). It was shown in [15] that such an unexpected property of the ratio  $I_1/I_2$  is caused by the dependence of the ratio of populations on SD and the partial cancellation of terms arising in the expression for intensity from the level population and the transition probability.

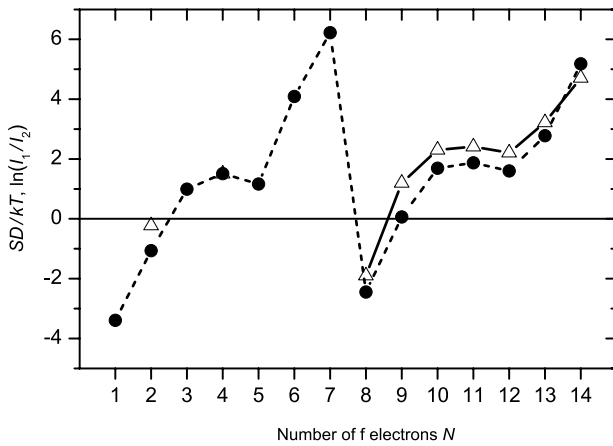


Fig. 3. System difference (SD) (●) [24] and the ratio of intensities  $\ln(I_1/I_2)$  (Δ) [25] in calibrated arcs for the neutral lanthanide atoms.  $I_1$  and  $I_2$  correspond to the strongest lines of the transitions (54). In order to plot both quantities on the same scale, the values of SD are divided by  $kT$ , where  $k$  is the Boltzman constant and  $T = 6440$  K is the approximate temperature in the arc at the local thermodynamic equilibrium.

The symmetry with respect to a quarter of shell also approximately holds for some chemical quantities (cohesive energy, enthalpy of decomposition or disproportionation,  $\alpha$  parameter for the reaction with formation of ion with smaller number of  $f$  electrons) related with the binding energy of a free atom (Fig. 4). Such symmetry is also the reason of interval rules for binding energies. These rules were formulated empirically for the ionization energies and oxidation potentials in [27] and derived theoretically for binding energies of free atoms in [14, 16]. They were proved by expanding the radial integrals  $E^i$  or  $F^k$ , the spin-

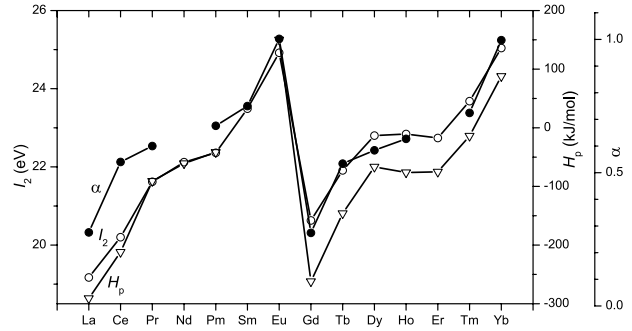


Fig. 4. The second ionization energy  $I_2$  (○) (experimental values) [24], the enthalpy of decomposition  $H_p$  (▽) and the  $\alpha$  parameter (●) in the lanthanide series. The semi-empirical data for  $H_p$  and  $\alpha$  correspond to the reaction  $nHaI_2 \rightarrow 1/3 Ln + 2/3 HaI_3$ , they are taken from [26].

orbit constant  $\xi_{nl}$  and the term-independent part of binding energy by the series in terms of the number of electrons as well as by using the symmetry properties for the coefficients  $\Delta e'_i$  and  $\Delta \chi_i$  [16]. Then the following expressions for the ratio of binding energies were obtained:

$$\frac{I_{nl}(l^{N_0-q}) + I_{nl}(l^{N_0+q})}{I_{nl}(l^{N_0})} = 2 + \Delta$$

$$(N_0 = l + 1, 3l + 2; q = 1, \dots, l), \quad (55)$$

$$\frac{I_{nl}(l^{N_0-q}) + I_{nl}(l^{N_0+q})}{I_{nl}(l^{N_0-q'}) + I_{nl}(l^{N_0+q'})} = 1 + \Delta$$

$$(N_0 = l + 1, 3l + 2; q, q' = 1, \dots, l). \quad (56)$$

The second term  $\Delta$  presents a correction which is mainly determined by the spin-orbit interaction.  $\Delta$  usually obtains a small value for neutral and several-times-ionized atoms.

## 5. Additional symmetry for the states of $n_1 l^{N_1} n_2 l^{N_2}$ configuration

Configuration with two open shells can obtain additional symmetry properties, especially at the same orbital quantum number. Let us consider the iso-electronic sequence of configurations (IC sequence) corresponding to the transfer of an electron from the second shell to the first one:

$$n_1 l^{N_1} n_2 l^{N_2} - n_1 l^{N_1+1} n_2 l^{N_2-1} - n_1 l^{N_1+2} n_2 l^{N_2-2} - \dots \quad (57)$$

This IC sequence ends with the  $n_1 l^{N_1+N_2}$  configuration when  $N_1 + N_2 \leq 4l + 2$ , or with the  $n_1 l^{4l+2} n_2 l^{N_1+N_2-4l-2}$  when  $N_1 + N_2 > 4l + 2$ . We assume that  $n_1 > n_2$  and

$N_1 \geq N_2$ , then the number of states of any configuration in the IC sequence is always larger than the number of states of the next configuration. Thus, the number of terms with the same final quantum numbers  $LS$  increases and the terms with the new  $LS$  appear in the IC sequence. This enables one to introduce the classification of terms according to their appearance in the IC sequence [12]. Terms are described by the additional quantum numbers  $i$  and  $\beta$ :  $i$  indicates the configuration in which the term with the given  $LS$  appears for the first time (it is taken equal to the number of electrons in the second shell of this configuration), while the  $\beta$  denotes the terms with the same  $LS$  values in the considered configuration. It is necessary to mention that it stands for the analogue of the seniority quantum number which designates the shell in which the given term appears for the first time.

The  $|\beta iLS\rangle$  wavefunctions can be presented in a form of linear combinations of functions in the  $LS$  coupling scheme:

$$\begin{aligned} &|n_1^{N_1} n_2^{N_2} \beta iLS\rangle = \\ &\sum_{\alpha_1 L_1 S_1 \alpha_2 L_2 S_2} \langle n_1^{N_1} n_2^{N_2} \alpha_1 L_1 S_1 \alpha_2 L_2 S_2 | \beta iLS \rangle \\ &\times |n_1^{N_1} n_2^{N_2} \alpha_1 L_1 S_1 \alpha_2 L_2 S_2\rangle. \end{aligned} \quad (58)$$

Wavefunctions of the IC sequence are expressed via the same spin-angular single-electron functions and differ only by the radial orbitals. Let us introduce the function

$$|n_1^{N_1+N_2-k} n_2^k \rightarrow n_1^{N_1} n_2^{N_2} \beta iLS\rangle, \quad (59)$$

which is obtained from  $|n_1^{N_1+N_2-k} n_2^k \beta iLS\rangle$  by replacing the  $N_2 - k$  radial orbitals  $R(\tilde{n}_1, l|r)$  with  $R(n_2, l|r)$  (it is a generalization of function  $\Psi$  introduced in [28]). Expression for the expansion coefficients in Eq. (58) can be obtained using the equality

$$|n_1^{N_1} n_2^{N_2} \beta iLS\rangle = |n_1^{N_1+N_2-k} n_2^k \rightarrow n_1^{N_1} n_2^{N_2} \beta iLS\rangle \quad (60)$$

as well as by expressing function (60) in terms of the fractional parentage coefficients and transformation matrix, as was considered in [28, 29]. For example, in the case  $N_2 = 1$  and  $i = 0$  the expansion coefficient in Eq. (58) is equal simply to the fractional parentage coefficient [12]:

$$\langle l^N \alpha_1 L_1 S_1 LS | \alpha (i = 0) LS \rangle = \langle l^{N+1} \alpha LS || l^N \alpha_1 L_1 S_1 l \rangle. \quad (61)$$

The other, more simple method to determine the  $|\beta iLS\rangle$  functions, follows from the diagonality of spin-angular coefficients  $g_0$  at the main radial integral

$G^0(nl, nl)$  in this basis. Indeed, the scalar term in the Coulomb energy expression corresponds to the zero-rank operator  $\sum_{i < j} (C_i^{(0)} \cdot C_j^{(0)}) r_{ij}^{-1}$  the angular part of which is the permutation operator of angular coordinates of electrons between shells. On the other hand, according to Eq. (60), the  $|\beta iLS\rangle$  wavefunctions must be invariant under such a permutation. Consequently, the expansion of  $|\beta iLS\rangle$  wavefunctions in the basis of usual functions can be obtained by the diagonalization of the  $||g_0||$  matrix.

The diagonal elements of  $||g_0||$  were found in [12] as follows:

$$g_0(l^{N_1} l^{N_2} \beta iLS) = -N_1 N_2 - i(N_1 + N_2) + i(i - 1). \quad (62)$$

Introduction of the new basis was reformulated in a more strict mathematical form using the isospin concept [30, 21, 7]. The  $n_1 l$  and  $n_2 l$  electrons can be treated as two states of  $l$  electron (an analogy with proton and neutron considered as two states of the same particle – nucleon). It is supposed that both states of  $l$  electron differ by the isospin quantum number, which obtains two possible values  $1/2$  and  $-1/2$ . Angular operators  $T^{(1)}$  and  $T^2$  acting in the additional isospin space are introduced. The operator  $T_1^{(1)}$  annihilates an electron in the first shell and creates an electron in the second one, while the operator  $T_{-1}^{(1)}$  does the reverse. The eigenvalue of  $T^2$  is  $T(T-1)$ , where the quantum number  $T$  is related with the earlier introduced:

$$T = (N_1 + N_2 - 2i) / 2. \quad (63)$$

Expression (62) for  $g_0$  (62) was obtained as an eigenvalue of some combination of isospin operators.

In the isospin formalism, the additional classification of repeating terms  $TLS$  was proposed using the irreducible representations of unitary group  $U_{8l+4}$  and its subgroups [21].

Some important properties of the new basis were established in [12]. If the  $n_1^{N_1} n_2^{N_2}$  configuration is the highest one among the configurations in the IC sequence (57), then the terms with  $i = N_2$  appear in this configuration for the first time and are absent in the other lower-lying configurations. Consequently, the  $|n_1^{N_1} n_2^{N_2} \beta (i = N_2) LS\rangle$  wavefunctions are automatically orthogonal to the lower configurations of the same symmetry. It is guaranteed by the correspondence of such functions to the absolute minimum of the functional when the variational method is applied for their calculation. The best functional of such a type presents the energy of configuration averaged over all terms appearing first in this configuration. Expressions for such average coefficients of the Coulomb interaction were obtained by supposing their



quadratic dependence on the number of electrons in the shells and using the explicit expressions for the simplest configurations  $l^{4l+1}$ ,  $l^{4l+1}l^{4l+1}$  and  $ll$ . The final result is the following [12]:

$$\tilde{f}_k(l^{N_1}l^{N_2}) = \frac{N_2(4l+2-N_1)}{(2l+1)(4l+1)(4l+3)} \times \langle l \| C^{(k)} \| l \rangle^2 \quad (k > 0), \quad (64)$$

$$\tilde{g}_k(l^{N_1}l^{N_2}) = -\frac{N_2[(4l+2)N_1-1]}{(2l+1)(4l+1)(4l+3)} \times \langle l \| C^{(k)} \| l \rangle^2 \quad (k > 0), \quad (65)$$

$$\tilde{g}_0(l^{N_1}l^{N_2}) = -N_2, \quad (66)$$

$$\tilde{f}_k(l^{N_i}) = -\frac{N_i(N_i-1)}{2(2l+1)(4l+1)} \times \langle l \| C^{(k)} \| l \rangle^2 \quad (i=1,2). \quad (67)$$

Such a functional takes into account also some correlation effects: in the isospin basis some inter-configuration matrix elements between the  $l^{N_1}l^{N_2}$  and  $l^{N_1-1}l^{N_2+1}$  configurations vanish [12, 31]. This property along with the diagonality of the main part of the Coulomb exchange energy demonstrate the advantages of the isospin basis in comparison with the usual basis for the  $n_1l^{N_1}n_2l^{N_2}$  configuration.

It is necessary to note that at the equal numbers of electrons in both open shells there exists an additional symmetry in the radial space: the Hartree-Fock functional is invariant under the rotation of  $R(n_1l|r)$  and  $R(n_2l|r)$  radial orbitals. The most exact functions for these electrons are the solutions of Hartree-Fock equations with the nondiagonal Lagrangean multiplier  $\varepsilon_{n_1l,n_2l}$  equal to 0. It was shown for  $nl n'l$  and  $n^{4l+1}n'l^{4l+1}$  configurations in [28] and extended for any  $N$  in [12]. An important relationship between the unitary transformations of radial wavefunctions and rotations in the isospin space was established in [21, 7].

## 6. Maximal values of Auger amplitudes and selection rules for their quantum numbers

The calculated Auger or radiative spectrum corresponding to the transitions between two configurations with open shells contains a large number of lines which intensities vary by many orders of the magnitude. While the initial levels are populated non-selectively, the intensities of lines are mainly determined by the amplitudes of transitions. Thus, their maximal values play an exceptional role in the formation of spectrum.

A general expression for the amplitude of the Auger transition has a rather complicated form. It contains fractional parentage coefficients,  $3nj$  coefficients and the summation over intermediate states. Thus, it seems rather probable that the maximal value of the amplitude varies non-regularly with the number of electrons in an open shell. However, the investigation of maximal values of Auger amplitudes performed in [18] showed that there exist hidden symmetry properties for these quantities too.

Let us consider one of the two main types of Auger transitions:

$$n_1l_1^{4l_1+1}n_2l_2^{N_2} - n_1l_1^{4l_2+2}n_2l_2^{N_2-1}\varepsilon l. \quad (68)$$

The amplitude of the Auger transition is defined as follows:

$$[g A(n_1l_1^{4l_1+1}j_1n_2l_2^{N_2}\gamma_2L_2S_2J_2J - n_1l_1^{4l_2+2}n_2l_2^{N_2-1}\gamma_2'L_2'S_2'J_2'lj)]^{1/2}, \quad (69)$$

where  $g$  is the statistical weight of the initial level equal to  $2J+1$ ,  $A$  is the rate of the Auger transition and  $\gamma$  denotes the additional many-electron quantum numbers of shell except when indicated explicitly. The square root of the rate is used instead of the matrix element in order to obtain a positive quantity.

The maximal value of Auger amplitudes (MVAA) between two configurations was selected from the set of amplitudes corresponding to all possible values of quantum numbers  $\gamma_2L_2S_2J_2J$  and  $\gamma_2'L_2'S_2'J_2'$  at the given numbers  $j_1$  and  $lj$ . These quantities were calculated in the single-configuration intermediate and pure coupling schemes using the quasirelativistic Hartree-Fock wavefunctions (the Cowan code) [6]. The following transitions involving various inner vacancies and outer open shells were considered:

$$3s3d^{N_2} - 3s^23d^{N_2-2}\varepsilon lj \quad Ti-Cu, \quad (70)$$

$$4s4p^{N_2} - 4s^24p^{N_2-2}\varepsilon lj \quad Ge-Kr, \quad (71)$$

$$2p^5j_13d^{N_2} - 2p^63d^{N_2-2}\varepsilon lj \quad Ti-Cu, \quad (72)$$

$$2p^5j_14d^{N_2} - 2p^64d^{N_2-2}\varepsilon lj \quad Zr-Pd, \quad (73)$$

$$3d^9j_14p^{N_2} - 3d^{10}4p^{N_2-2}\varepsilon lj \quad Ge-Kr. \quad (74)$$

All in all, 303 sets of amplitudes with the given values of  $N_2$ ,  $j_1$  and  $lj$  were examined. For all considered transitions MVAA vary within a relatively narrow interval and rather smoothly with  $N$  in both intermediate and pure coupling schemes; a typical example is given in Fig. 5.

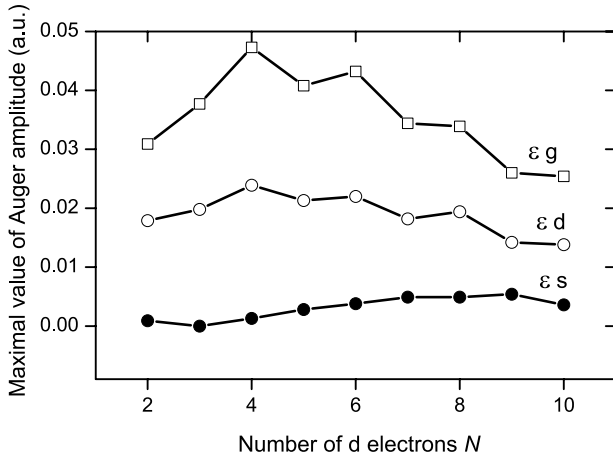


Fig. 5. Dependence of the maximal values of Auger amplitude (MVAA) for various channels of Auger transitions  $3s3d^{N_2} - 3s^23d^{N_2-2}\epsilon l$  [18]. The data are given for the sets with both values of the total moment of Auger electron  $j = l \pm 1/2$ , however, in all cases MVAA corresponds to  $j = l + 1/2$ .

Variation of many-electron quantum numbers of MVAA on  $N$  was considered in the pure coupling scheme, only then strict selection rules are possible. Symmetry with respect to the number of electrons  $N = 2l + 2$  is evident for the quantum numbers of the open shell in the initial and final configurations (Fig. 6). It corresponds to the electron-vacancy symmetry, which centre is shifted by 1 from a half-filled shell due to the difference of electron numbers in both configurations. Thus, this symmetry follows from the two-electron fractional parentage coefficient – the single multiplier in the expression for the transition amplitude having such a property. Values of many-electron quantum numbers of MVAA depend on  $N$  very regularly. For the majority of considered sets (297 from 303) the difference of spins obeys the rule:

$$\Delta S_2 = S'_2 - S_2 = 0. \quad (75)$$

Differences of orbital and total quantum numbers often correspond to the similar rule:

$$\Delta L_2 = \Delta J_2 = 0, \quad (76)$$

but for the sets of amplitudes with the  $l = l_1$  and  $j = j_1$  the other rule is valid:

$$\Delta L_2 = \Delta J_2 = N - 2l_2 - 2. \quad (77)$$

However, the both rules are violated in about the fourth part of sets.

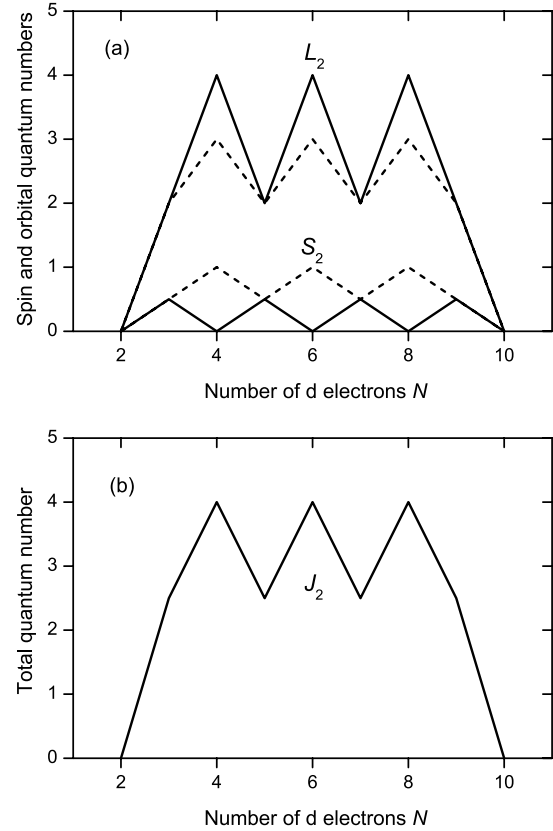


Fig. 6. Dependence of the quantum numbers  $L_2$ ,  $S_2$  and  $J_2$  of the open  $d^N$  and  $d^{N-2}$  shells for the MVAA when the selection rules  $\Delta L_2 = 0$  and  $\Delta S_2 = 0$  are fulfilled: solid line, transitions  $3s3d^{N_2} - 3s^23d^{N_2-2}\epsilon s$  and  $2p^5_{3/2}nd^{N_2} - 2p^63d^{N_2-2}\epsilon p_{3/2}$ ; broken line,  $2p^5_{1/2}nd^{N_2} - 2p^63d^{N_2-2}\epsilon p_{1/2}$ . (a) variation of  $L_2$ ,  $S_2$ ; (b) variation of  $J_2$  [18].

Validity of such rules does not follow from the known properties of matrix elements and indicates the existence of hidden symmetries.

## 7. Conclusions

The many-electron atom is a very complex system, thus, it is important to use its symmetry properties for the investigation of an electronic structure of an atom and regularities of atomic quantities. In this review, several additional symmetry properties of some atomic states are considered. The atom with one open shell in its highest multiplicity state can be considered as having one open spin-polarised subshell. This reduction enables one to derive the explicit expressions for the quantum numbers and the matrix elements of physical operators for the ground state of an atom. These expressions obtain a very simple form of the  $N$  degree polynomial. It is demonstrated that such a model successfully explains the symmetry with respect to a quarter of shell, which is characteristic

of the binding energies, system difference and other physical and chemical quantities. This symmetry is not distorted by some important many-electron effects.

Configuration with two open shells with the same orbital quantum number also obtains additional symmetry properties. For such a configuration the new more exact wavefunction basis can be introduced, where the classification of terms according to their parentage in the isoelectronic sequence of configurations is used. In this basis, the main coefficient of the Coulomb exchange energy  $g_0$  becomes diagonal as well as some correlation effects are taken into account. Such a classification enables one to obtain the functional, which automatically guarantees the orthogonality of wavefunctions to the functions of the lower states of the same symmetry. Description of the new basis was later reformulated in a more strict mathematical form using the isospin concept: the  $n_1l$  and  $n_2l$  electrons can be considered as two states of the  $l$  electron corresponding to two possible values  $1/2$  and  $-1/2$  of the isospin quantum number.

The amplitudes of Auger transitions have a rather complex expression and for the transitions between two configurations differ by several orders. However, the maximal values of Auger amplitudes vary with  $N$  in a rather regular manner and their quantum numbers obey the unexpected selection rules. It indicates the existence of still unknown symmetries for inter-configuration matrix elements.

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## ATOMŲ SU VIENU IR DVIEM ATVIRAIS SLUOKSNIAIS PAPILDOMOS SIMETRIJOS SAVYBĖS

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### Santrauka

Darbe nagrinėjamos atomo pagrindinės būsenos ir su ja susijusių dydžių, taip pat konfigūracijų, turinčių du atvirus elektronų sluoksnius su tuo pačiu orbitiniu kvantiniu skaičiumi, bei Ožė šuolių maksimalių amplitudžių papildomos simetrijos savybės. Pateiktos aukščiausio multiplietiškumo termų, pagrindinio ir aukščiau-

siojo lygmenų energijos išraiškos esant vienam atviram sluoksniui. Nagrinėjama konfigūracijos  $n_1^{N_1} n_2^{N_2}$  būsenų klasifikacija, naudojantis jų kilme izoelektronėje konfigūracijų sekoje, ir tokios banginių funkcijų bazės savybės. Aptariamos maksimalių Ožė šuolių amplitudžių atrankos taisyklės.