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SUMMATION OF ATOMIC QUANTITIES OVER ALL MANY-ELECTRON QUANTUM NUMBERS

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A general group-diagrammatic summation method for obtaining explicit expressions for the averages of the products of operators is described. It is based on the properties of irreducible representations of continuous groups and application of special summation diagrams. The simple rules formulated are convenient for implementation of this method in a computer code for automatic derivation of expressions. The formulae for the averages of the products of some physical operators (spin-orbit interaction, projection of the total momentum, unit standard operators) are presented.

1. Introduction

Various mean characteristics of atoms — the averages of Hamiltonian or effective operators, the total line strengths, the main measures of configuration interaction (CI) in the electronic shells — are expressed by the sums over all many-electron quantum numbers. Such sums also appear in the formulae for global characteristics (average energy, variance, skewness, excess, and others) of the energy level spectra, including all levels of one configuration (configuration complex), and of the characteristic emission or Auger spectra, corresponding to the transitions between all levels of two configurations (configuration complexes). All these quantities may be expressed in terms of averages of a product of operators.

Let us take k operators $O_1, O_2, \ldots, O_{k-1}, O_k$ in the second quantization representation acting in the space of one configuration or between two configurations. The average of the product of these operators with respect to configuration K_1 is defined as follows:

$$\langle O_1 O_2 \ldots O_{k-1} O_k \rangle^{K_1} = \frac{1}{g(K_1)} \sum_{\gamma_1 \ldots \gamma_k} \langle K_1\gamma_1 | O_1 | K_2\gamma_2 \rangle \langle K_2\gamma_2 | O_2 | K_3\gamma_3 \rangle \ldots \langle K_{k-1}\gamma_{k-1} | O_{k-1} | K_k\gamma_k \rangle \langle K_k\gamma_k | O_k | K_1\gamma_1 \rangle, \quad (1)$$

where $\gamma_1, \gamma_2, \ldots, \gamma_k$ are the states of configurations. Some of the configurations $K_1, K_2, \ldots, K_k$ or even they all may be the same. The average is independent of the coupling scheme; some pure coupling is commonly used.

From the definition (1), such symmetry properties for the average follow:

$$\langle O_1 O_2 \ldots O_{k-1} O_k \rangle^{K_1} = \frac{g(K_2)}{g(K_1)} \langle O_2 O_3 \ldots O_k O_1 \rangle^{K_2}, \quad (2)$$

$$\langle O_1 O_2 \ldots O_{k-1} O_k \rangle^{K_1} = \langle O_k^\dagger O_{k-1}^\dagger \ldots O_2^\dagger O_1^\dagger \rangle^{K_1}, \quad (3)$$

where $O_i^\dagger$ is the operator Hermitian adjoint to O_i.

The averages may also be defined in the CI approximation. Then all (or some) configurations K_i in Eq. (1) are replaced by configuration complexes $K_i^* \equiv K_{i1} + K_{i2} + \ldots$, and γ_i has a meaning

of the state of the complex; the summation in the average is carried out over all states of the complexes. The averages in this approximation may be expressed in terms of the averages (1). This is illustrated by the following example ($K_1^* \equiv K$, $K_2^* = K_3^* = K_1 + K_2$):

$$\langle OO'O'' \rangle^K = \frac{1}{g(K)} \sum_{\gamma\gamma'\gamma''} \langle K\gamma|O|K_1+K_2\gamma'\rangle\langle K_1+K_2\gamma'|O'|K_1+K_2\gamma''\rangle\langle K_1+K_2\gamma''|O''|K\gamma\rangle$$

$$= \langle O_{KK_1}O'_{K_1}O''_{K_1K}\rangle^K + \langle O_{KK_2}O'_{K_2}O''_{K_2K}\rangle^K + \langle O_{KK_1}O'_{K_1K_2}O''_{K_2K}\rangle^K + \langle O_{KK_2}O'_{K_2K_1}O''_{K_1K}\rangle^K, \quad (4)$$

where the subscripts of the operators in the averages on the right side of equality indicate the spaces of configurations in which or between which the operator is acting.

An explicit or algebraic expression for the average may be obtained under the assumption that all radial orbitals are term-independent — then the summations over the spin-angular parts of matrix elements can be performed algebraically. However, the matrix elements contain fractional parentage coefficients, which have no standard expressions, and their sums together with the $3nj$ coefficients are unknown.

In Refs. [1, 2], a general group theory method for deriving averages of many-fermion systems was proposed and special summation diagrams suggested. The diagrammatic form of this method was elaborated [3, 4] and applied to electronic shells of atoms [5–7]. The aim of this paper is to present a comprehensive review of this method and to show some applications to physical operators.

2. Dependence of averages on the number of electrons in shells or subshells

The general method for deriving explicit expressions for the averages of operators may be formulated using properties of the irreducible representations (IR) of higher continuous groups: the special orthogonal group $SO_{3\Omega+1}$ and its unitary subgroup U_Ω, where Ω is the number of single-electron states in a shell $(4l + 2)$ or subshell $(2j + 1)$. The states of all nl^N shells (or nlj^N subshells) with the same quantum numbers nl (nlj) and $0 \le N \le \Omega$ belong to the same IR of $SO_{3\Omega+1}$, and the states of a single shell or subshell with the given number of electrons N form a basis of the same IR of U_Ω. These groups are not convenient for classification of the states because of the very large number of repeating terms, but this is not so important when averaging over all the states. On the other hand, it is very important that every IR of U_Ω appears once and only once for the given IR of $R_{3\Omega+1}$. This provides the opportunity to determine explicitly the dependence of the average on the number of electrons N. For the configuration with one open shell (subshell), the average of the operator O reads

$$\langle O \rangle^N = \binom{\Omega}{N}^{-1} \sum_\alpha \langle \Delta\delta_N\alpha|O|\Delta\delta_N\alpha\rangle, \quad (5)$$

where Δ is spinor IR of $SO_{3\Omega+1}$, δ_N is IR of U_Ω contained in Δ and α labels the states in δ_N. The superscript of the average indicates only the number of electrons N instead of configuration K.

For applying the Wigner-Eckart theorem to the matrix element in Eq. (5), the operator O must transform under some IR Λ_p of $SO_{3\Omega+1}$ and IR $\lambda_{\nu,\mu}$ of U_Ω. Such an operator will be called hereafter as an irreducible operator and designated by a had. IR $\lambda_{\nu,\mu}$ also appears only once in Λ_p. According to the Racah lemma, the Clebsch-Gordan coefficient for the group $SO_{3\Omega+1}$ can be factorized as

$$\begin{bmatrix} \Delta & \Lambda_p & \Delta \\ \delta_N\alpha & \lambda_{\nu,\mu}\beta & \delta_N\alpha \end{bmatrix} = \begin{bmatrix} \delta_N & \lambda_{\nu,\mu} & \delta_N \\ \alpha & \beta & \alpha \end{bmatrix} \begin{bmatrix} \Delta & \Lambda_p & \Delta \\ \delta_N & \lambda_{\nu,\mu} & \delta_N \end{bmatrix}. \quad (6)$$

Here the first multiplier is the Clebsch-Gordan coefficient for the group U_Ω, and the second one is the unitary scalar coefficient independent of additional labels of the basic states α and β.

When averaging over α, the Clebsch-Gordan coefficient does not vanish only at $\nu = \mu = \beta = 0$. In this special case, the unitary scalar coefficient has the following simple algebraic expression in terms of binomial coefficients:

$$\begin{bmatrix} \Delta & \Lambda_p & \Delta \\ \delta_N & \lambda_{0,0} & \delta_N \end{bmatrix} = 2^{-\frac{\Omega}{2}} \sum_q (-2)^q \binom{\Omega}{q}^{-1} \binom{p}{q} \binom{N}{q}. \quad (7)$$

The reduced matrix element may be expressed via the average of the operator with respect to the vacuum state with $N = 0$, and the average $\langle \hat{O}^p \rangle^N$ is presented in the form [1]

$$\langle \hat{O}^p \rangle^N = \sum_{q=0}^{\Omega} (-2)^q \binom{\Omega}{q}^{-1} \binom{p}{q} \binom{N}{q} \langle \hat{O}^p \rangle^0. \quad (8)$$

For the configuration with several open shells (subshells), the averaging is accomplished independently in the space of each shell (subshell).

In order to expand the physical operator O in terms of irreducible operators $\hat{O}^p$, the following operator C is constructed:

$$CO = \frac{1}{4} \sum_{\rho} \left\{ \left[a_\rho^\dagger, \left[a_\rho, O \right] \right] + \left[a_\rho, \left[a_\rho^\dagger, O \right] \right] \right\}, \quad (9)$$

where $a^\dagger$ and a are the electron creation and annihilation operators. The irreducible operator $\hat{O}^p$ is an eigenoperator of C:

$$C\hat{O}^p = p\hat{O}^p. \quad (10)$$

Using Eq. (9), the projection operator P^p may be constructed, which projects out $\hat{O}^p$ from O:

$$P^p = \sum_{q} (-1)^{p+q} \binom{C}{q} \binom{q}{p}. \quad (11)$$

Expansions for the general one- and two-electron operators in terms of irreducible parts are given in Refs. [1, 8] and for particular operators of atomic quantities they are given in Ref. [3]. An irreducible one-electron operator acting in the space of a single configuration is obtained by excluding its average from the operator. The average of the spin-orbit interaction operator H^{so} vanishes. Therefore, this operator itself is irreducible:

$$H^{so} \equiv \hat{H}^{so}. \quad (12)$$

Scalar one-electron operators, such as kinetic energy and the Coulomb interaction of electrons with a nucleus in the nonrelativistic approximation or the Dirac Hamiltonian in the relativistic single-configuration approximation, may be simply taken out from the average, because their matrix elements are term-independent. On the other hand, such operators acting between two configurations K, K' must be treated as irreducible one-electron traceless operators. The same holds for the one-electron radiative transition operator D in the dipole approximation or the two-electron Auger transition operator usually approximated by the Coulomb interaction operator H^C:

$$D_{KK'} \equiv \hat{D}_{KK'}, \quad H^C_{KK'} \equiv \hat{H}^C_{KK'}. \quad (13)$$

The operator of the Coulomb interaction between electrons acting within the single-configuration space is expanded into the scalar part, equal to the average energy of configuration $\bar{E}(K)$, and the two-electron part obtained by subtracting the average energy from the operator:

$$\hat{H}^C_K = H^C - \bar{E}(K). \quad (14)$$

Only the reduction of the two-electron operator acting between two configurations which differ by the state of one electron is more complicated. Such an operator splits into one-electron and two-electron parts with their expressions given in Ref. [3].

The product of k irreducible operators $\hat{O}_1 \ldots \hat{O}_k$ may be reduced using projection operator (11). Considering the commutators between electron creation ($a^\dagger$) and annihilation (a) operators, two kinds of contractions appear: left contractions, when the operator $a^\dagger$ stands to the left of the operator a contracted with it, and right contractions, when $a^\dagger$ stands to the right of a. Only the terms containing contractions between all creation and annihilation operators give a contribution to vacuum expectation. Finally, the result is given by

$$\langle \hat{O}_1 \hat{O}_2 \ldots \hat{O}_k \rangle^N = \binom{\Omega}{N}^{-1} \sum_{t=0}^{\min(p,N)} \binom{\Omega - p}{N - t} \hat{D}^p_t, \quad (15)$$

where p is the number of contractions in each term of the average (number of pairs of creation and annihilation operators in the averaged operators), t is the number of left contractions, and $\hat{D}^p_t$ is the vacuum expectation in which all creation and annihilation operators are contracted among themselves.

If the operators act on the states of different shells or subshells, the numbers p_i and t_i are determined for every space independently, and the whole average is obtained as product of the averages in all spaces.

The creation and annihilation operators must be contracted in all possible ways (except of contractions between $a^\dagger$ and a in the same operator $\hat{O}_i$, since they have already been taken into account when reducing the operators O_i). The problem of finding all possible contraction schemes is considerably simplified by using special summation diagrams.

3. Diagrammatic method for finding expressions of the averages

In the second quantization representation, one- and two-electron operators take the following form:

$$\hat{F} = \sum_{\nu\zeta} a_\nu^\dagger a_\zeta \langle \nu | \hat{f} | \zeta \rangle, \tag{16}$$

$$\hat{G} = \frac{1}{4} \sum_{\nu\xi\zeta\eta} a_\nu^\dagger a_\xi^\dagger a_\eta a_\zeta \langle \nu\xi | \hat{g} | \zeta\eta \rangle^a. \tag{17}$$

Here the Greek letters stand for the sets of single-electron quantum numbers. In the *LS* coupling, $\nu \equiv n_\nu l_\nu m_\nu \mu_\nu$, where m_ν is the projection of orbital momentum and μ_ν is the projection of spin momentum. The last multiplier on the right side is the one- or two-electron matrix element. Though the validity of the Pauli principle is ensured by anticommutation properties of the operators $a^\dagger$ and a, the two-electron matrix element is nevertheless defined with respect to the antisymmetric wave functions

$$\langle \nu\xi | x_1 x_2 \rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \langle \nu | x_1 \rangle & \langle \nu | x_2 \rangle \\ \langle \xi | x_1 \rangle & \langle \xi | x_2 \rangle \end{vmatrix} \tag{18}$$

in order to simplify properties of the diagrams. Since only two-electron matrix elements with respect to antisymmetric wave functions are used in this paper, the superscript a will be omitted in all formulae below.

The one-electron operator is represented by a vertex (dot), the two-electron operator by two vertices arranged in turn (Fig. 1). The operators

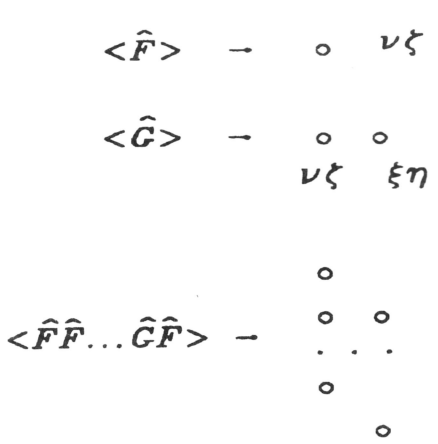

Fig. 1. Graphical representation of one-electron (16), two-electron operator (17) as well as of a product of several operators in the average

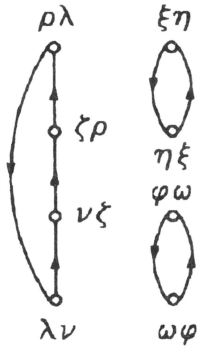

Fig. 2. One of the diagrams for the average of the product of four two-electron operators $\langle \hat{G}\hat{G}\hat{G}\hat{G} \rangle$

in the diagram are displayed from the bottom up to the top, corresponding to their arrangement in the average from the left to the right. Each contraction is shown as a directed line, going by convention from a to $a^\dagger$ (Fig. 2). Since the contractions within the same irreducible operator are excluded, the diagram contains no horizontal lines or the lines beginning and ending at the same vertex. The left contraction is represented by a downward line, and the right one by an upward line. The second single-electron state indicated beside the vertex, from which the line begins, must coincide with the first state at the vertex, on which this line ends.

Because all operators in the average must be contracted, all vertices in the diagram are linked by one or several closed loops (each vertex belongs to only one loop, all arrows in the loop have the same direction), and the summation diagram is always closed. The relation between two-electron matrix elements with respect to antisymmetric wave functions

$$\langle \nu\xi | \hat{g} | \zeta\eta \rangle = \langle \xi\nu | \hat{g} | \eta\zeta \rangle \tag{19}$$

allows one to exclude contractions between vertices of different columns, thus only vertices of the same column must be linked together.

One diagram represents one possible distribution of contractions, so the average with respect to the configuration $K \equiv n_1 l_1^{N_1} \ldots n_q l_q^{N_q}$ or $n_1 l_1 j_1^{N_1} \ldots n_q l_q j_q^{N_q}$ is expressed by the following sum:

$$\langle \hat{O}_1 \hat{O}_2 \ldots \hat{O}_k \rangle^K = \sum_{\text{diagr}} N_{\text{diagr}} M_{\text{diagr}}, \tag{20}$$

where summation is accomplished over all non-equivalent diagrams. N_{diagr} is the N-multiplier containing entire dependence on the number of electrons in the shells:

$$N_{\text{diagr}} = (-1)^{h+t} \prod_{i=1}^{q} \binom{\Omega_i}{N_i}^{-1} \binom{\Omega_i - p_i}{N_i - t_i}$$

$$= (-1)^{h+t} \prod_i \frac{N_i(N_i-1)\dots(N_i-t_i+1)(\Omega_i-N_i)(\Omega_i-N_i-1)\dots(\Omega_i-N_i-p_i+t_i-1)}{\Omega_i(\Omega_i-1)\dots(\Omega_i-p_i+1)} \quad (t_i \le N_i), \tag{21}$$

where t_i is the number of left contractions ($t = \sum_i t_i$), p_i is the total number of contractions in the space of the i-th shell (subshell), h is the number of loops in the diagram. The index i runs over all shells and/or subshells acted on by the operators. Since the averaging is performed independently in the space of each shell or subshell, some of the shells may be treated within LS coupling while the others are divided into subshells. According to Eq. (21), the multiplier $N_i(N_i-1)\dots(N_i-t_i+1)$ in the numerator corresponds to t_i left contractions, and the multiplier $(\Omega_i-N_i)(\Omega_i-N_i-1)\dots(\Omega_i-N_i-p_i+t_i-1)$ to p_i-t_i right contractions.

It should be noted that for avoiding uncertainties of the type 0 divided by 0 in Eq. (21), the multipliers in the numerator must be canceled with the identical multipliers in the denominator for particular N_i before specifying quantum numbers l_i.

The minimal sum M_{diagr} is the sum over all one-electron or two-electron matrix elements contained in the product of operators $\hat{O}_1\hat{O}_2\dots\hat{O}_k$ in the second quantization form. The additional multiplier 2^{-v}, where v is the number of equal bra and ket two-electron states (e. g. $\langle\nu\varphi|$ and $|\nu\varphi\rangle$), also appears. For example, the minimal sum corresponding to the diagram in Fig. 2 has the following expression:

$$2^{-2} \sum_{\lambda\omega\nu\varphi\zeta\eta\xi\rho} \langle\lambda\omega|\hat{g}|\nu\varphi\rangle\langle\nu\varphi|\hat{g}|\zeta\omega\rangle\langle\zeta\eta|\hat{g}|\rho\xi\rangle\langle\rho\xi|\hat{g}|\lambda\eta\rangle. \tag{22}$$

The numbers of the left and the right contractions may be simply determined from the minimal sum. It is necessary to consider every one-electron ket state, and if the same bra state stands to the left, then it is a left contraction, if to the right, then it is a right contraction. For example, according to expression (22), the contractions corresponding to the states $\omega\lambda\eta$ are left contractions and the ones corresponding to $\nu\varphi\zeta\rho\xi$ are right contractions.

All nonequivalent diagrams for the average of the product of k one-electron operators may be constructed linking them by the $1, 2, \dots, \{k/2\}$ loops in all possible ways, where $\{k/2\}$ is an integer part of $k/2$. Such diagrams for $k = 2, 3, 4$ are presented in Fig. 3 and for $k = 5$ in Fig. 4.

All nonequivalent diagrams for the product of several two-electron operators or two-electron and one-electron operators are obtained in the following way. First, all combinations of nonequivalent diagrams for the first and the second columns are constructed (vertices of one-electron operators are placed in both possible positions). Then, existing equivalent diagrams should be excluded from the obtained set. The diagrams are equivalent, if they can be transformed one to another by a mirror reflection with respect to a

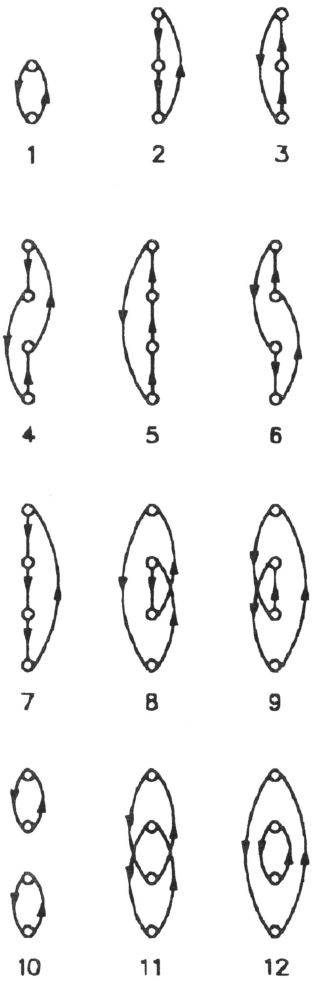

Fig. 3. Nonequivalent diagrams for the averages of the products of two (1), three (2, 3), and four (4–12) one-electron operators

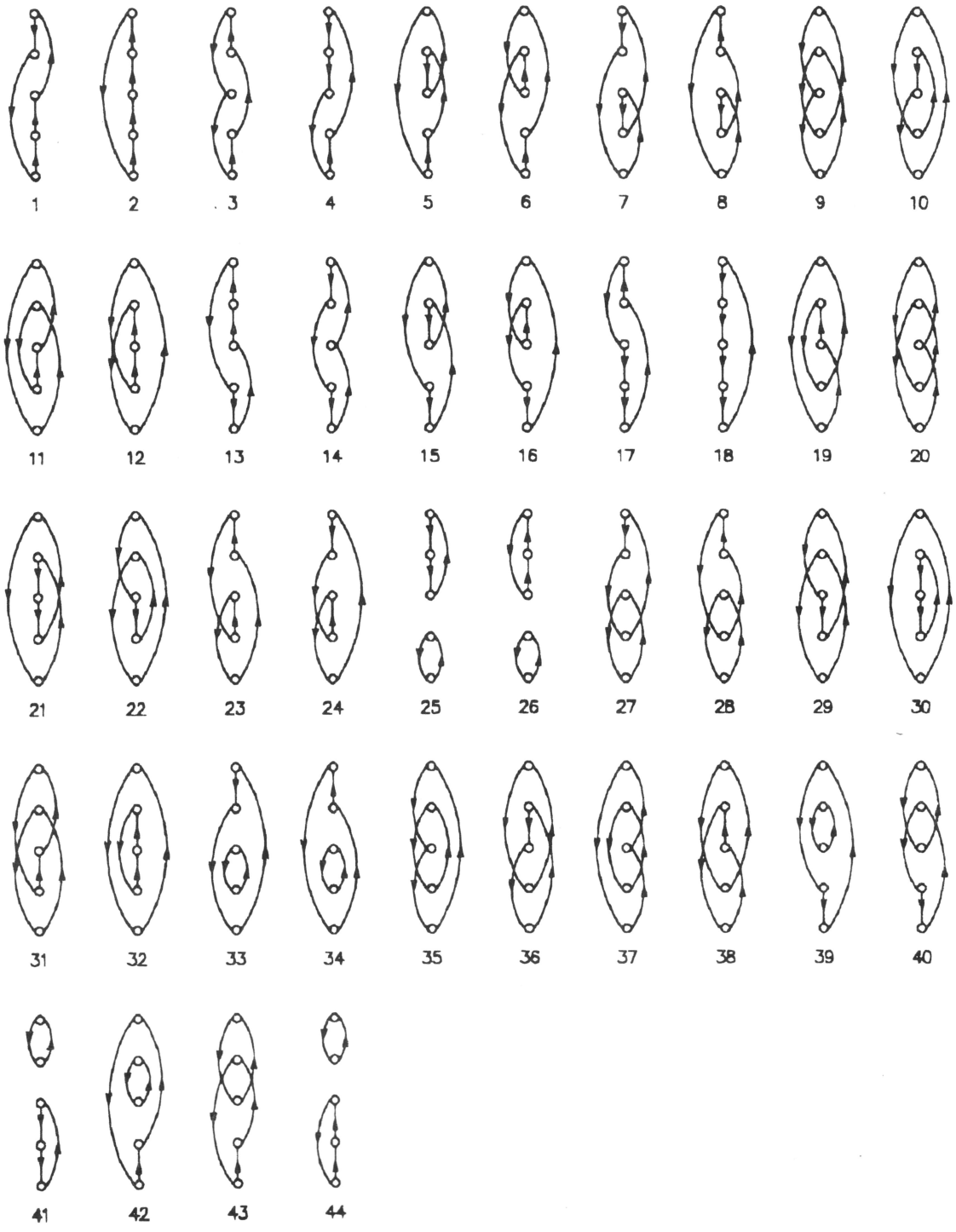

Fig. 4. Nonequivalent diagrams for the average of the product of five one-electron operators $\langle \hat{F}\hat{F}\hat{F}\hat{F}\hat{F} \rangle$.

vertical line between columns or by deformation of the diagram without changing positions of vertices (Fig. 5). The rest equivalent diagrams, corresponding to the symmetry property of matrix elements

$$\langle \nu\xi | \hat{g} | \zeta\eta \rangle = -\langle \nu\xi | \hat{g} | \eta\zeta \rangle = -\langle \xi\nu | \hat{g} | \zeta\eta \rangle, \quad (23)$$

may be obtained by cyclic permutation of the single-electron states in the minimal sum. Two single-electron states are permuted in any two-electron state, for example, states $\zeta\lambda$ in the minimal sum

$$\sum \langle \nu | \hat{f} | \zeta \rangle \langle \zeta\lambda | \hat{g} | \eta\omega \rangle \langle \rho\omega | \hat{g} | \nu\lambda \rangle \langle \eta | \hat{f} | \rho \rangle \quad (24)$$

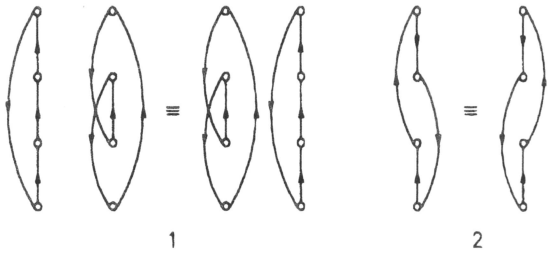

Fig. 5. Some of the equivalent diagrams

corresponding to the diagram 1 in Fig. 6, then λ is permuted with ν in the third matrix element and so on, generally, until reaching the initial state ζ. When during such a permutation the state ν in the one-electron matrix element $\langle \nu|\hat{f}|\zeta\rangle$ is reached, the order of permutation is simply transmitted to the next state ζ of this matrix element. When the cyclic permutation involves all single-electron states of the minimal sum except equal two-electron bra and ket states, the diagram is transformed into itself and, consequently, has no equivalent diagrams in the obtained set. Otherwise, if the permutation involves only some of the states, it produces an equivalent diagram which must be excluded from the set.

All nonequivalent diagrams for the averages of the product of two and three two-electron operators are shown in Fig. 7, and of some products of one-electron and two-electron operators in Fig. 8. The number of diagrams and minimal sums increases rapidly with the number of operators (Table 1). The number of minimal sums (principal diagrams) is smaller and increases slower

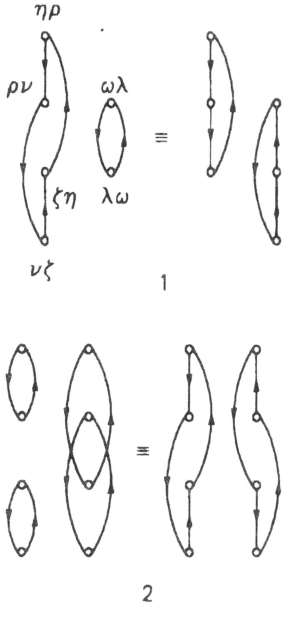

Fig. 6. Examples of diagrams, whose equivalency follows from the cyclic permutation of operators

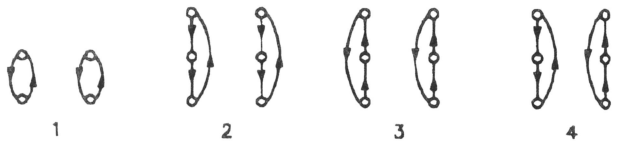

Fig. 7. Nonequivalent diagrams for the averages $\langle \hat{G}\hat{G}\rangle$ (1) and $\langle \hat{G}\hat{G}\hat{G}\rangle$ (2–4)

than the number of nonequivalent diagrams because the same minimal sum corresponds to a certain group of diagrams that may be transformed to each other by a vertical permutation of vertices corresponding to various operators (for example, the diagrams 1–24 and 25–44 in Fig. 4). The contribution of the whole such group of diagrams may be presented in terms of permutation operators acting on the minimal sum. One arbitrarily chosen diagram in the group is called a principal diagram and the arrangement of matrix elements in the minimal sum corresponding to the principal diagram is called to be the normal order (the matrix elements obtain ordinal numbers corresponding to their place in this minimal sum $M_i \equiv M_i(1, 2, \ldots, n)$).

The arrangement of matrix elements corresponding to other diagrams of this group is obtained by acting on the matrix elements in the normal order with the permutation operator:

$$M(ij \ldots pq) = P(ij \ldots pq)M(12 \ldots k-1k). \qquad (25)$$

Table 1. Number of nonequivalent diagrams (D) and minimal sums (M) for the averages of the products of one- and two-electron operators

Average	D	M	Average	D	M
$\langle \hat{F}\hat{F}\rangle$	1	1	$\langle \hat{F}\hat{F}\hat{F}\hat{F}\hat{F}\rangle$	44	2
$\langle \hat{G}\hat{G}\rangle$	1	1	$\langle \hat{F}\hat{F}\hat{F}\hat{F}\hat{G}\rangle$	42	3
$\langle \hat{F}\hat{F}\hat{F}\rangle$	2	1	$\langle \hat{F}\hat{F}\hat{F}\hat{G}\hat{G}\rangle$	74	8
$\langle \hat{F}\hat{F}\hat{G}\rangle$	1	1	$\langle \hat{F}\hat{F}\hat{G}\hat{G}\hat{G}\rangle$	144	17
$\langle \hat{F}\hat{G}\hat{G}\rangle$	3	2	$\langle \hat{G}\hat{G}\hat{G}\hat{G}\hat{G}\rangle$	870	15
$\langle \hat{F}\hat{F}\hat{F}\hat{F}\rangle$	9	2	$\langle \hat{F}\hat{F}\hat{F}\hat{F}\hat{F}\hat{F}\rangle$	265	4
$\langle \hat{F}\hat{F}\hat{F}\hat{G}\rangle$	6	1	$\langle \hat{F}\hat{F}\hat{F}\hat{F}\hat{F}\hat{G}\rangle$	320	4
$\langle \hat{F}\hat{F}\hat{G}\hat{G}\rangle$	11	5	$\langle \hat{F}\hat{F}\hat{F}\hat{F}\hat{G}\hat{G}\rangle$	616	24
$\langle \hat{G}\hat{G}\hat{G}\hat{G}\rangle$	42	6	$\langle \hat{F}\hat{F}\hat{F}\hat{G}\hat{G}\hat{G}\rangle$	1314	47
			$\langle \hat{F}\hat{F}\hat{G}\hat{G}\hat{G}\hat{G}\rangle$	3297	93
			$\langle \hat{G}\hat{G}\hat{G}\hat{G}\hat{G}\hat{G}\rangle$	28140	73

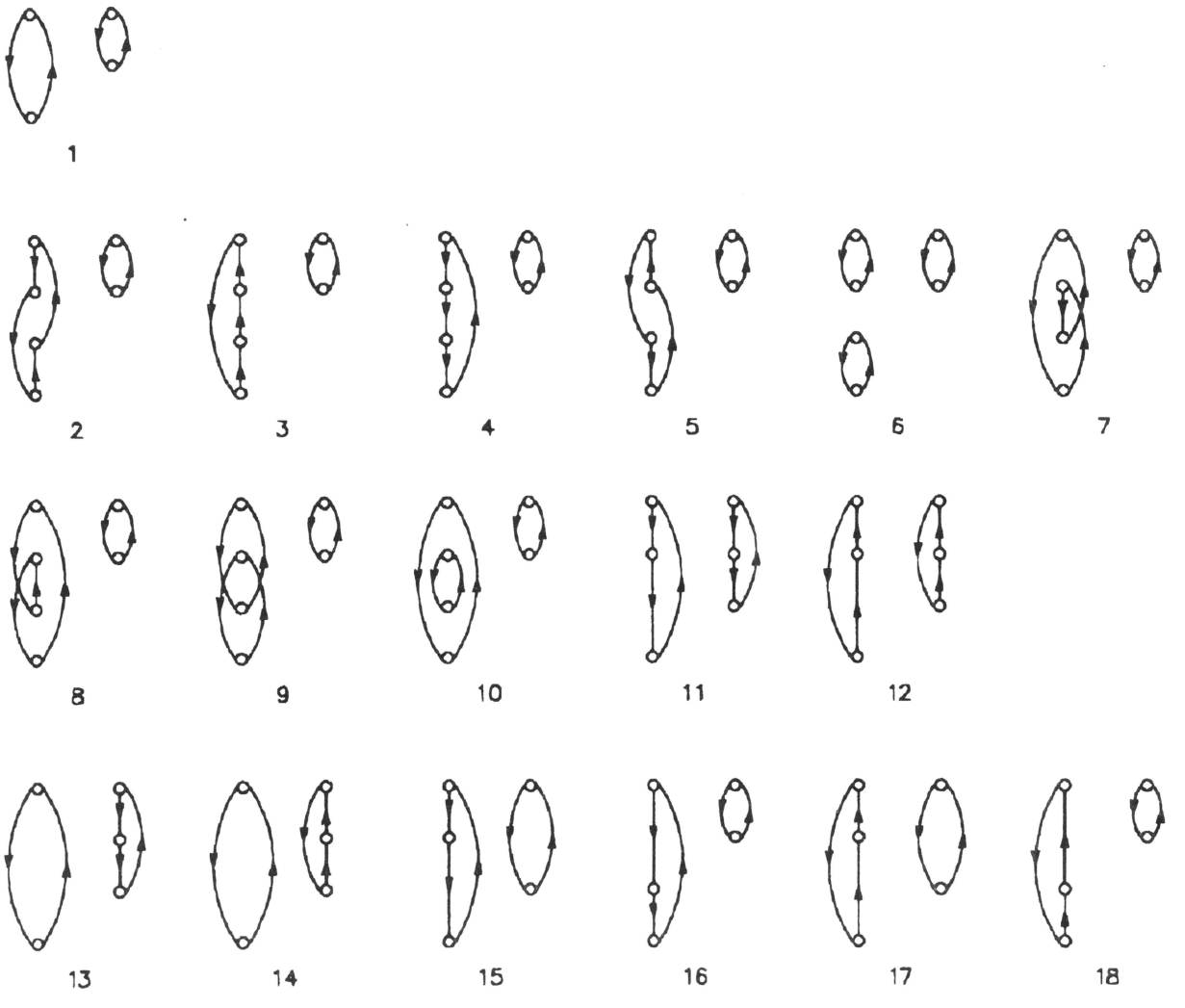

Fig. 8. Nonequivalent diagrams for the averages $\langle \hat{F}\hat{F}\hat{G} \rangle$ (1), $\langle \hat{F}\hat{F}\hat{G}\hat{G} \rangle$ (2–12), and $\langle \hat{F}\hat{F}\hat{F}\hat{G} \rangle$ (13–18)

The order of the matrix elements in the minimal sum is significant for obtaining the N-multiplier. When several permutation operators act on the same minimal sum, the matrix elements are supposed to have fixed numbers corresponding to their normal order:

$$P(2134)P(1324)M(1234) = \begin{pmatrix} 2 & 1 & 3 & 4 \\ 1 & 2 & 3 & 4 \end{pmatrix} \begin{pmatrix} 1 & 3 & 2 & 4 \\ 1 & 2 & 3 & 4 \end{pmatrix} M(1234) = P(2314)M(1234) = M(2314). \quad (26)$$

The principle diagrams and the expressions for the averages of the products of three, four and five one- and two-electron operators are given in Appendix.

While specifying the averages for a given configuration, the operators in the average turn into operators acting within the definite shell or between shells (transition operator) or into the sums of such operators (Hamiltonian). Thus, the averages of operators acting on definite shells are in practice considered. Nevertheless, summation over quantum numbers of shells or subshells sometimes remains in the average because matrix elements with respect to antisymmetric wave functions for the two-electron operator in the second quantization form of Eq. (17) are used. For example, let us consider the contribution of the diagram in Fig. 9 to the average $\langle \hat{G}_{12}\hat{G}_{12}\hat{G}_{12}\hat{G}_{12} \rangle$, where $\hat{G}_{12}$ is the irreducible two-electron operator corresponding to interaction between electrons of the shells $n_1 l_1^{N_1}$ and $n_2 l_2^{N_2}$ in the configuration K. The minimal sum takes the form

$$\sum_{\substack{\lambda\omega\rho\varphi \\ \nu\xi\zeta\eta}} \langle\lambda\omega|\hat{g}|\nu\varphi\rangle\langle\nu\xi|\hat{g}|\zeta\eta\rangle\langle\zeta\eta|\hat{g}|\rho\omega\rangle\langle\rho\varphi|\hat{g}|\lambda\xi\rangle. \tag{27}$$

Taking out quantum numbers $n_i l_i$ from the sets $\lambda, \omega, \ldots$ and performing summation over $n_i l_i$, we rewrite expression (27) in the form

$$\begin{aligned}
&\sum_{\substack{\lambda\omega\rho\varphi \\ \nu\xi\zeta\eta}} \langle l_1\lambda l_2\omega|\hat{g}|l_1\nu l_2\varphi\rangle\langle l_1\nu l_2\xi|\hat{g}|l_1\zeta l_2\eta\rangle\langle l_1\zeta l_2\eta|\hat{g}|l_1\rho l_2\omega\rangle\langle l_1\rho l_2\varphi|\hat{g}|l_1\lambda l_2\xi\rangle \\
&+\langle l_1\lambda l_2\omega|\hat{g}|l_1\nu l_2\varphi\rangle\langle l_1\nu l_2\xi|\hat{g}|l_2\zeta l_1\eta\rangle\langle l_2\zeta l_1\eta|g|l_1\rho l_2\omega\rangle\langle l_1\rho l_2\varphi|g|l_1\lambda l_2\xi\rangle \\
&+\langle l_2\lambda l_1\omega|\hat{g}|l_2\nu l_1\varphi\rangle\langle l_2\nu l_1\xi|\hat{g}|l_1\zeta l_2\eta\rangle\langle l_1\zeta l_2\eta|\hat{g}|l_2\rho l_1\omega\rangle\langle l_2\rho l_1\varphi|\hat{g}|l_2\lambda l_1\xi\rangle \\
&+\langle l_2\lambda l_1\omega|\hat{g}|l_2\nu l_1\varphi\rangle\langle l_2\nu l_1\xi|\hat{g}|l_2\zeta l_1\eta\rangle\langle l_2\zeta l_1\eta|\hat{g}|l_2\rho l_1\omega\rangle\langle l_2\rho l_1\varphi|\hat{g}|l_2\lambda l_1\xi\rangle,
\end{aligned} \tag{28}$$

where Greek letters denote the sets of the projections $m_i\mu_i$ only.

Due to relations (19) and (23), the all four terms in expression (28) are equal, but the N-multipliers differ for terms 1, 2 and 3, 4. Thus, summation over quantum numbers $n_i l_i$ must be taken out from the minimal sum. In Refs. [3, 6], a special operator $\hat{L}$ was introduced, which acted on the minimal sum and produced all possible summations over the quantum numbers of shells or subshells before the determination of N-multiplier.

The summation over the projections of single-electron moments in the minimal sum may be accomplished algebraically or graphically (using topological equivalence of the angular momentum and summation diagrams) [3]. The transformation of minimal sums to the coupled-momenta basis considerably simplifies their calculation, because in this basis the matrix elements of the Hamiltonian are independent of the projections of angular momenta.

Transforming the matrix element of the irreducible operator of the Coulomb interaction between electrons to the LS coupling scheme, the following quantity is obtained:

$$V^{LS}_{l_\nu l_\xi, l_\omega l_\eta} = V^{LS}_{n_\nu l_\nu n_\xi l_\xi, n_\omega l_\omega n_\eta l_\eta} = \frac{1}{2} N^{-1}_{n_\nu l_\nu, n_\xi l_\xi} N^{-1}_{n_\omega l_\omega, n_\eta l_\eta} \langle n_\nu l_\nu n_\xi l_\xi LS|\hat{h}^C|n_\omega l_\omega n_\eta l_\eta LS\rangle$$

$$= \begin{cases} \left[1+(-1)^{L+S}\right]\sum\limits_{k>0}\left[(-1)^L\begin{Bmatrix} l & l & L \\ l & l & k \end{Bmatrix} + \dfrac{1}{(2l+1)(4l+1)}\right]\langle l\|C^{(k)}\|l\rangle^2 F^k(nl,nl), & \text{if } n_\nu l_\nu = n_\omega l_\omega = n_\xi l_\xi = n_\eta l_\eta = nl, \\ \sum\limits_{k>0}(-1)^{l_1+l_2+L}\begin{Bmatrix} l_1 & l_2 & L \\ l_2 & l_1 & k \end{Bmatrix}\langle l_1\|C^{(k)}\|l_1\rangle\langle l_2\|C^{(k)}\|l_2\rangle F^k(n_1l_1,n_2l_2) + \sum\limits_k\left[(-1)^S\begin{Bmatrix} l_1 & l_2 & L \\ l_1 & l_2 & k \end{Bmatrix} + \dfrac{1}{2(2l_1+1)(2l_2+1)}\right] \\ \times\langle l_1\|C^{(k)}\|l_2\rangle^2 G^k(n_1l_1,n_2l_2), \quad \text{if } n_\nu l_\nu = n_\omega l_\omega = n_1l_1,\ n_\xi l_\xi = n_\eta l_\eta = n_2l_2, \end{cases} \tag{29}$$

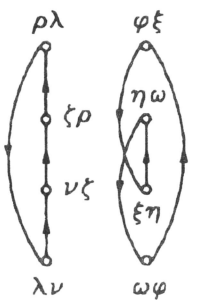

Fig. 9. Diagram for the average $\langle\hat{G}_{12}\hat{G}_{12}\hat{G}_{12}\hat{G}_{12}\rangle$, in the contribution of which the summation over the quantum numbers of shells remains

where F^k and G^k are radial integrals of the Coulomb interaction, $\hat{h}^C$ is the irreducible (traceless) Coulomb interaction operator, $N_{n_\nu l_\nu, n_\xi l_\xi}$ is the normalization multiplier

$$N_{n_\nu l_\nu, n_\xi l_\xi} = \begin{cases} 1/2 & \text{if } n_\nu l_\nu = n_\xi l_\xi, \\ 1/\sqrt{2} & \text{if } n_\nu l_\nu \neq n_\xi l_\xi. \end{cases} \tag{30}$$

It must be excluded from the matrix element because of the same normalization condition used for equivalent and nonequivalent electrons in Eq. (18). The matrix elements of the irreducible

operators of the spin-orbit interaction and the radiative dipole transition coincide with their usual expressions.

The group-diagrammatic method described above has been implemented in a general computer code which derives the formulae for the averages in terms of minimal sums and performs their calculation. A special code for the transformation of the minimal sums to the coupled-momenta basis has been written by V. Jonauskas.

4. General expression for the average of the product of one-electron operators. Averages of spin-orbit interaction, projection of the angular momentum, and standard unit operators

The group diagrammatic summation method was applied for finding explicit expressions of the main global characteristics of energy levels, emission and Auger spectra [4–6]. The general expression for the average of the product of one-electron operators was obtained in Ref. [1] and simplified using the diagrammatic method in Ref. [3]. Here we present also some applications of this expression for physical operators.

The diagram for the average of the product of k one-electron operators consists of one or several loops (Figs. 3 and 4). Let us designate the number of loops h and the number of vertices in the i-th loop, or its length, by k_i.

The number of all possible ways to link k_i vertices by one loop with the t_i $(1 \le t_i \le k_i - 1)$ downward segments is equal to the number of permutations of $k_i - 1$ elements during which the element with the larger number is replaced t_i times by the element with the smaller number and is equal to the Euler number A_{k_i,t_i-1} [1]:

$$A_{k_i,t_i-1} = \sum_{p_i=0}^{t_i-1} (-1)^{p_i+t_i+1}(p_i+1)^{k_i-1}\binom{k_i}{t_i-p_i-1}. \tag{31}$$

The number of ways to link k vertices by the loops of length $k_1, k_2, \ldots, k_h$ can be expressed as

$$K_k^{k_1k_2..k_h} = \frac{k!}{k_1!k_2!\ldots k_h!}\frac{1}{\nu(2)!\nu(3)!\ldots\nu(\{k/2\})!}, \tag{32}$$

where $\nu(i)$ is the number of loops of the same length linking up i vertices, $\{k/2\}$ is the integer part of the number $k/2$.

The minimal sum B_k may be factorized into h parts corresponding to the separate loops:

$$B_k = B_{k_1}B_{k_2}\ldots B_{k_h}. \tag{33}$$

Consequently, the average of the product of k one-electron operators acting on the electrons of the same shell or subshell with the number of states Ω and the number of electrons N is expressed as

$$\langle\hat{F}_1\ldots\hat{F}_k\rangle^N = \binom{\Omega}{N}^{-1}\sum_{h=1}^{\{k/2\}}\sum_{t=h}^{k-h}(-1)^{h+t}\binom{\Omega-k}{N-t}\sum_{\substack{k_1..k_h\\(2\le k_1..\le k_h\le k)}}K_k^{k_1..k_h}\sum_{t_1=1}^{k_1-1}A_{k_1,t_1-1}\cdots\sum_{t_h=1}^{k_h-1}A_{k_h,t_h-1}$$

$$\times\,\delta(t_1+\ldots+t_h,t)\,\delta(k_1+\ldots+k_h,k)\,B_{k_1}\ldots B_{k_h}. \tag{34}$$

For two, three, and four operators acting on the electrons of the single shell or subshell the average takes the following simple form:

$$\langle\hat{F}\hat{F}\rangle^N = \frac{N(\Omega-N)}{\Omega(\Omega-1)}B_2, \tag{35}$$

$$\langle\hat{F}\hat{F}\hat{F}\rangle^N = \frac{N(\Omega-N)(\Omega-2N)}{\Omega(\Omega-1)(\Omega-2)}B_3, \tag{36}$$

$$\langle\hat{F}\hat{F}\hat{F}\hat{F}\rangle^N = \frac{N(\Omega-N)}{\Omega(\Omega-1)(\Omega-2)(\Omega-3)}$$

$$\times\left\{\left[(\Omega-N-1)(\Omega-N-2)-4(N-1)(\Omega-N-1)+(N-1)(N-2)\right]B_4+3(N-1)(\Omega-N-1)B_2^2\right\}. \tag{37}$$

In the case of spin-orbit interaction, the minimal sum B_k is expressed as

$$B_k^{so} = \sum_j (2j+1)\langle nlj|h^{so}|nlj\rangle^k = 2^{-k+1}l(l+1)\left[l^{k-1}+(-1)^k(l+1)^{k-1}\right]\zeta_{nl}^k, \tag{38}$$

where ζ_{nl} is the spin-orbit parameter.

The number of levels of configuration K with the given total momentum J and the number of lines of radiative dipole transitions between all

levels of two configurations can be approximately calculated using the formulae [9]

$$N(K,J) = \frac{g(K)[J]}{\alpha_2(8\pi\alpha_2)^{1/2}}\left\{1+\frac{\alpha_4-3\alpha_2^2}{24\alpha_2^2}\left[15-\frac{[J]^2}{2\alpha_2}+\frac{[J]^4}{16\alpha_2^2}\right]\right\}\exp\left[-\frac{[J]^2}{8\alpha_2}\right], \tag{39}$$

$$N(K,K') = \frac{3g(K)g(K')}{8\alpha_2(\pi\alpha_2)^{1/2}}\left[1-\frac{1}{2\alpha_2}+\frac{\alpha_4-3\alpha_2^2}{\alpha_2^2}\left(\frac{5}{16}-\frac{35}{96\alpha_2}\right)\right]. \tag{40}$$

Here $g(K)$ is the statistical weight of configuration K; $[J] \equiv 2J+1$ and $\alpha_2 = [\alpha_2(K)+\alpha_2(K')]/2$, $\alpha_4 = [\alpha_4(K)+\alpha_4(K')]/2$, where $\alpha_2(K)$, $\alpha_4(K)$ are the moments of the distribution of eigenvalues of the operator $J_0^{(1)}$ or its averages:

$$\alpha_k = \frac{\sum_{\gamma JM}\langle K\gamma JM|J_0^{(1)}|K\gamma JM\rangle^k}{g(K)} = \langle J_0^{(1)}\ldots J_0^{(1)}\rangle^K_{k \text{ operators}}. \tag{41}$$

For this operator the minimal sum B_k is expressed as

$$B_k = \sum_{jm}\langle nljm|j_0^{(1)}|nljm\rangle^k = \sum_j\sum_{m=-j}^{j} m^k. \tag{42}$$

The minimal sums B_2 and B_4, which appear in Eq. (41), have the following form for the shell l^N:

$$B_2 = \frac{1}{6}(2l+1)(4l^2+4l+3), \tag{43}$$

$$B_4 = \frac{1}{120}(2l+1)(48l^4+96l^3+152l^2+104l+15), \tag{44}$$

and for the subshell j^N:

$$B_2 = \frac{j(j+1)(2j+1)}{3}, \tag{45}$$

$$B_4 = \frac{2j+1}{240}\left[3(2j+1)^4-10(2j+1)^2+7\right]. \tag{46}$$

Various physical operators or effective operators are often expressed in terms of standard unit operators $U^{(k)}$, $V^{(kk')}$ (k is the rank in the orbital space, and k' in the spin space), for which the single electron reduced matrix elements are defined as

$$\langle nl\|u^{(k)}\|nl\rangle = \{llk\}, \tag{47}$$

$$\langle nls\|v^{(kk')}\|nls\rangle = \{llk\}\left\{\tfrac{1}{2}\tfrac{1}{2}k'\right\}. \tag{48}$$

Here $\{j_1j_2j_3\}$ is the triangle delta-function, which requires the triangle relations for the quantum numbers j_1, j_2, and j_3 to be satisfied.

The averages of the operators $U^{(k)}$ or $V^{(kk')}$ do not vanish only at $k=0$ or $k=k'=0$, therefore the irreducible one-electron operators acting on the electrons of the shell l^N are given by

$$\hat{U}^{(k)} = U^{(k)} - \delta(k,0)\frac{N}{\sqrt{2l+1}}, \tag{49}$$

$$\hat{V}^{(kk')} = V^{(kk')} - \delta(k,0)\delta(k',0)\frac{N}{\sqrt{4l+2}}. \tag{50}$$

The minimal sums of the product of operators $V^{(kk')}$ are expressed in terms of the sum of the Clebsch-Gordan coefficients:

$$\begin{aligned} B_t &= \sum_{m\mu}\langle m_1\mu_1|v^{(k_1k_1')}_{q_1q_1'}|m_2\mu_2\rangle\langle m_2\mu_2|v^{(k_2k_2')}_{q_2q_2'}|m_3\mu_3\rangle\ldots\langle m_{t-1}\mu_{t-1}|v^{(k_{t-1}k_{t-1}')}_{q_{t-1}q_{t-1}'}|m_t\mu_t\rangle\langle m_t\mu_t|v^{(k_tk_t')}_{q_tq_t'}|m_1\mu_1\rangle \\ &= [l,s]^{-t/2}\{llk_1\}\{ssk_1'\}\ldots\{llk_t\}\{ssk_t'\}\sum_{\substack{m_1m_2\ldots m_t\\ \mu_1\mu_2\ldots\mu_t}}\begin{bmatrix} l & k_1 & l\\ m_2 & q_1 & m_1\end{bmatrix}\begin{bmatrix} l & k_2 & l\\ m_3 & q_2 & m_2\end{bmatrix}\ldots\begin{bmatrix} l & k_{t-1} & l\\ m_t & q_{t-1} & m_{t-1}\end{bmatrix}\begin{bmatrix} l & k_t & l\\ m_1 & q_t & m_t\end{bmatrix} \\ &\quad\times\begin{bmatrix} 1/2 & k_1' & 1/2\\ \mu_2 & q_1' & \mu_1\end{bmatrix}\begin{bmatrix} 1/2 & k_2' & 1/2\\ \mu_3 & q_2' & \mu_2\end{bmatrix}\ldots\begin{bmatrix} 1/2 & k_{t-1}' & 1/2\\ \mu_t & q_{t-1}' & \mu_{t-1}\end{bmatrix}\begin{bmatrix} 1/2 & k_t' & 1/2\\ \mu_1 & q_t' & \mu_t\end{bmatrix}. \end{aligned} \tag{51}$$

The tensor operators with nonzero ranks in the orbital and spin spaces may be joined in scalar or tensorial products. Let us suppose that the final rank in both spaces is 0. Performing summation of the Clebsch-Gordan coefficients arising from the minimal sum and tensorial product, we obtain for the averages of two and three operators

$$\langle (\hat{V}^{(kk')} \cdot \hat{V}^{(kk')}) \rangle^N = \frac{N(4l+2-N)}{(4l+2)(4l+1)} \{llk\}\{\tfrac{1}{2}\tfrac{1}{2}k'\}[1-\delta(k,0)\delta(k',0)], \tag{52}$$

$$\left\langle \left[\left[\hat{V}^{(k_1k_1')} \times \hat{V}^{(k_2k_2')} \right]^{(k_3k_3')} \times \hat{V}^{(k_3k_3')} \right]^{(00)} \right\rangle^N = -\frac{N(4l+2-N)}{(4l+2)(4l+1)4l} \begin{Bmatrix} k_1 & k_2 & k_3 \\ l & l & l \end{Bmatrix} \begin{Bmatrix} k_1' & k_2' & k_3' \\ 1/2 & 1/2 & 1/2 \end{Bmatrix}$$

$$\times \left[(4l+1-N) - (-1)^{k_1+k_2+k_3}(N-1) \right] \left[1-\delta(k_1,0)\delta(k_1',0) \right] \left[1-\delta(k_2,0)\delta(k_2',0) \right] \left[1-\delta(k_3,0)\delta(k_3',0) \right]. \tag{53}$$

Using the relations (49) and (50), the averages of the standard unit operators may be found, for example,

$$\langle (V^{(kk')} \cdot V^{(kk')}) \rangle^N = \left[\frac{N(4l+2-N)}{(4l+2)(4l+1)} + \delta(k,0)\delta(k',0)\frac{N(N-1)}{4l+1} \right] \{l\,l\,k\}\{\tfrac{1}{2}\tfrac{1}{2}k'\}, \tag{54}$$

$$\left\langle \left[\left[U^{(k_1)} \times U^{(k_2)} \right]^{(k_3)} \times U^{(k_3)} \right]^{(0)} \right\rangle^N = \frac{N}{(4l+2)(4l+1)2l} \begin{Bmatrix} k_1 & k_2 & k_3 \\ l & l & l \end{Bmatrix} \Big\{ (4l+2-N) \Big[(4l+1-N) - (-1)^{k_1+k_2+k_3}(N-1)$$

$$+ (4l+2)(N-1)\left(\delta(k_1,0) + \delta(k_2,0) + \delta(k_3,0) \right) \Big] + \delta(k_1,0)\delta(k_2,0)\delta(k_3,0)(4l+2)^2(N-1)(N-2) \Big\}. \tag{55}$$

Two- and three-electron operators may be expressed in terms of the products of one-electron operators:

$$\sum_{i<j} \left(v_i^{(kk')} \cdot v_j^{(kk')} \right) = \frac{1}{2} \left(V^{(kk')} \cdot V^{(kk')} \right) - \frac{1}{2} \sum_i \left(v_i^{(kk')} \cdot v_j^{(kk')} \right), \tag{56}$$

$$\sum_{i<j<p} \left[\left[u_i^{(k_1)} \times u_j^{(k_2)} \right]^{(k_3)} \times u_p^{(k_3)} \right]_0^{(0)} = \frac{1}{6} \left[\left[U^{(k_1)} \times U^{(k_2)} \right]^{(k_3)} \times U^{(k_3)} \right]_0^{(0)}$$

$$- \frac{1}{6} \begin{Bmatrix} k_1 & k_2 & k_3 \\ l & l & l \end{Bmatrix} \left[\left(U^{(k_1)} \cdot U^{(k_1)} \right) + (-1)^{k_1+k_2+k_3} \left(U^{(k_2)} \cdot U^{(k_2)} \right) + \left(U^{(k_3)} \cdot U^{(k_3)} \right) - \frac{N}{2l+1} \left(1 + (-1)^{k_1+k_2+k_3} \right) \right]. \tag{57}$$

From Eqs. (56) and (57), the expressions follow for the averages of two- and three-electron operators with the complex inner structure:

$$\left\langle \sum_{i<j} (v_i^{(kk')} \cdot v_j^{(kk')}) \right\rangle^N = \frac{N(N-1)}{2(4l+2)(4l+1)} \left[(4l+2)\delta(k,0)\delta(k',0) - 1 \right] \{llk\}\{\tfrac{1}{2}\tfrac{1}{2}k'\}, \tag{58}$$

$$\left\langle \sum_{i<j<p} \left[\left[u_i^{(k_1)} \times u_j^{(k_2)} \right]^{(k_3)} \times u_p^{(k_3)} \right]^{(0)} \right\rangle^N = \frac{N(N-1)(N-2)}{3(4l+2)(4l+1)4l} \begin{Bmatrix} k_1 & k_2 & k_3 \\ l & l & l \end{Bmatrix}$$

$$\times \left\{ 1 + (-1)^{k_1+k_2+k_3} - (4l+2)\left[\delta(k_1,0) + \delta(k_2,0) + \delta(k_3,0) \right] + \delta(k_1,0)\delta(k_2,0)\delta(k_3,0)(4l+2)^2 \right\}. \tag{59}$$

A four-electron operator may have a various tensorial structure. The following effective operator often appears:

$$\sum_{i<j<p<q} \left(u_i^{(k_1)} \cdot u_j^{(k_1)} \right) \left(u_p^{(k_2)} \cdot u_q^{(k_2)} \right) = \frac{1}{24} \Big\{ \left(U^{(k_1)} \cdot U^{(k_1)} \right) \left(U^{(k_2)} \cdot U^{(k_2)} \right) - 4(-1)^{k_1+k_2} \sum_x \begin{Bmatrix} k_1 & k_2 & x \\ l & l & l \end{Bmatrix} \times$$

$$\times \left[6[x]^{1/2} \sum_{i<j<p} \left(\left[u_i^{(k_1)} \times u_j^{(k_2)} \right]^{(x)} \cdot u_p^{(x)} \right) + (-1)^x [x] \begin{Bmatrix} k_1 & k_2 & x \\ l & l & l \end{Bmatrix} \sum_{i<j} \left(u_i^{(x)} \cdot u_j^{(x)} \right) \right]$$

$$- \frac{2N}{2l+1} \sum_{i<j} \left[\left(u_i^{(k_1)} \cdot u_j^{(k_1)} \right) + \left(u_i^{(k_2)} \cdot u_j^{(k_2)} \right) \right] - \frac{N^2}{(2l+1)^2} \Bigg\}. \tag{60}$$

Its average is expressed as

$$\left\langle \sum_{i<j<p<q} \left(u_i^{(k_1)} \cdot u_j^{(k_1)} \right) \cdot \left(u_p^{(k_2)} \cdot u_q^{(k_2)} \right) \right\rangle^N = \frac{1}{6} \frac{N(N-1)(N-2)(N-3)}{(4l+2)(4l+1)4l(4l-1)} \left\{ \frac{2\delta(k_1,k_2)}{2k_1+1} - (-1)^{k_1+k_2} \begin{Bmatrix} l & l & k_1 \\ l & l & k_2 \end{Bmatrix} + \frac{2l-1}{2l+1} \right.$$

$$\left. - (4l-2)[\delta(k_1,0)+\delta(k_2,0)] - \frac{2}{4l+1} \left[1 - (-1)^{k_1+k_2} \right] [\delta(k_1,0)+\delta(k_2,0)] + \delta(k_1,0)\delta(k_2,0)(4l-2)(4l+2) \right\} \{llk_1\}\{llk_2\}. \tag{61}$$

These formulae may be useful when introducing mean characteristics of atomic quantities which correspond to the averages of some effective operators.

Conclusions

The general group-diagrammatic summation method allows summation of atomic quantities to be performed over all many-electron quantum numbers in either nonrelativistic or relativistic, single-configuration or CI approximations. The only assumption made is that the radial orbitals are term-independent. The simple rules of this method are convenient for deriving the expressions using a computer. This gives the possibility to obtain explicit expressions for the main global characteristics of the energy level, emission and Auger spectra, for the mean characteristics of configuration interaction in atoms and other quantities, which can be expressed by the averages of the products of operators.

Acknowledgements

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Appendix

Expressions for the averages of the products of one- and two-electron operators

Here we present expressions for the averages of the products of three, four, and five two-electron operators as well as of two-electron and one-electron operators (except $\langle \hat{F}\hat{F}\hat{G} \rangle$ which is described by only one diagram). The average of the product of one-electron operators is expressed by the explicit formula (34). The principal diagrams corresponding to the minimal sums in the normal form are given in Figs. 10–17. In all formulae below, $P(i \ldots q)$ is the permutation operator (25), its abbreviated notation $P(ij)$ means that only the i-th and the j-th matrix elements are interchanged. $\Pi(i \ldots q)$ denotes the sum of the operators of all possible permutations of $i \ldots q$ matrix elements in the minimal sum on which the operator is acting. The operator $\hat{L}$ produces summation over quantum numbers $n_i l_i$ or $n_i l_i j_i$ (see the comment below Eq. (28)). N_{diagr} is the N-multiplier defined by Eq. (21).

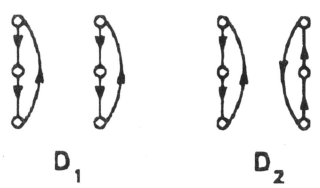

Fig. 10. Principle diagrams for the average $\langle \hat{G}\hat{G}\hat{G} \rangle$. The letter under the diagram designates the corresponding minimal sum

Figure 11. Principle diagram for the average $\langle \hat{F}\hat{F}\hat{F}\hat{G} \rangle$

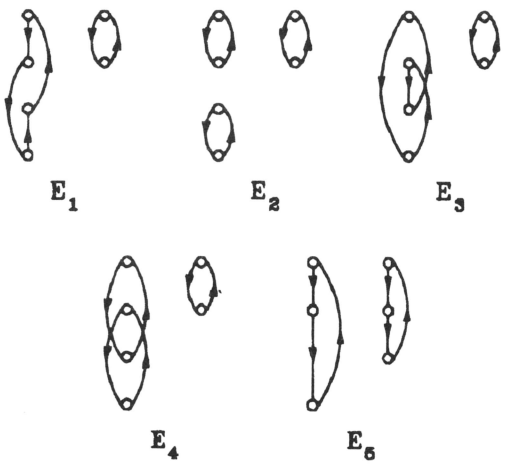

Fig. 12. Principle diagrams for the average $\langle \hat{F}\hat{F}\hat{G}\hat{G} \rangle$

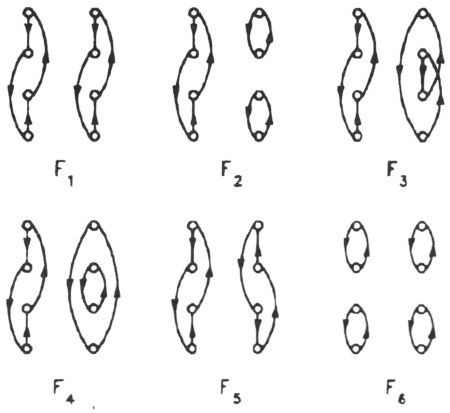

Fig. 13. Principle diagrams for the average $\langle \hat{G}\hat{G}\hat{G}\hat{G} \rangle$

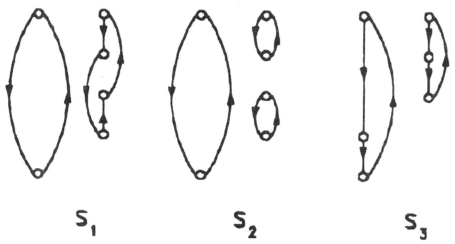

Fig. 14. Principle diagrams for the average $\langle \hat{F}\hat{F}\hat{F}\hat{F}\hat{G} \rangle$

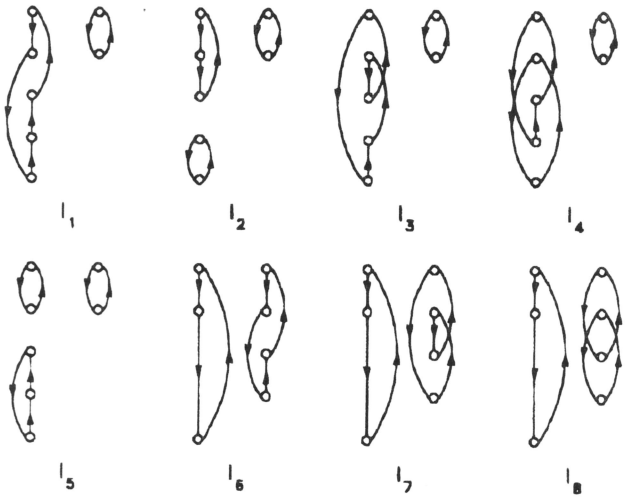

Fig. 15. Principle diagrams for the average $\langle \hat{F}\hat{F}\hat{F}\hat{G}\hat{G} \rangle$

$$\langle \hat{G}\hat{G}\hat{G} \rangle^K = N_{\text{diagr}} \hat{L} \{[1 + P(12)]D_1 + D_2\} \quad \text{(A 1)}$$

$$\langle \hat{F}\hat{F}\hat{F}\hat{G} \rangle^K = N_{\text{diagr}} \hat{L} \Pi(123) M_1 \quad \text{(A 2)}$$

$$\langle \hat{F}\hat{F}\hat{G}\hat{G} \rangle^K = N_{\text{diagr}} \hat{L} \{[1 + P(12)][1 + P(34)]E_1 + E_2 + [1 + P(34)](E_3 + E_4 + E_5)\} \quad \text{(A 3)}$$

$$\langle \hat{G}\hat{G}\hat{G}\hat{G} \rangle^K = N_{\text{diagr}} \hat{L} \{\Pi(234)(F_1 + F_2 + F_3 + F_4) + P(12)\Pi(234)F_2 + [P(12) + P(14)][P(23) + P(24) + P(34)]F_3 + [P(23) + P(24) + P(34)](F_5 + F_6)\} \quad \text{(A 4)}$$

$$\langle \hat{F}\hat{F}\hat{F}\hat{F}\hat{G} \rangle^K = N_{\text{diagr}} \hat{L} \{\Pi(1234)S_1 + [1 + P(12)]\{[P(23) + P(24) + P(34)]S_2 + \Pi(234)S_3\}\} \quad \text{(A 5)}$$

$$\langle \hat{F}\hat{F}\hat{G}\hat{G}\hat{G} \rangle^K = N_{\text{diagr}} \hat{L} \{\Pi(123)[1 + P(45)](I_1 + I_3 + I_4 + I_6 + I_8) + [1 + P(13) + P(23)][1 + P(45)]I_2 + [1 + P(12)]I_5 + [1 + P(12) + P(23)][1 + P(45)]I_7\} \quad \text{(A 6)}$$

$$\langle \hat{F}\hat{F}\hat{G}\hat{G}\hat{G} \rangle^K = N_{\text{diagr}} \hat{L} \{1 + P(12)]\Pi(345)(H_1 + H_2 + H_5 + H_6 + H_7 + H_8 + H_9 + H_{11} + H_{12}) + [1 + P(34)](H_3 + H_{16}) + H_4 + \Pi(345)(H_{10} + H_{13} + H_{14} + H_{15} + H_{17}) + [1 + P(34) + P(35)]H_{16}\} \quad \text{(A 7)}$$

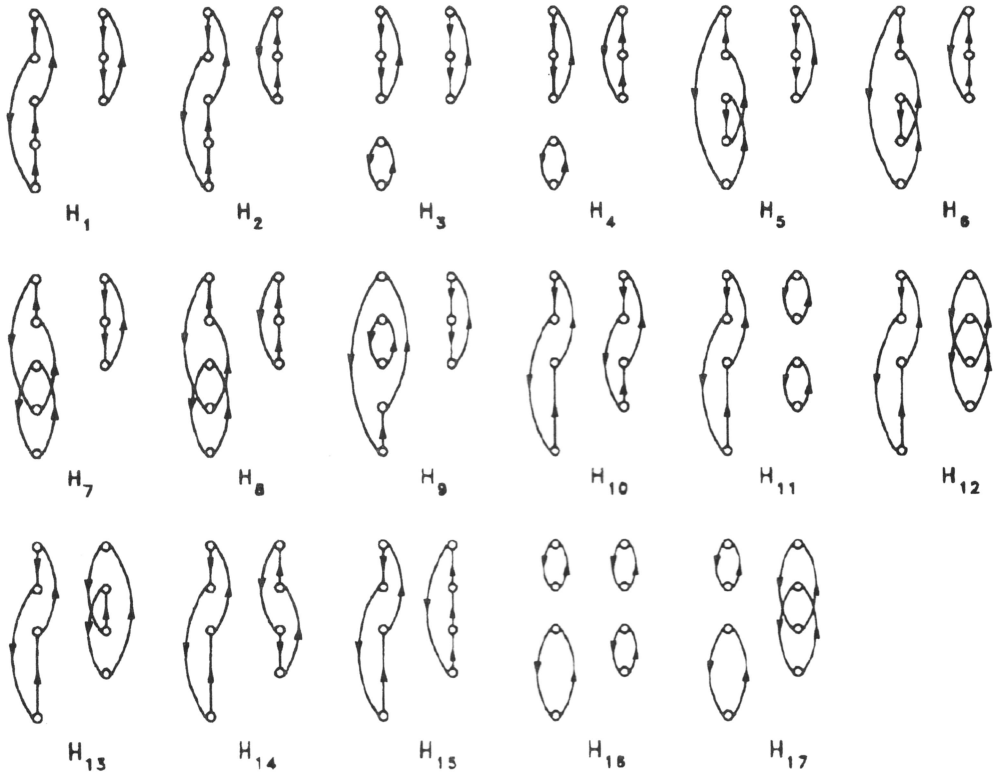

Fig. 16. Principle diagrams for the average $\langle \hat{\hat{F}}\hat{\hat{F}}\hat{\hat{G}}\hat{\hat{G}}\hat{G} \rangle$

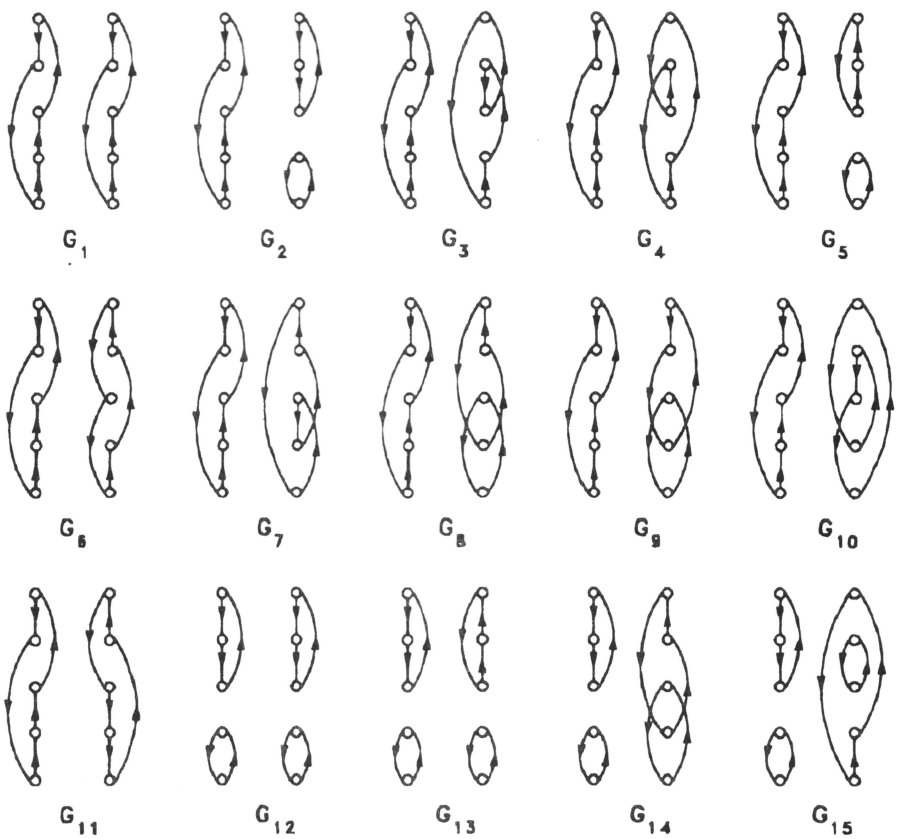

Fig. 17. Principle diagrams for the average $\langle \hat{G}\hat{G}\hat{G}\hat{G}\hat{G}\hat{G} \rangle$

$$\langle \hat{G}\hat{G}\hat{G}\hat{G}\hat{G}\hat{G} \rangle^K = N_{\text{diagr}} \hat{L} \{ \Pi(2345)(G_1 + G_{10}) + \Pi(12345)(G_2 + G_5 + G_9) + P(14)[1 + P(24)]\Pi(345)G_3$$

$$+ [P(13) + P(15)]\Pi(2345)[G_3 + G_7 + G_8 + G_{14}) + P(23)[1 + P(13) + P(14)]\Pi(345)G_4$$

$$+ \Pi(124)[1 + P(34) + P(45)]G_4 + P(13)\Pi(2345)(G_4 + G_6) + P(23)[1 + P(13) + P(15)]\Pi(345)G_6$$

$$+ \Pi(125)[1 + P(35) + P(45)]G_6 + [1 + P(24)]\Pi(345)(G_7 + G_{14})$$

$$+ P(12)[1 + P(24)]\Pi(345)G_8 + [P(15) + P(24)]\Pi(345)(G_{11} + G_{12}) + [1 + P(45)]G_{12}$$

$$+ P(23)P(14)[1 + P(35) + P(45)]G_{12} + P(24)P(13)[1 + P(35) + P(45)](G_{12} + G_{13})$$

$$+ [1 + P(13) + P(14) + P(15) + P(23) + P(24) + P(25)]G_{13} \} \qquad \text{(A 8)}$$

If one-electron and two-electron operators are arranged in the average in another than in the formulae above order such average is described by the same minimal sums. Its diagrams can be obtained by interchanging the corresponding vertices and its expression contains an additional permutation operator of matrix elements of different operators.

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