JOURNAL OF COMPUTATIONAL PHYSICS 91, 460–477 (1990)

Configuration Average of General n-Body Symmetrical Tensor Operators

J. OREG* AND W. H. GOLDSTEIN

High Temperature Physics Division,
Lawrence Livermore National Laboratory, Livermore, California 94550

A. BAR-SHALOM*

Department of Physcis and Space Science Laboratory,
University of California, Berkeley, California 94704

AND

M. KLAPISCH†

High Temperature Physics Division,
Lawrence Livermore National Laboratory, Livermore, California 94550

Received May 16, 1989; December 5, 1989

A new method for calculating configuration averages of n-body operators is presented. The method is easily adapted for calculations of high spectral moments, average cross sections of atomic processes, etc. We present a general explicit expression for the dependence of the configuration average on the occupation numbers. An algorithm based on the angular momentum graphical technique is then applied to obtain the dependence of the average on the quantum numbers of the orbitals involved. This algorithm is easily adapted to numerical applications using a newly developed angular momentum code. A detailed analytic example is presented for the case of average of a three-body effective interaction. © 1990 Academic Press, Inc.

I. INTRODUCTION

The calculation of configuration average of n-body symmetrical tensor operators (nBSTO) is essential to a variety of atomic physics problems. In particular, these averages turn up repeatedly in models for the atomic kinetics and the interpretation of emission spectra of highly ionized heavy atoms in hot plasma. For example, the

* Permanent address: Nuclear Research Center of the Negev, P. O. Box 9001, Beer Sheva, 84190, Israel.

† Permanent address: Racah Institute of Physics, Hebrew University, Jerusalem 91904, Israel.

0021-9991/90 $3.00

unresolved transition array (UTA) model [1] characterizes unresolved spectra by the moments of transition arrays that reduce to configuration averages nBSTOs. Another example occurs in the collisional-radiative model for atomic level populations in a plasma, where level-configuration and configuration–configuration average rates can be used (in addition to level–level rates) to reduce configurations to effective levels. It has been shown [2] that these average rates involve nBSTOs with $n<4$. In many cases the second quantization technique [1] provides a convenient procedure for averaging operators. But when equivalent electrons are involved, it can become cumbersome as n increases. In fact, in the UTA analysis only the first and second moments were fully investigated. For higher moments this procedure becomes impracticable. In this work we present an alternative method for evaluating configuration averages of nBSTOs based on traditional electron coordinate indices. We introduce the concept of "minimal configuration" for the nBSTO and derive a general relation connecting the original and minimal configuration averages. This relation yields an explicit general expression for the occupation number dependence of the average in a general N-electron system ($N \geqslant n$). The dependence of the average on the configuration orbital quantum numbers is then obtained by calculating the minimal configuration average. For this purpose we present a simple algorithm based on the angular momenta graphical rules yielding closed diagrams. This algorithm may be easily connected to the recently developed NJGRAF code [3], yielding the algebraic expressions and numerical values of the various graphs.

In Section II we define the nBSTO and present our notations. In Section III we introduce the concept of an n-electron "minimal configuration" and present the fundamental relation that relates configuration averages over the actual (N-electron) to that in the minimal (n-electron) configuration. The algorithm using graphical technique is described in Section IV to derive the dependence of average on the orbital quantum numbers in terms of closed diagrams. The method is applied in Section V to calculate the configuration average shifts due to configuration interaction [4, 5]. In Section VI we present the various steps of a computer code based on the algorithm of Section IV.

II. Definitions and Notations

For an N-electron system, an elementary n-body symmetrical tensor operator (nBSTO) is defined by

$$S \equiv \sum^{(N)} S_{i_1 i_2 \cdots i_n} \tag{1}$$

$$S_{i_1 i_2 \cdots i_n} = [Z^{(k_1)}_{i_1}(\mathbf{j}_1, \mathbf{j}'_1) \times Z^{(k_2)}_{i_2}(\mathbf{j}_2, \mathbf{j}'_2) \times \cdots \times Z^{(k_n)}_{i_n}(\mathbf{j}_n, \mathbf{j}'_n)]^{[K]}, \tag{2}$$

where $\sum^{(N)}$ indicates the symmetrical sum $\sum_{i_1=1}^{N} \sum_{i_2=1}^{N} \cdots \sum_{i_n=1}^{N}$ with the restriction

$i_1 \neq i_2 \cdots \neq i_n$, and $Z_i^{(k)}(\mathbf{j}, \mathbf{j}')$ is the unit tensor operator of rank k of the ith electron, defined by its (k independent) reduced matrix element,

$$\langle \mathbf{j}_a \| Z^{(k)}(\mathbf{j}, \mathbf{j}') \| \mathbf{j}_b \rangle = \delta_{\mathbf{j}\mathbf{j}_a} \delta_{\mathbf{j}'\mathbf{j}_b} \tag{3}$$

and $\mathbf{j} \equiv nlj$ are the orbital quantum numbers.

In Eq. (2) $[K]$ stands for a specific set of $n-1$ triangle conditions defining the coupling order of intermediate tensorial ranks $\mathbf{k}_1, \mathbf{k}_2, ..., \mathbf{k}_{n-1}$ of the **n**-body operator. (Of course, these operators must be coupled to a total rank of zero in order that the configuration average of S does not vanish). For example, the two couplings

$$[K] \equiv [(k_1, k_2, \mathbf{k}_1), (\mathbf{k}_1, k_3, \mathbf{k}_2) \cdots (\mathbf{k}_{n-1}, k_n, 0)] \tag{4a}$$

and

$$[K] \equiv [(k_1, k_2, \mathbf{k}_1), (k_3, k_4, \mathbf{k}_2), (\mathbf{k}_1, \mathbf{k}_2, 0)] \tag{4b}$$

indicate respectively the operators:

$$S = \sum^{(N)} [[[Z_{i_1}^{(k_1)}(\mathbf{j}_1, \mathbf{j}_1') \times Z_{i_2}^{(k_2)}(\mathbf{j}_2, \mathbf{j}_2')]^{(\mathbf{k}_1)} \times Z_{i_3}^{(k_3)}(\mathbf{j}_3, \mathbf{j}_3')]^{(\mathbf{k}_2)} \cdots]^{(0)} \tag{5a}$$

$$S = \sum^{(N)} [[Z_{i_1}^{(k_1)}(\mathbf{j}_1, \mathbf{j}_1') \times Z_{i_2}^{(k_2)}(\mathbf{j}_2, \mathbf{j}_2')]^{(\mathbf{k}_1)} \times [Z_{i_3}^{(k_3)}(\mathbf{j}_3, \mathbf{j}_3') \times Z_{i_4}^{(k_4)}(\mathbf{j}_4, \mathbf{j}_4')]^{(\mathbf{k}_2)}]^{(0)} \tag{5b}$$

The coupling $[K]$ of the operator S is defined explicitly, in terms of the components $Z_{iq}^{(k)}$ ($q = -k, -k+1, ..., k$) of the operators $Z_i^{(k)}$, as

$$S_{i_1 i_2 \cdots i_n} = \sum_{\text{all } q} (k_1 q_1, k_2 q_2, ..., k_n q_n | [K]) \prod_{\alpha=1}^{n} Z_{i_\alpha q_\alpha}^{(k_\alpha)}(\mathbf{j}_\alpha, \mathbf{j}_\alpha'), \tag{6}$$

where $(k_1 q_1, k_2 q_2, ..., k_n q_n | [K])$ is a recoupling coefficient.

It is easy to show that any atomic interaction can be expressed in terms of nBSTOs combined with one electron reduced matrix elements of the spherical harmonics $C_q^{(k)}$ and radial integrals. In Appendix A, in addition to a few simple examples, we express the spectral moments of a transition array, used in the UTA model, in terms of nBSTOs. A detailed discussion on the use of the operators $Z^{(k)}$ is presented in the appendix of Ref. [6].

We adopt the standard representation of an N electron configuration C,

$$C \equiv \prod_s \mathbf{j}_s^{N_s}, \qquad \sum_s N_s = N, \tag{7}$$

where N_s is the number of electrons occupied in the shell "s" whose orbital quantum numbers are $\mathbf{j}_s \equiv n_s l_s j_s$ and the sum is over different shells s.

Finally, we define the configuration average of S by

$$\langle S\rangle_C \equiv \sum_{\psi\in \mathbf{C}} \langle\psi\,|S|\,\psi\rangle/g_c, \tag{8}$$

where

$$g_c = \prod_s \binom{2j_s+1}{N_s} \tag{9}$$

is the statistical weight of C, $\binom{2j_s+1}{N_s}$ is a binomial coefficient, and ψ runs over all its allowed states.

III. The Occupation Number Dependence of the nBSTOs Average

Clearly, $\langle S\rangle_c$ vanishes unless $N\geqslant n$. Referring to Eq. (2) we define the "minimal configuration" of S as the $N=n$ electron configuration C_n constructed by its orbitals, i.e.,

$$C_n = \mathbf{j}_1\mathbf{j}_2\cdots\mathbf{j}_n = \mathbf{p}:\mathbf{j}'_1\mathbf{j}'_2\cdots\mathbf{j}'_n. \tag{10}$$

This definition makes explicit the requirement that the "primed" orbitals can differ from the "unprimed" set by at most a specific permutation $\mathbf{p}$ that is unique to the operator S. Otherwise the configuration average of S will vanish.

In general, we may have equivalent orbitals in C_n ($\mathbf{j}_i=\mathbf{j}_j$). Renumbering the different shells, s, using the standard occupation number representation we may write

$$C_n = \prod_s \mathbf{j}_s^{n_s}, \qquad \sum_s n_s = n \tag{11}$$

and the actual configuration for averaging is

$$C = \prod_s \mathbf{j}_s^{N_s} \qquad \text{with} \quad N_s\geqslant n_s. \tag{12}$$

Using the identities [7],

$$\sum_{i\neq j} [Z_i^{(k_1)}(\mathbf{j}_1,\mathbf{j}'_1)\times Z_j^{(k_2)}(\mathbf{j}_2,\mathbf{j}'_2)]^{(k)}$$

$$= (-1)^{(k_1+k_2-k)} \sum_{i\neq j} [Z_j^{(k_2)}(\mathbf{j}_2,\mathbf{j}'_2)\times Z_i^{(k_1)}(\mathbf{j}_1,\mathbf{j}'_1)]^{(k)} \tag{13a}$$

$$= \sum_{t_1,t_2} f(\mathbf{j}_i,k_i,t_i) \sum_{i\neq j} [Z_i^{(t_1)}(\mathbf{j}_1,\mathbf{j}'_2)\times Z_j^{(t_2)}(\mathbf{j}_2,\mathbf{j}'_1)]^{(k)}, \tag{13b}$$

where $f(\mathbf{j}_i,k_i,t_i)$ is an explicit recoupling coefficient, we may perform the permuta-

tion $\mathbf{p}:\mathbf{j}'_1\mathbf{j}'_2\cdots\mathbf{j}'_n$ step by step and rewrite the operator S in terms of "direct type" operators D:

$$S=\sum_{[T]}(K|T)\,D \tag{14}$$

$$D=\sum^{(N)}[Z^{(t_1)}_{i_1}(\mathbf{j}_1,\mathbf{j}_1)\times Z^{(t_2)}_{i_2}(\mathbf{j}_2,\mathbf{j}_2)\times\cdots\times Z^{(t_n)}_{i_n}(\mathbf{j}_n,\mathbf{j}_n)]^{[T]}, \tag{15}$$

where $(K|T)$ is a combination of the recoupling coefficients $f(\mathbf{j}_i, k_i, t_i)$, and $[T]$ defines *any chosen set of intermediate coupling scheme* of the operators $Z^{(t)}_i(\mathbf{j},\mathbf{j})$. In Eq. (14) $\sum_{[T]}$ stands for summation over all possible values of the ranks of $[T]$.

The details of $(K|T)$ are not important here. The only point that counts here is that they do not involve electronic coordinates.

In Appendix B we show that

$$\langle D\rangle_c=\varphi\langle D\rangle_{c_n}, \tag{16}$$

where

$$\varphi=\prod_s\binom{N_s}{n_s}. \tag{17}$$

Clearly from Eq. (14) we also have the general relation

$$\langle S\rangle_c=\varphi\langle S\rangle_{c_n}. \tag{18}$$

This relation is a generalization of the well-known expression for the configuration average of the electrostatic interaction [11], *a special case with* $n=2$. *It reduces the calculation of the configuration average from a general N-electron system into an* $n\leqslant N$ *electron , usually much simpler, system.*

The algorithm for calculating the configuration average within the "minimal configuration" ($N=n$ system), yielding analytic expressions for the averages in terms of the orbitals quantum numbers, is described in the next section.

IV. Configuration Average of C_n: The Dependence on Orbital Angular Momenta

Since the configuration average forms a matrix trace it is independent of the choice of angular momentum coupling scheme of the states $\psi\in c_n$. For convenience we will work in the "*jm*" Slater determinant (SD) scheme in which

$$|\psi\rangle=(1/n!)^{1/2}\sum_p(-1)^p\,p\colon|\mathbf{m}_1(1)\,\mathbf{m}_2(2)\cdots\mathbf{m}_n(n)\rangle, \tag{19}$$

where $\mathbf{m}_i$, $i=1, 2, n$ represents the different individual orbital sets

$$\mathbf{m}\equiv\mathbf{j}m\equiv nljm, \tag{20}$$

and p permutes the $\mathbf{m}_i$ sets leaving electronic coordinates (1), (2), ..., (n), fixed.

From Eqs. (8), (19), and (1), we have

$$g_{c_n}\langle S\rangle_{c_n} = \sum_{\psi\in c_n}\langle\psi\,|S|\,\psi\rangle$$
$$= \sum_{\{\mathbf{m}_i\}}\sum_{p,\,\underline{p}}(-1)^{\underline{p}} \tag{21}$$
$$\times\langle p{:}\mathbf{m}_1(1)\,\mathbf{m}_2(2)\cdots\mathbf{m}_n(n)\,|S_{12\ldots n}|\,\underline{pp}{:}\mathbf{m}_1(1)\,\mathbf{m}_2(2)\cdots\mathbf{m}_n(n)\rangle,$$

where $\{\mathbf{m}_i\}$ is the allowed set $\mathbf{m}_1\neq\mathbf{m}_2\neq\cdots\neq\mathbf{m}_n$, defining each SD state $\psi\in C_n$ in the sum.

It can be easily seen that the summation over all $\psi\equiv\{\mathbf{m}_i\}\in C_n$ and over p in Eq. (21) amounts to summing each m value from $-j$ to j with the fixed $\mathbf{j}\equiv nlj$ values of Eq. (11). Further, since the orbitals $\mathbf{j}\equiv nlj$ of each electron (1), (2), ..., (n) in Eq. (21) is fixed by the definition of $S_{12\ldots n}$, the nonvanishing terms in Eq. (21) result from permutations of equivalent electrons only, specifically,

$$g_{\mathbf{c}_n}\langle S\rangle_{c_n} = \sum_{\text{all } m=-j}^{j}\sum_{p'}(-1)^{p'}\langle\mathbf{m}_1(1)\,\mathbf{m}_2(2)\cdots\mathbf{m}_n(n)$$
$$\times|S_{12\ldots n}|\,p'{:}\mathbf{m}_1(1)\,\mathbf{m}_2(2)\cdots\mathbf{m}_n(n)\rangle. \tag{22}$$

In Eq. (22) the sum is over $p'=p\mathbf{p}$, where $\mathbf{p}$ is the permutation of Eq. (10) and p permutes only m symbols ($\mathbf{m}\equiv\mathbf{j}m$) of equivalent electrons. The sum over all m means that for all $i=1, n$, m_i runs over all possible values from j_i to $-j_i$.

The restriction $\mathbf{m}_1\neq\mathbf{m}_2\neq\cdots\neq\mathbf{m}_n$ has been removed in Eq. (22) as contributions of $\mathbf{m}_i=\mathbf{m}_j$ vanish owing to the antisymmetry of the determinantal wavefunctions.

From Eq. (22), Eq. (2), and Eq. (6) we now obtain the following working formula in terms of one-electron matrix elements:

$$g_{\mathbf{c}_n}\langle S\rangle_{c_n} = \sum_{p'}(-1)^{p'}\Bigg\{\sum_{\text{all }m}\sum_{\text{all }q}(k_1q_1, k_2q_2, \ldots k_nq_n|\,[K])$$
$$\times\prod_{\alpha=1}^{n}\langle\mathbf{m}_\alpha(\alpha)\,|Z^{(k_\alpha)}_{\alpha q_\alpha}(\mathbf{j}_\alpha,\mathbf{j}'_\alpha)|\,p'{:}\mathbf{m}_\alpha(\alpha)\rangle\Bigg\}. \tag{23}$$

The evaluation of the contribution to Eq. (23) from each permutation $p'\equiv p\mathbf{p}$ proceeds now using graphical representation of the matrix element in accordance with the intermediate couplings $[K]$ of the various operators $\mathbf{Z}^{(k)}$ of Eq. (2).

The graphical rules have been described in details by Lindgren and Morrison [8] and we will only sketch the derivation briefly. Using the conventions of Lindgren and Morrison [8] (with negative junctions), the matrix element $\langle\mathbf{m}\,|Zq^{(k)}(\mathbf{j},\mathbf{j}')|\,\mathbf{m}'\rangle$ and the recoupling coefficients $(k_1q_1, k_2q_2|k_{12}q_{12})$ are represented by the graphs of Fig. 1.

The summation over all q is removed by combining lines having the same kq symbols so that the k lines form a tree-like diagram which is constructed simply

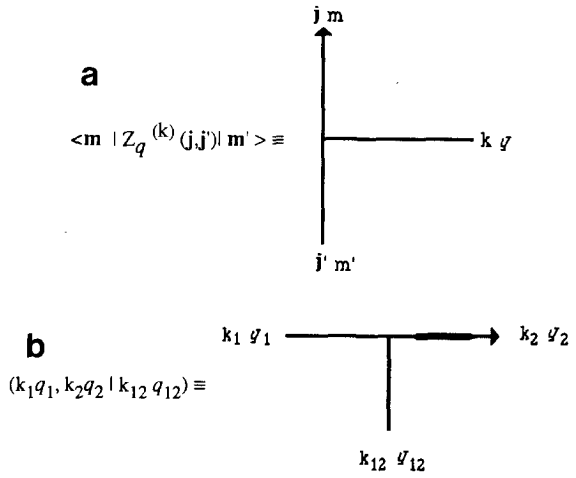

FIG. 1. Graphical representations of: (a) a single electron matrix element; (b) a two angular momenta recoupling coefficient. The heavy line on a k line stands for a multiplication factor of $(2k+1)^{1/2}$.

according to the triangle conditions in $[K]$. The two examples of Eq. (5a) and Eq. (5b) yield the graphs of Fig. 2. In these graphs, the line corresponding to the resultant zero rank of Eqs. (4a) and (4b) has been removed, canceling the factor $(2k+1)^{1/2}$ from the line to which it was connected.

Note that since in the ket $p' \equiv p\mathbf{p}$ permutes the m symbols of the bra, each m symbol appears exactly twice in Fig. 2, one from the bra (with an arrow) and one from the ket. Summation over all m_i yields closed loops formed by joining the ends of lines that share a summed index. Each closed graph is then assigned an algebraic expression in terms of n-j symbols according to the graphical rules. The application of this procedure is demonstrated analytically in the Section VI. The algorithm we propose for computer evaluation of the average of S is based on the above procedure, using the recently presented NJGRAF code [3] which evaluates the algebraic expressions and numerical values of any closed diagram. This will be described in detailes in Section VI.

VI. EXAMPLES

(a) *Configuration Average of a Three-Body Effective Interaction in* $\mathbf{j}^N$

Our method is applied in this section to calculate analytically the configuration average of a three-body effective interaction in a configuration of the type $\mathbf{j}^N$. It can be shown that the three-body effective operator has the form:

$$S_{\text{eff}} = \sum_{i \neq k \neq 1} [[Z_i^{(t)}(\mathbf{j}_1, \mathbf{j}_a) \times Z_k^{(t')}(\mathbf{j}_a, \mathbf{j}_1)]^{(t'')} \times Z_1^{(t'')}(\mathbf{j}_b, \mathbf{j}_b)]^{(0)}. \tag{24}$$

The interaction $(\mathbf{j}^{N-1}\mathbf{j}' - \mathbf{j}^N)$ of Ref. [4] is the special case with $\mathbf{j}_a = \mathbf{j}_b = \mathbf{j}_1 \equiv \mathbf{j}$.

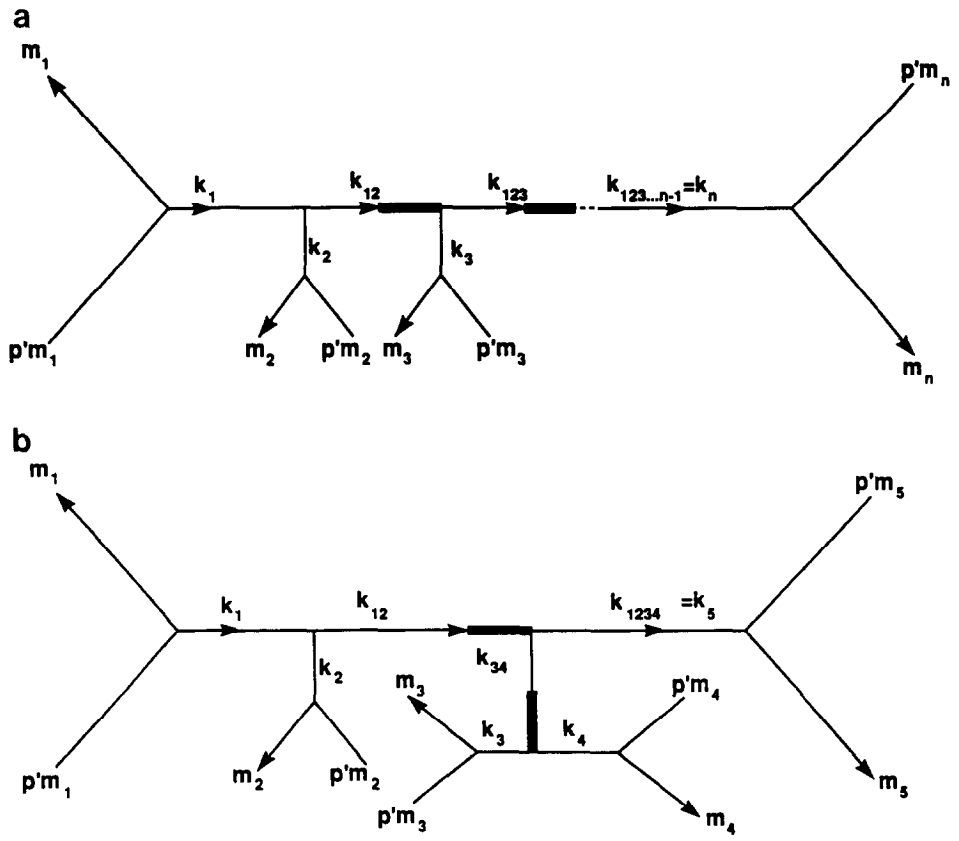

FIG. 2. Graphical representation of a N-electron matrix element corresponding to one of the permutations p' of Eq. (23): (a) $[K]$ coupling as in Eq. (5a); (b) $[K]$ coupling as in Eq. (5b).

In order to calculate $\langle S_{\text{eff}} \rangle_C$ we start with the minimal configuration ($n=3$)

$$C_3 = \mathbf{j}_1 \mathbf{j}_a \cdot \mathbf{j}_b = \mathbf{p} : \mathbf{j}_a \mathbf{j}_1 \cdot \mathbf{j}_b \tag{25}$$

$$\mathbf{p} = \begin{cases} a \leftrightarrow 1 & \text{for} \quad \mathbf{j}_a \neq \mathbf{j}_1 \\ I & \text{for} \quad \mathbf{j}_a = \mathbf{j}_1. \end{cases} \tag{26}$$

The statistical weight of C_3 is:

$$g_{c_3} = [(2j_1+1)(2j_a+1-\delta_{a1})(2j_b+1-\delta_{b1}-\delta_{ab})]/[\delta_{a1}+\delta_{b1}+\delta_{ab}]!. \tag{27}$$

The average is to be taken over a configuration given by

$$C = \mathbf{j}_1^{N_1} \mathbf{j}_a^{N_a} \cdot \mathbf{j}_b^{N_b} \cdots \mathbf{j}^{N_c}, \tag{28}$$

where $\mathbf{j}^{N_c}$ is any other shell not included in C_3.

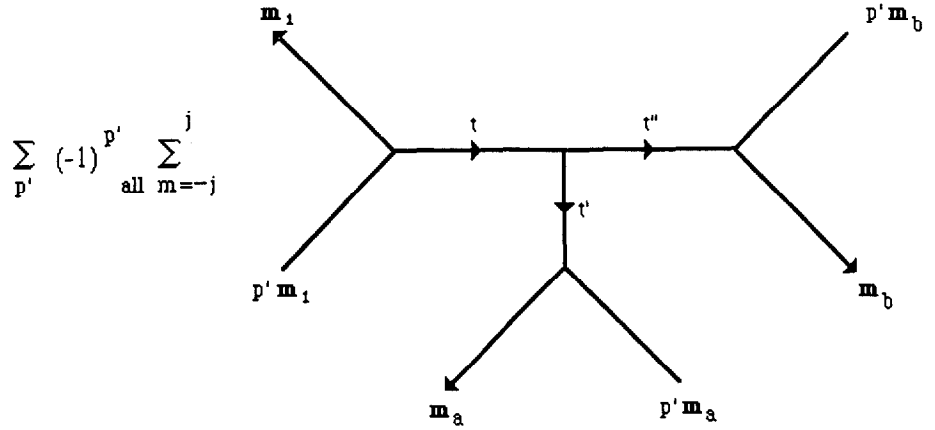

FIG. 3. Graphical representation of the configuration average of the three-body operator corresponding to Eq. (24). The summation is over the permutation p' of Table I.

The dependence of $\langle S_{\text{eff}} \rangle_c$ on the occupation numbers $N_1 N_a N_b$ is obtained from Eq. (21),

$$\langle S_{\text{eff}} \rangle_c = f g_{c_3} \langle S_{\text{eff}} \rangle_{c_3}, \tag{29}$$

where

$$f = \varphi / g_{c_3}$$
$$= [N_1(N_a - \delta_{a1})(N_b - \delta_{b1} - \delta_{ab})]/[(2j_1 + 1)(2j_a + 1 - \delta_{a1})(2j_b + 1 - \delta_{b1} - \delta_{ab})]. \tag{30}$$

The graph representing this configuration average is presented in Fig. 3. The 3-electron permutations $p' = p\mathbf{p}$ (p permutes equivalent electrons only), over which there is a summation, are listed in Table I and the corresponding closed diagrams

TABLE I

The Equivalent Electron Permutations That Contribute to the Configuration Average of the 3-Body Effective Interaction Operator S_{eff} in Fig. 4 and Eq. (31).

No.	p': $\mathbf{m}_1(1)$	$\mathbf{m}_a(2)$	$\mathbf{m}_b(3)$	$(-1)^{p'}$	Vanishes unless
1	$\mathbf{m}_a$	$\mathbf{m}_1$	$\mathbf{m}_b$	-1	
2	$\mathbf{m}_1$	$\mathbf{m}_a$	$\mathbf{m}_b$	$+1$	δ_{a1}
3	$\mathbf{m}_a$	$\mathbf{m}_b$	$\mathbf{m}_1$	$+1$	δ_{b1}
4	$\mathbf{m}_b$	$\mathbf{m}_1$	$\mathbf{m}_a$	$+1$	δ_{ab}
5	$\mathbf{m}_1$	$\mathbf{m}_b$	$\mathbf{m}_a$	-1	$\delta_{a1}\delta_{ab}$
6	$\mathbf{m}_b$	$\mathbf{m}_a$	$\mathbf{m}_1$	-1	$\delta_{a1}\delta_{ab}$

G_i (the index i enumerates the permutations p') are obtained from Fig. 3 by joining lines that share a summed index. In the convention of Ref. [8] a phase factor of $(-1)^{2j}$ is introduced for each reversal in arrow direction of a j line and a factor of $(-1)^{j_1+j_2+j_3}$ for each anticyclic permutation of j_1, j_2, j_3 lines that share a common junction. These operations are required to match the lines in Fig. 3. The resulting closed diagrams G_i and their algebraic expressions are given in Fig. 4. The desired algebraic expression for the average effective interaction is:

$$\langle S_{\text{eff}} \rangle_c = \mathbf{f} \sum_i (-1)\, p'_i G_i. \tag{31}$$

(b) *Configuration Average Shifts Due to Configuration Interaction*

We present here the calculation of configuration average shifts due to configuration interaction observed experimentally by Sugar and Kaufman [5] in copper plasma. The mixed configurations under consideration: $C = 3s3p^3$ and $C' = 3s^23p3d$ are comprised of the following relativistic configurations;

$$\begin{aligned} C &= \{c_1 = sp^2_{1/2}\, p_{3/2} + c_2 = sp_{1/2}\, p^2_{3/2} + c_3 = sp^3_{3/2}\} \\ C' &= \{c'_1 = s^2 p_{1/2} d_{3/2} + c'_2 = s^2 p_{1/2} d_{5/2} \\ &\quad + c'_3 = s^2 p_{3/2} d_{3/2} + c'_4 = s^2 p_{3/2} d_{5/2}\}. \end{aligned} \tag{32}$$

In the non-relativistic limit the radial orbitals depend only on nl and not on j and the $j-j$ spliting is small. The shift $\Delta_{C,C'}$ of C due to C' may then be written in term of the relativistic configuration shifts [9] $\Delta_{C,C'}$ by

$$\Delta_{C,C'} = (1/g_C) \sum_{i,j} g_{c_i} \Delta_{c_i, c'_j}. \tag{33}$$

We will present in detail here only the shift of c_1 due to c'_1. As can be seen from Section II of Ref. [10] this shift can be written as

$$\Delta_{c_1, c'_1} = [R^1(pp, ds)]^2 \langle Y \rangle_{c_1} / \Delta E_{C,C'}, \tag{33}$$

where $R^1((pp, ds))$ is a Slater integral, $\Delta E_{C,C'}$ is the average energy difference between C and C', and

$$\begin{aligned} Y \equiv \sum_{i \neq j} \sum_{k \neq l} &(\mathbf{Z}^{(1)}_i (p_{1/2} d_{3/2}) \cdot \mathbf{Z}^{(1)}_j (p_{3/2} s_{1/2})) \\ &\times (\mathbf{Z}^{(1)}_k (s_{1/2}\, p_{3/2}) \cdot \mathbf{Z}^{(1)}_l (d_{3/2}\, p_{1/2})). \end{aligned} \tag{34}$$

By recoupling the $\mathbf{Z}$ operators, Y can be expressed in terms of two types of nbSTOs one three-body (for $i = l$) and the other two body (for $i = l$ and $j = k$), i.e.,

$$Y = \sum_{T=0}^{1} \{a_T S_T + b_T S'_T\}, \tag{35}$$

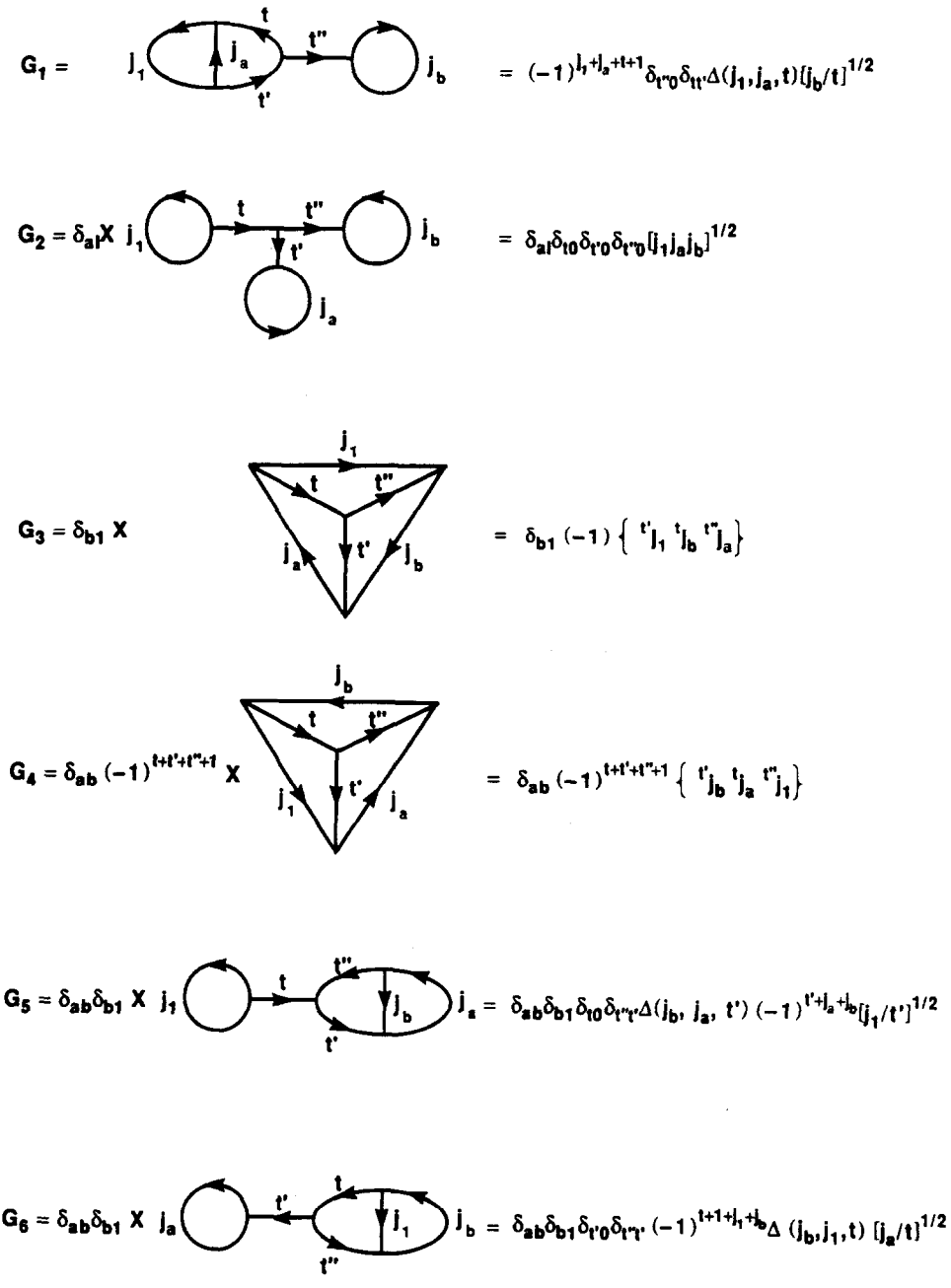

FIG. 4. Graphical and algebraic representations of the six permutations, enumerated in Table I, that contribute to $\langle S_{\text{eff}} \rangle_{C_3}$ of Eq. (31). In this figure, $[j] \equiv 2j + 1$,

$[j_1, j_2] \equiv (2j_1 + 1)(2j_2 + 1)$ and $[j_1/j_1] \equiv (2j_1 + 1)/(2j_2 + 1)$.

where a_T and b_T are given in terms of $6j$ symbols as

$$a_T=(-1)^{T+1}(2T+1)^{1/2}\begin{Bmatrix}1 & T & 1\\ 1/2 & 3/2 & 1/2\end{Bmatrix}$$
$$b_T=(-1)^{T+1}(2T+1)^{1/2}\begin{Bmatrix}1 & T & 1\\ 3/2 & 1/2 & 3/2\end{Bmatrix} \tag{36}$$

and

$$S_T=\sum_{i\neq j\neq k}[\mathbf{Z}_i^{(T)}(p_{1/2}p_{1/2})\,\mathbf{Z}_j^{(1)}(p_{3/2}s_{1/2})\,\mathbf{Z}_k^{(1)}(s_{1/2}p_{3/2})]^{(0)}$$
$$S'_T=\sum_{i\neq j}[\mathbf{Z}_i^{(T)}(p_{1/2}p_{1/2})\,\mathbf{Z}_j^{(T)}(p_{3/2}p_{3/2})]^{(0)}. \tag{37}$$

The corresponding minimal configurations are $A=s_{1/2}p_{1/2}p_{3/2}$ and $B=p_{1/2}p_{3/2}$ and from Eq. (18), the occupation number dependence, φ yields for the two nbSTOs a factor of 2. Therefore,

$$\langle Y\rangle_{c_1}=2\left[\sum_T\{a_T\langle S_T\rangle+b_T\langle S'_T\rangle\}\right]. \tag{38}$$

For both $\langle S_T\rangle$ and $\langle S'_T\rangle$ only a single permutation in Eq. (23) contributes, leading to the graphs of Fig. 5 yielding

$$\langle S_T\rangle=-\delta_{T,0}(2/3)^{1/2}/g_A$$
$$\langle S'_T\rangle=\delta_{T,0}(8)^{1/2}/g_B. \tag{39}$$

The Slater integral $R^1(pp,ds)=156\times10^3\,\mathrm{cm}^{-1}$ and the average energy shifts $\Delta E_{C,C'}=-167\times10^3\,\mathrm{cm}^{-1}$ for copper were obtained from least square fit from the experiment. This together with

$$g_A=16, \qquad g_B=8$$
$$a_0=-(1/6)^{1/2}, \qquad b_0=(1/72)^{1/2} \tag{40}$$

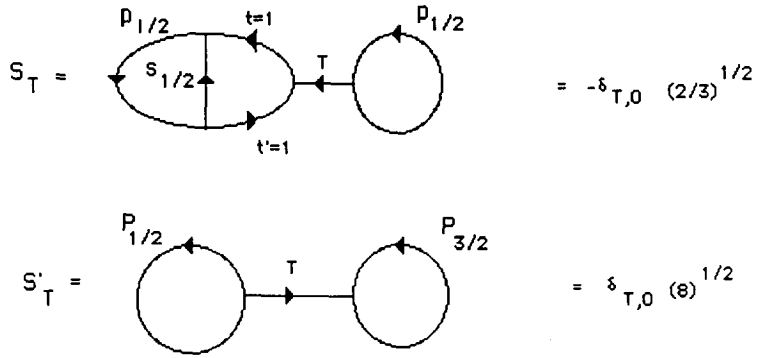

FIG. 5. The graphical and algebraic representations of $\langle S_T\rangle$ and $\langle S'_T\rangle$ of Eq. (38).

leads to

$$\Delta_{c_1,c_1'} = (1/8)[R^1(pp, ds)]^2/\Delta E_{C,C'} = -18.3 \times 10^3 \text{ cm}^{-1}. \tag{41}$$

The other shifts on c_1 are

$$\begin{aligned} &\Delta_{c_1,c_2'} = \Delta_{c_1,c_4'} = 0 \qquad \text{(selection rules)} \\ &\Delta_{c_1,c_3'} = (1/9)[R^1(pp, ds)]^2/\Delta E_{C,C'} = -16.2 \times 10^3 \text{ cm}^{-1}. \end{aligned} \tag{42}$$

It turns out that all the other pair-contributions c, c' of Eq. (32) again contain only the single Slater integral $R^1(pp, ds)$ and their summation over c' and average over c according to Eq. (33) yields the result,

$$\Delta_{C,C'} = (8/60)[R^1(pp, ds)]^2/\Delta E_{C,C'} = -19{,}5 \times 10^3 \text{ cm}^{-1}, \tag{43}$$

in excellent agreement with the experiment [10] ($19.0 \times 10^3 \text{ cm}^{-1}$).

VI. The Various Steps of a Computer Program

The various steps of a computer flowchart are described below:

(a) *Read Input*

1. *N*Shell. The number of occupied shells in the configuration for averaging C.

2. ($n(i)$, $l(i)$, $j(i)$, $N(i)$, $i = 1$, *N*Shell). The orbitals and occupation numbers defining $C = \prod_s \mathbf{j}_s^{N_s}$.

3. n. The number of electron indices of the averaged operator S.

4. ($ns(i)$, $ls(i)$, $js(i)$, $i = 1, n$). The set of orbitals $\mathbf{j}_1\mathbf{j}_2 \cdots \mathbf{j}_n$ defining S.

5. ($\mathbf{p}(i)$, $i = 1, n$). The permutation $\mathbf{p}: \mathbf{j}_1'\mathbf{j}_2' \cdots \mathbf{j}_n' = \mathbf{j}_1\mathbf{j}_2 \cdots \mathbf{j}_n$ defining S.

6. ($k(i)$, $i = 1, n$). The ranks of the operators $Z^{(k)}$ defining S.

7. ($k(i)$, $i = n+1, 2n-1$). The ranks $\mathbf{k}_1, \mathbf{k}_2, \ldots, \mathbf{k}_{n-1}$ of intermediate couplings identified by the next read.

8. ((kcoup(jt, jn), $jt = 1, 3$) $jn = 1, n-1$). The indices defining the $\mathbf{n}-1$ triangle conditions of $[K]$. The three indices $i_1 = \text{kcoup}(1, jn)$, $i_2 = \text{kcoup}(2, jn)$, $i_3 = \text{kcoup}(3, jn)$ define the jnth triangle condition $(k(i_1), k(i_2), k(i_3))$.

(b) *Define the "Minimal Configuration"*

Calculate:

1. NSmin. The number of different orbitals in $C_n = \mathbf{j}_1\mathbf{j}_2 \cdots \mathbf{j}_n$.

2. ($n(i)$, $l(i)$, $j(i)$, $n(i)$, $i = 1$, NSmin). The orbitals and occupation numbers in the standard representation $C_n = \prod_s \mathbf{j}_s^{n_s}$.

(c) *Calculate the Occupation Numbers Dependence φ of $\langle S \rangle_c$*

$$\varphi = \prod_s \binom{N_s}{n_s}.$$

(d) *Perform Loop on Permutations of Equivalent Electrons*

1. Define $p'(i)$ the electron index into which "i" is moved by the permutation p'

$$p'(i) = p:/\mathbf{p}:1, 2, ..., n_1/\mathbf{p}:n_1+1, ..., n_1+n_2/\mathbf{p}:\cdots i\cdots/\mathbf{p}:n_1+n_2+\cdots n_{n-1}, \cdots n/.$$

Each Shell $/\cdots/$ is permuted separately.

2. For each permutation p' create **n** triangle conditions $\mathbb{P}(3, n)$, involving the orbitals,

$$\big(\mathbb{P}(1, n) = (k(i), \mathbb{P}(2, n) = j(i), \mathbb{P}(3, n) = j(p'(i)), i = 1, n\big).$$

3. Call NJGRAF. The input is the triangle conditions kcoup$(3, n)$ $\mathbb{P}(3, n)$ defining a closed loop. The output is algebraic expressions and numerical values for the contribution of p' to the average.

Summary and Discussion

In this work we have presented a new method for calculating the configuration average of a general symmetrical n-body tensor operator. The method presents an explicit expression for the dependence of the averages on the occupation numbers of the configuration, while the dependence on the orbitals angular momenta is obtained by graphical techniques. The contribution to the configuration average of a three-body effective interaction was calculated as an example. We have demonstrated the applicability of the method as an algorithm for computer calculations. Such a program is essential for cases with high n-values, in particular for the transition array spectral moments μ^r with $r > 2$, where the application of traditional methods become impractical. Although we have presented the method for j–j configurations, it is easily applied in the LS scheme as well. In this case the operators $Z_i^{(k)}(\mathbf{j}, \mathbf{j}')$ of Eqs. (2) and (3) are replaced by double tensors $Z_i^{(\kappa,k)}(\mathbf{j}, \mathbf{j}')$ of ranks κ, k with respect to the spin and orbital angular momentum spaces. Shells are defined by the quantum numbers $l = nsl$. Results in LS coupling can be obtained by performing the appropriate sum over j–j configurations or more simply by the substitutions:

$$\mathbf{j}^N \Rightarrow \boldsymbol{l}^N, \qquad [j] \equiv 2j+1 \Rightarrow [sl] \equiv (4l+2),$$

$$G_i \equiv G_i(p', k_i j_i) \Rightarrow G_i(p', k_i l_i)\, G_i(p', \kappa_i s_i = 1/2).$$

APPENDIX A: EXAMPLES FOR nBSTOs

(a) Three well-known simple examples of nBSTOs are:

(1) *One-body.* Electric dipole interaction $\mathbf{d}=\mathbf{r}\mathbf{C}^{(1)}$,

$$\mathbf{d}=\sum_{\mathbf{j}\mathbf{j}'}\left[\sum_i Z_i^{(1)}(\mathbf{j},\mathbf{j}')\right]P_{\mathbf{j}\mathbf{j}'}, \tag{A1}$$

where $P_{\mathbf{j}\mathbf{j}'}$ is the dipole radial integral multiplied by $\langle \mathbf{j}\|C^{(1)}\|\mathbf{j}'\rangle$.

(2) *Two-body.* The electrostatic interaction [5]

$$\sum_{i<j} e/r_{ij}=\sum_{\{\mathbf{j}_1\mathbf{j}_1'\mathbf{j}_2\mathbf{j}_2'\}}\sum_k\sum_{i\neq j}(Z_i^{(k)}(\mathbf{j}_1,\mathbf{j}_1')\cdot Z_j^{(k)}(\mathbf{j}_2,\mathbf{j}_2')\,X^k(\mathbf{j}_1\mathbf{j}_1',\mathbf{j}_2\mathbf{j}_2'), \tag{A2}$$

where

$X^k(\mathbf{j}_1\mathbf{j}_1',\mathbf{j}_2\mathbf{j}_2')$ are the Slater integrals $R^k(\mathbf{j}_1\mathbf{j}_1',\mathbf{j}_2\mathbf{j}_2')$ times $\langle \mathbf{j}_1\|C^{(k)}\|\mathbf{j}_1'\rangle$ $x\langle \mathbf{j}_2\|C^{(k)}\|\mathbf{j}_2'\rangle$.

(3) *Three-body.* Effective interaction [4] $(\mathbf{j}^{N-1}\mathbf{j}\cdots\mathbf{j}^N)$

$$\sum_{k,k',k''}\sum_{i\neq j\neq k}[[Z_i^{(k)}(\mathbf{j},\mathbf{j})\,Z_j^{(k')}(\mathbf{j},\mathbf{j})]^{(k'')}\,Z_\kappa^{(k'')}(\mathbf{j},\mathbf{j})]^{(0)}\,X^k(\mathbf{j}\mathbf{j}',\mathbf{j}\mathbf{j})\,X^{k'}(\mathbf{j}\mathbf{j}',\mathbf{j}\mathbf{j}). \tag{A3}$$

(b) The spectral moments of a transition array:

We now show that the spectral moments of a transition array are configuration averages of nBSTOs with higher n.

The rth moment of a transition array between two configurations A and B, is defined by [1a]

$$\mu^{(r)}=\sum_{\substack{a\in A\\ b\in B}}\mathbf{d}_{ab}^2(\mathbf{H}_{aa}-\mathbf{H}_{bb})^r, \tag{A4}$$

where the sum is over all states of the configurations A and B. In Eq. (A1) $\mathbf{d}$ and $\mathbf{H}$ are the dipole and Hamiltonian operators and $\mathbf{d}_{ab}=\langle a\,|\mathbf{d}|\,b\rangle$, etc. In the following we will take $\mathbf{H}=\sum_{i<j}e/r_{ij}$.

We define the "curtailed" operators $\mathbf{d}^{AB}$, $\mathbf{H}^{AA}$, and $\mathbf{H}^{BB}$ by the representations of Eqs. (A1), (A2), where the orbitals in the summations are restricted to the respective configurations. Specifically, in Eq. (A1) for $\mathbf{d}^{AB}$ the summation orbitals are $\mathbf{j}\in A$, $\mathbf{j}'\in B$, and in Eq. (A2) for $\mathbf{H}^{AA}$ $(\mathbf{H}^{BB})$ all $\mathbf{j}\in A(B)$. Thus

$$\mu^{(r)}=\sum_{a,b}(\mathbf{d}^{AB})_{ab}^2\,(\mathbf{H}_{aa}^{AA}-\mathbf{H}_{bb}^{BB})^r \tag{A5}$$

with no restriction on the states a, b.

Using the complete set of configuration eigenstates of **H** and the closure theorem we obtain the representation for the spectral moments,

$$\mu^{(r)} = \sum_a \langle a | \mu_r^{AB} | a \rangle = \sum_b \langle b | \mu_r^{BA} | b \rangle, \tag{A6}$$

where

$$\mu_r^{AB} = \sum_{s=0}^{r} \binom{r}{s} (-1)^s \mathbf{d}^{AB} (\mathbf{H}^{BB})^s \mathbf{d}^{BA} (\mathbf{H}^{AA})^{r-s}. \tag{A7}$$

From Eqs. (A6), (A7), (A1), and (A2) it is seen immediately that μ_r^{AB} can be decomposed in terms of n-body symmetrical operators of the type S, where the highest n is $2r+1$, and that the spectral moments are configuration (scheme independent) averages of such operators $\mu^{(r)}$.

APPENDIX B: The Relation between the Averages within the Minimal and Any General Configurations

In this appendix we will derive the relation between the configuration averages of the "direct type" operator D within the configuration

$$C \equiv \prod_s \mathbf{j}_s^{N_s}, \qquad \sum_s N_s = N \tag{B1}$$

and the minimal configuration

$$C_n = \prod_s \mathbf{j}_s^{n_s}, \qquad \sum_s n_s = \mathbf{n}, \qquad n_s \leqslant N_s. \tag{B2}$$

Specifically, we will show that

$$\langle D \rangle_c = \varphi \langle D \rangle_{c_n}, \tag{B3}$$

where

$$\varphi = \prod_s \binom{N_s}{n_s} \tag{B4}$$

and

$$\begin{aligned} D &= \sum^{(N)} Z_{i_1 q_1}^{(t_1)}(\mathbf{j}_1, \mathbf{j}_1) \times Z_{i_2 q_2}^{(t_2)}(\mathbf{j}_2, \mathbf{j}_2) \times \cdots \times Z_{i_n q_n}^{(t_n)}(\mathbf{j}_n, \mathbf{j}_n) \\ &\equiv \sum^{(N)} \prod_{\alpha=1}^{n} Z_{i_\alpha}^{(t_\alpha)}(\mathbf{j}_\alpha, \mathbf{j}_\alpha), \end{aligned} \tag{B5}$$

where we have chosen the $[T]=[t_i, q_i]$ coupling scheme and $\sum^{(N)}$ indicates the symmetrical summation of Eq. (1). For simplicity of notation we hereafter omit the component indices q_α. In the occupation number notation of Eqs. (B1) and (B2), where s enumerates different shells,

$$D=\sum_{s}^{(N)}\prod\left\{\prod_{\alpha\in s} Z_{i_\alpha}^{(t_\alpha)}(\mathbf{j}_s,\mathbf{j}_s)\right\}, \tag{B6}$$

where $\alpha\in s$ indicate indices for which $\mathbf{j}_\alpha=\mathbf{j}_s$.

Owing to the antisymmetry of the state vectors $\psi\in C$, each set of values of the indices $i_1\neq i_2\cdots\neq i_n$ in D contribute equally to the matrix element $\langle\psi|D|\psi\rangle$. In particular, we can let the indices i_α of each operator $Z_{i_\alpha}^{(t_\alpha)}(\mathbf{j}_s,\mathbf{j}_s)$ run only on specific N_s coordinates and multiply the matrix element by $\mathcal{N}=N!/\prod_s N_s!$, the number of terms that were factored out. The same factor $\mathcal{N}$ appears also in the following expression for ψ in terms of antisymmetrical shell-states ψ_s of $\mathbf{C}_s\equiv\mathbf{j}_s^{N_s}$:

$$|\psi\rangle=(1/\mathcal{N})^{1/2}\sum_{\underline{p}}(-1)^{\underline{p}}\underline{p}:\prod_s\psi_s, \tag{B7}$$

where the sum runs over all the permutations $\underline{p}$ which *do not* involve equivalent electrons. It is then easily seen from Eq. (3) that

$$\langle\psi|D|\psi\rangle=\prod_s\langle\psi_s|D_s^{(N_s)}|\psi_s\rangle, \tag{B8}$$

where

$$D_s^{(N_s)}=\sum_{\alpha\in s}^{(N_s)}\prod Z_{i_\alpha}^{(t_\alpha)}(\mathbf{j}_s,\mathbf{j}_s). \tag{B9}$$

To complete the derivation we will show now that for single shell configurations:

$$\langle|D_s^{(N_s)}|\rangle_{\mathbf{C}_s}=\binom{N_s}{n_s}\langle|D_s^{(n_s)}|\rangle_{C_s}, \tag{B10}$$

where the averages on the left- and right-hand sides of Eq. (B10) is on the "shell configuration" $\mathbf{C}_s\equiv\mathbf{j}_s^{N_s}$ and $C_s\equiv\mathbf{j}_s^{n_s}$, respectively.

We first notice that for each $\psi_s\in\mathbf{C}_s$,

$$\langle\psi_s|D_s^{(N_s)}|\psi_s\rangle=\sum\langle\phi_s|D_s^{(n_s)}|\phi_s\rangle,\qquad \phi_s\in\psi_s, \tag{B11}$$

where ϕ_s is an n_s electron SD of C_s, and the sum is over all ϕ_s that can be constructed from the orbitals of ψ_s. When summing over ψ_s, each ϕ_s appears exactly

$$\binom{2j_s+1-n_s}{n_s}=g_{\mathbf{C}_s}/g_{C_s}\binom{N_s}{n_s} \tag{B12}$$

times. Thus

$$\sum \psi_s \langle \psi_s | D_s^{(N_s)} | \psi_s \rangle = \binom{2j_s + 1 - n_s}{N_s - n_s} \sum \phi_s \langle \phi_s | D_s^{(n_s)} | f\psi_s \rangle. \tag{B13}$$

From the Eqs. (B11) and (B13) we obtain Eq. (B10), leading to the desired relation (B3).

ACKNOWLEDGMENT

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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