Theoret. Chim. Acta (Berl.) 51, 175–188 (1979)

THEORETICA CHIMICA ACTA

Original Investigations

Coupling Constants in the Direct Configuration Interaction Method

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A general algorithm of evaluation of the coefficients of molecular integrals (coupling constants) appearing in the direct configuration interaction method is derived. The configurations are assumed to be spin-adapted antisymmetrized products of orthonormal orbitals. No limitation is imposed either upon the reference state (the number of the singly occupied orbitals may be arbitrary) or upon the excitation multiplicity.

Key words: Configuration interaction method, coupling constants in the direct ~

1. Introduction

Trends towards using in the configuration interaction (CI) method as long expansions as possible stimulate search of efficient methods of constructing the wavefunctions. A method formulated by Roos [1], and then developed by Roos and Siegbahn [2–4], known as the Direct CI method from Molecular Integrals (CIMI), seems to be most attractive. The wavefunction $\langle \boldsymbol{r}, \boldsymbol{\sigma} \mid \Psi\rangle$ of an N-electron system is expressed as a superposition of Configuration State Functions (CSFs), $\langle \boldsymbol{r}, \boldsymbol{\sigma} \mid k\rangle$,

$$\langle \boldsymbol{r}, \boldsymbol{\sigma} \mid \Psi\rangle = \sum_{k=0}^{M} C_k \langle \boldsymbol{r}, \boldsymbol{\sigma} \mid k\rangle, \tag{1}$$

where $\boldsymbol{r}$ and $\boldsymbol{\sigma}$ stand collectively for all space $(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ and spin $(\sigma_1, \sigma_2, \ldots, \sigma_N)$ coordinates, respectively. It is convenient to take the CSFs as Spin Adapted Antisymmetrized Products (SAAPs) of orthonormal orbitals $\varphi_1, \varphi_2, \ldots, \varphi_K$. Matrix elements $H_{kl} = \langle k|\mathscr{H}|l\rangle$ of a Hamiltonian

$$\mathscr{H} = \sum_{i=1}^{N} \hbar_1(\boldsymbol{r}_i) + \sum_{i<j}^{N} \hbar_2(\boldsymbol{r}_i, \boldsymbol{r}_j) \tag{2}$$

may then be expressed as linear combinations of integrals

$$[pq] = \int \varphi_p(\boldsymbol{r}_1)^* \hbar_1(\boldsymbol{r}_1) \varphi_q(\boldsymbol{r}_1)\, dv_1 \tag{3}$$

and

$$[pq \mid rs] = \int \varphi_p(\boldsymbol{r}_1)^* \varphi_r(\boldsymbol{r}_2)^* h_2(\boldsymbol{r}_1, \boldsymbol{r}_2) \varphi_q(\boldsymbol{r}_1) \varphi_s(\boldsymbol{r}_2)\, dv_{12}. \tag{4}$$

In the CI procedure the vector $\boldsymbol{C} = \{C_0, C_1, \ldots, C_M\}$ and the corresponding eigenvalue of the Hamiltonian matrix are obtained from a diagonalization procedure. Efficient iteration methods, recently formulated by Nesbet [5], Shavitt [6], and Davidson [7], all have a bottleneck in common: one must construct the Hamiltonian matrix $\boldsymbol{H}$ and then, in each iteration, multiply it by the vector:

$$b_k^{(n+1)} = \sum_{l=0}^{M} H_{kl} C_l^{(n)}, \tag{5}$$

where $(n + 1)$ and (n) refer to the iteration number. All the other steps in the iteration scheme require negligible time [7]. The CIMI method is, in fact, a method of finding the product vector $\boldsymbol{b}^{(n+1)} = (b_0^{(n+1)}, b_1^{(n+1)}, \ldots, b_M^{(n+1)})$ without the construction of the matrix H_{kl}, but directly from the list of the integrals (3) and (4). The formula (5) may be rewritten as:

$$\begin{aligned} b_k^{(n+1)} = {} & \sum_{pq} [pq] \sum_{l=0}^{M} A_1(kl; pq) C_l^{(n)} \\ & + \sum_{pqrs} [pq \mid rs] \sum_{l=0}^{M} A_2(kl; pqrs) C_l^{(n)}, \end{aligned} \tag{6}$$

where the coupling constants $A_1(kl; pq)$ and $A_2(kl; pqrs)$ are defined by the relation

$$H_{kl} = \sum_{pq} A_1(kl; pq)[pq] + \sum_{pqrs} A_2(kl; pqrs)[pq \mid rs], \tag{7}$$

According to (6) every integral has to be multiplied by the sum of products of the coupling constants A_1 or A_2 and the components of the vector $\boldsymbol{C}^{(n)}$ and then added to the appropriate component of the vector $\boldsymbol{b}^{(n+1)}$. Hence, a single reading of the list of the integrals allows us to compute the vector $\boldsymbol{b}^{(n+1)}$ without the time- and memory-consuming construction of the Hamiltonian matrix.

In the original formulation of the CIMI method [1] the coupling constants are given in a tabular form. It restricts an applicability of the method to the case of $|k\rangle$ being at most doubly excited relatively to a closed-shell reference configuration. In order to generalize the computational scheme one has to formulate an algorithm of evaluation of the coupling constants. Since most of the coupling constants are equal 0, the problem to solve is: given p, q (or p, q, r, s) find k and l for which A_1 $(kl; pq)$ (or $A_2(kl; pqrs)$) do not vanish and determine their values. The aim of the present paper is to derive a general algorithm of evaluation of the coupling constants for an arbitrary set of configurations[1].

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[1] An effective alternative method has recently been formulated by Shavitt [8]. In the Shavitt's method some graph theoretical concepts have been introduced to the unitary group approach developed by Paldus [9], resulting in a simple diagrammatical procedure for evaluation of the coupling constants.

2. Wavefunction

Usually the CSFs are expressed as linear combinations of Slater determinants. However, as shown by Ruedenberg and Salmon [10] and by Karwowski [11], a more compact and general formulation is possible, when CSFs are chosen as SAAPs, i.e.

$$\langle \boldsymbol{r}, \boldsymbol{\sigma} \mid k\rangle \equiv \langle \boldsymbol{r}, \boldsymbol{\sigma} \mid SM, m; \lambda\rangle = D\mathscr{A}[\langle \boldsymbol{\sigma} \mid SM, m\rangle\langle \boldsymbol{r} \mid \lambda\rangle], \tag{8}$$

where

$$\mathscr{A} = \frac{1}{\sqrt{N!}} \sum_{\mathscr{P}} \varepsilon(\mathscr{P})\mathscr{P} \tag{9}$$

is the antisymmetrization operator ($\mathscr{P}$ is an operator of permutation of the electron coordinates and $\varepsilon(\mathscr{P})$ its parity), $\langle \boldsymbol{\sigma} \mid SM, m\rangle$ is an eigenfunction of $\mathscr{S}^2$ and $\mathscr{S}_z$, depending on the spin coordinates only, $\langle \boldsymbol{r} \mid \lambda\rangle$ is the orbital part, and D is a normalization constant.

The orbital function has the form

$$\langle \boldsymbol{r} \mid \lambda\rangle = \prod_{i=1}^{N} \varphi_{\lambda i}(\boldsymbol{r}_i). \tag{10}$$

Index λ is an abbreviation for the set $\{\lambda_1, \lambda_2, \ldots, \lambda_N\}$ and describes the electronic configuration corresponding to a given CSF. In an electronic configuration λ there are, in general, p_λ singly and $(N - p_\lambda)/2$ doubly occupied orbitals. A doubly occupied orbital appears twice in the product. We shall use the name *single* for a singly occupied orbital, *double* for a doubly occupied one, and *virtual* for an unoccupied orbital. In the case of singles the indices of the orbitals are designated $s_\lambda(s_{\lambda 1}, s'_\lambda, \ldots)$, in the case of doubles $d_\lambda(d_{\lambda 1}, d'_\lambda, \ldots)$, and in the case of virtuals $v_\lambda(v_{\lambda 1}, v'_\lambda, \ldots)$. If there is no risk of confusion, the subscript λ is omitted. In the product (10) we always place singles in front of doubles. Moreover, the orbitals forming a double are adjacent in (10).

The spin functions $\langle \boldsymbol{\sigma} \mid SM, m\rangle$ are eigenfunctions of the $\mathscr{S}^2$ and $\mathscr{S}_z$ operators belonging to the eigenvalues $S(S + 1)$ and M respectively. Index m distinguishes different states with the same S,M quantum numbers. As known [12], $m = 1, 2, \cdots f(S, N)$, where $f(S, N) = (2S + 1)N!/(N/2 + S + 1)!\,(N/2 - S)!$, and the vectors $|SM, m\rangle$ form a basis for an irreducible representation of the permutation group, i.e.

$$\mathscr{P} \mid SM, m\rangle = \varepsilon(\mathscr{P}) \sum_{n=1}^{f(S,N)} U_S^N(\mathscr{P})_{nm} \mid SM, m\rangle, \tag{11}$$

where $U_S^N(\mathscr{P})$ is the irreducible representation matrix. It is convenient to choose an orthonormal set of the functions. The U_S^N matrices are then unitary. Moreover, in the following we assume that the parts of $\langle \boldsymbol{\sigma} \mid SM, m\rangle$ corresponding to doubly occupied pairs form two-electron singlets. Both Yamanouchi-Kotani [12] and Serber [13] spin functions fulfill this condition. Then, for a given λ, there are only

$f(S, p_\lambda)$ independent spin functions. If $\mathcal{P}^s$ denotes a permutation operator acting on the electrons occupying singles in (10), then

$$\langle SM, n|\mathcal{P}^s|SM, m\rangle = \varepsilon(\mathcal{P}^s)U^p_S(\mathcal{P}^s)_{nm}, \qquad m, n = 1, 2, \ldots, f(S, p) \equiv f, \tag{12}$$

where $U^p_S(\mathcal{P}^s) = [U^N_S(\mathcal{P}^s)]^{ff}$. The symbol $[U^N_S]^{ff'}$ denotes the rectangular $f \times f'$ matrix being a part of the U^N_S matrix and consisting of the elements of its first f rows and f' columns.

3. Configuration State Functions

One of the configurations we define as the reference configuration. The corresponding CSF vector is designated $|SM, m; 0\rangle$, and its orbital part $|0\rangle$. It is convenient to number orbitals according to their positions in $\langle \boldsymbol{r} \mid 0\rangle$, i.e. in such a way that $s_0 = 1, 2, \ldots, p$, $d_0 = p + 1, p + 2, \ldots, (N + p)/2$, and $v_0 = (N + p)/2 + 1, (N + p)/2 + 2, \ldots, K$, where s_0, d_0, and v_0 refer, respectively, to the singles, doubles and virtuals. The orbital function $\langle \boldsymbol{r} \mid 0\rangle$ is then:

$$\langle \boldsymbol{r} \mid 0\rangle = \prod_{s=1}^{p} \varphi_s(s) \prod_{d=p+1}^{(N+p)/2} \varphi_d(2d - p - 1)\varphi_d(2d - p), \tag{13}$$

where $\varphi(k) \equiv \varphi(\boldsymbol{r}_k)$.

An arbitrary configuration may be considered as an excitation from the reference state. The corresponding orbital function has the form:

$$|\lambda\rangle = \mathcal{P}_\lambda\mathcal{R}_\lambda \mid 0\rangle, \tag{14}$$

where $\mathcal{R}_\lambda = \begin{bmatrix} i & j & k & \cdots \\ a & b & c & \cdots \end{bmatrix}$ is a replacement operator which puts the orbitals $\varphi_a, \varphi_b, \varphi_c, \ldots$ in place of $\varphi_i, \varphi_j, \varphi_k, \ldots$ respectively, and $\mathcal{P}_\lambda$ is a permutation operator rearranging the electron coordinates in such a way that all the singles stand in front of the doubles in $\langle \boldsymbol{r} \mid \lambda\rangle$. A $\mathcal{P}_\lambda$ permutation always exists, however it is not unique. The explicit form of $\mathcal{P}_\lambda$, irrelevant for the present discussion, may be determined for each particular case in a way being the most convenient from the point of view of an implementation of the method.

In order to define $\mathcal{R}_\lambda$ in a unique way we require the orbitals to appear in each row of $\mathcal{R}_\lambda$ in ascending order of their occupation numbers in $|0\rangle$ and, within a group of the orbitals with the same occupation number, in ascending order of their indices, i.e.

$$\mathcal{R}_\lambda = \begin{bmatrix} s_{01} & s_{02} & \cdots & s_{0k} & d_{01} & d_{02} & \cdots & d_{0l} \\ v_{01} & v_{02} & \cdots & v_{0m} & s'_{01} & s'_{02} & \cdots & s'_{0n} \end{bmatrix}, \tag{15}$$

$$v_{01} \leqslant v_{02} \leqslant \cdots \leqslant v_{0m}, \qquad s_{01} < s_{02} < \cdots < s_{0k},$$
$$s'_{01} < s'_{02} < \cdots < s'_{0n}, \qquad d_{01} \leqslant d_{02} \leqslant \cdots \leqslant d_{0l}.$$

If $d_{0i} = d_{0,i+1}$, $i = 1, 2, \ldots, l - 1$, then d_{0i} corresponds to the first electron from the double and $d_{0,i+1}$ to the second one. Moreover, $s_{0i} \neq s'_{0j}$ for $i = 1, 2, \ldots, k$; $j = 1, 2, \ldots, n$. Of course, $k + l = m + n$.

The formulae (8), (9), and (14) yield

$$|SM, m; \lambda\rangle = D(N!)^{-1/2} \sum_{\mathscr{P}} \varepsilon(\mathscr{P})(\mathscr{P} \mid SM, m\rangle)(\mathscr{P}\mathscr{P}_\lambda \mathscr{R}_\lambda \mid 0\rangle, \tag{16}$$

or substituting $\mathscr{P}$ for $\mathscr{P}\mathscr{P}_\lambda$

$$|SM, m; \lambda\rangle = D(N!)^{-1/2} \sum_{\mathscr{P}} \varepsilon(\mathscr{P}\mathscr{P}_\lambda^+)(\mathscr{P}\mathscr{P}_\lambda^+ \mid SM, m\rangle)\mathscr{P} \mid \mathscr{R}_\lambda\rangle, \tag{17}$$

where

$$|\mathscr{R}_\lambda\rangle \equiv \mathscr{R}_\lambda \mid 0\rangle. \tag{18}$$

4. Matrix Elements

A matrix element between two CSFs (17) is:

$$\begin{aligned} &\langle SM, m; \lambda \mid \mathscr{H} \mid SM, m'; \lambda'\rangle \\ &\quad = DD' \sum_{\mathscr{P}} \varepsilon(\mathscr{P}_\lambda \mathscr{P}\mathscr{P}_{\lambda'}^+)\langle SM, m \mid \mathscr{P}_\lambda \mathscr{P}\mathscr{P}_{\lambda'}^+ \mid SM, m'\rangle\langle \mathscr{R}_\lambda \mid \mathscr{P}\mathscr{H} \mid \mathscr{R}_{\lambda'}\rangle. \end{aligned} \tag{19}$$

Making use of (12) we may rewrite (19) in the form:

$$H^{\lambda\lambda'} = DD' \sum_{\mathscr{P}} [U_S^N(\mathscr{P}_\lambda \mathscr{P}\mathscr{P}_{\lambda'}^+)]^{ff'}\langle \mathscr{R}_\lambda \mid \mathscr{P}\mathscr{H} \mid \mathscr{R}_{\lambda'}\rangle \tag{20}$$

where $f = f(S, p)$, $f' = f(S, p')$, and $H^{\lambda\lambda'}$ is the appropriate part of the H matrix. The integral over space variables may be transformed as follows [11]:

$$\langle \mathscr{R}_\lambda \mid \mathscr{P}\mathscr{H} \mid \mathscr{R}_{\lambda'}\rangle = \langle \mathscr{P}^{-1}\mathscr{R}_\lambda \mid \mathscr{H} \mid \mathscr{R}_{\lambda'}\rangle = \langle \bar{\mathscr{P}}\mathscr{R}_\lambda \mid \mathscr{H} \mid \mathscr{R}_{\lambda'}\rangle \tag{21}$$

where $\bar{\mathscr{P}}$ is an operator acting on the orbital indices rather than on the electron coordinates and $\langle \boldsymbol{r} \mid \bar{\mathscr{P}}\mathscr{R}_\lambda\rangle$ is the orbital product in which the orbital indices have been properly permuted. Since $\mathscr{H}$ contains only one- and two-electron terms, then due to orthogonality of the orbitals, the integrals (21) vanish unless $|\bar{\mathscr{P}}\mathscr{R}_\lambda\rangle$ and $|\mathscr{R}_{\lambda'}\rangle$ differ by two or less orbitals.

The permutation which brings orbitals of $|\mathscr{R}_\lambda\rangle$ into maximum coincidence with orbitals of $|\mathscr{R}_{\lambda'}\rangle$ we denote $\bar{\mathscr{P}}_R$. It is an identity operator except the cases when both in $\mathscr{R}_\lambda$ and in $\mathscr{R}_{\lambda'}$ there are excitations to the same orbital from different orbitals. The permutation $\bar{\mathscr{P}}_R$ may be easily expressed as a product of cycles when $\mathscr{R}_\lambda$ and $\mathscr{R}_{\lambda'}$ are given. For example, if

$$\mathscr{R}_\lambda = \begin{bmatrix} \ldots a \ldots e \ldots c \ldots \\ \ldots x \ldots y \ldots z \ldots \end{bmatrix}$$

and

$$\mathscr{R}_{\lambda'} = \begin{bmatrix} \ldots b \ldots f \ldots e \ldots \\ \ldots x \ldots y \ldots z \ldots \end{bmatrix},$$

then

$$\mathscr{P}_R = (j_a j_b)(j_c j_e j_f),$$

where $(j_c j_e j_f)$ is a cycle and j_a is the consecutive number of the electron described by φ_a in the product (13), i.e.

$$j_a = \begin{cases} a, & \text{if} \quad a = s_{0i}, \quad i = 1, 2, \ldots, k; \quad \text{i.e.} \quad \text{if } a \leqslant p, \\ 2a - p - 1, & \text{if} \quad a = d_{0i} \quad \text{and} \quad i = 1, \quad \text{or} \quad d_{0i} \neq d_{0,i-1}, \\ & \qquad\qquad\qquad\qquad\qquad\qquad i = 2, 3, \ldots, l, \\ 2a - p, & \text{if} \quad a = d_{0i} \quad \text{and} \quad d_{0i} = d_{0,i-1}, \quad i = 2, 3, \ldots, l. \end{cases}$$

We assumed here that when only one electron is excited from a double then it is the first electron. The permutation

$$\overline{\mathscr{P}}_0 = \mathscr{P}_\lambda \overline{\mathscr{P}}_R \mathscr{P}_{\lambda'}^+ \tag{22}$$

is identical with the line-up permutation defined by Ruedenberg and Salmon [10] and with the reference permutation introduced by Karwowski [11].

Let $n(p)$ and $n'(p)$ be the occupation numbers of the orbital φ_p in $\langle \boldsymbol{r} \mid \lambda \rangle$ and in $\langle \boldsymbol{r} \mid \lambda' \rangle$ respectively. The number of orbitals by which the functions $\langle \boldsymbol{r} \mid \overline{\mathscr{P}}_R \mathscr{R}_\lambda \rangle$ and $\langle \boldsymbol{r} \mid \mathscr{R}_{\lambda'} \rangle$ differ is equal to

$$\rho = \frac{1}{2} \sum_{p=1}^{K} |n(p) - n'(p)|. \tag{23}$$

Since the orbitals form an orthonormal set and only one- and two-electron operators appear in the Hamiltonian (2), the matrix elements (20) vanish unless $\rho = 2, 1, 0$. After some algebra ([10], [11]) we obtain:

1. $\rho = 2$.

Let, respectively, φ_p and φ_r be the orbitals which in $\langle \boldsymbol{r} \mid \overline{\mathscr{P}}_R \mathscr{R}_\lambda \rangle$ occupy the same positions as φ_q and φ_s in $\langle \boldsymbol{r} \mid \mathscr{R}_{\lambda'} \rangle$. For our purposes it is convenient to individualize three cases:

a) The indices p, q, r, s are all different. The formula (20) yields

$$\boldsymbol{H}^{\lambda\lambda'} = 2^u \{ [\boldsymbol{U}_S^N(\overline{\mathscr{P}}_0)]^{ff'} [pq \mid rs] + [\boldsymbol{U}_S^N(\overline{\mathscr{P}}_1)]^{ff'} [ps \mid rq] \} \tag{24}$$

where

$$u = (n(p) + n(r) + n'(q) + n'(s))/2 - 2 \tag{25}$$

and

$$\overline{\mathscr{P}}_1 = \mathscr{P}_\lambda (k_p k_r) \overline{\mathscr{P}}_R \mathscr{P}_{\lambda'}^+ \tag{26}$$

with k_p and k_r, respectively, equal to the consecutive numbers of the electrons described by φ_p and φ_r in $\langle \boldsymbol{r} \mid \mathscr{R}_\lambda \rangle$.

b) Either $p = r$ and $q \neq s$ or $p \neq r$ and $q = s$. In this case

$$\boldsymbol{H}^{\lambda\lambda'} = 2^{u-1/2} [\boldsymbol{U}_S^N(\overline{\mathscr{P}}_0)]^{ff'} [pq \mid rs]. \tag{27}$$

c) Both $p = r$ and $q = s$. Then

$$\boldsymbol{H}^{\lambda\lambda'} = [\boldsymbol{U}_S^N(\bar{\mathscr{P}}_0)]^{ff'}[pq \mid pq]. \tag{28}$$

2. $\rho = 1$

Let φ_p occupy the same position in $\langle \boldsymbol{r} \mid \bar{\mathscr{P}}_R\mathscr{R}_\lambda\rangle$ as φ_q in $\langle \boldsymbol{r} \mid \mathscr{R}_\lambda'\rangle$. Then from (20) results

$$\boldsymbol{H}^{\lambda\lambda'} = 2^t \sum_{\substack{m=1 \\ (m \neq p, m \neq q)}}^{K} n(m)\{[\boldsymbol{U}_S^N(\bar{\mathscr{P}}_0)]^{ff'}[pq \mid mm] + [\boldsymbol{U}_S^N(\bar{\mathscr{P}}_2)]^{ff'}[pm \mid mq]\}$$

$$+ 2^t[\boldsymbol{U}_S^N(\bar{\mathscr{P}}_0)]^{ff'}\{[pq] + n(q)[pq \mid qq] + (n(p) - 1)[pq \mid pp]\}, \tag{29}$$

where

$$t = (n(p) + n'(q))/2 - 1 \tag{30}$$

and

$$\bar{\mathscr{P}}_2 = \mathscr{P}_\lambda(k_p k_m)\bar{\mathscr{P}}_R\mathscr{P}_{\lambda'}^{+}. \tag{31}$$

3. $\rho = 0$

In this case $\langle \boldsymbol{r} \mid \mathscr{R}_\lambda\rangle = \langle \boldsymbol{r} \mid \mathscr{R}_{\lambda'}\rangle$ and

$$\boldsymbol{H}^{\lambda\lambda} = \sum_{l<m}^{K} n(l)n(m)\{[mm \mid ll] + [\boldsymbol{U}_S^N(\mathscr{P}_\lambda(k_l k_m)\mathscr{P}_\lambda^{+})]^{ff}[ml \mid lm]\}$$

$$+ \sum_{m=1}^{K} n(m)\{[mm] + \tfrac{1}{2}(n(m) - 1)[mm \mid mm]\}. \tag{32}$$

As it is seen, in order to determine the matrix elements of $\mathscr{H}$, only the blocks $[\boldsymbol{U}_S^N]^{ff'}$ corresponding to single transpositions, to $\mathscr{P}_0$, and to the permutations $\mathscr{P}_1$ and $\mathscr{P}_2$, being composed of $\mathscr{P}_0$ and a transposition, are needed. The blocks may either be constructed directly for each permutation [10] or obtained by a matrix multiplication of the $\boldsymbol{U}_S^g$ matrices (12) corresponding to transpositions, constructed in advance and stored in the computer memory [11]. In both the cases an advance reduction of $[\boldsymbol{U}_S^N(\mathscr{P})]^{ff}$ to $\boldsymbol{U}_S^g(\mathscr{P}^s)$ greatly simplifies the numerical work. An algorithm for this kind of reduction is given in Refs. [11] and [12].

5. Two-Electron Integrals

We assume that all the two-electron integrals (4) are real. The case when they are complex may be treated in a slightly modified way. The two-electron integrals may be divided into 5 groups:

1. All the indices p, q, r, s are different. The integrals of this group couple configurations differing by two orbitals. The matrix element (24) is always a combination of two integrals: $[pq \mid rs]$ and $[ps \mid rq]$. Therefore it is convenient to group these integrals into pairs. Since $h_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is Hermitean and symmetric in electron coordinates, the following relations hold:

$$[pq \mid rs] = [rs \mid pq] = [qp \mid sr] = [sr \mid qp]. \tag{33}$$

Hence, among $4! = 24$ integrals corresponding to a given set of four different orbitals, only 6 are different:

$$\begin{aligned} J_1(pqrs) &= [pq \mid rs], & J_1'(pqrs) &= [ps \mid rq], \\ J_2(pqrs) &= [pr \mid sq], & J_2'(pqrs) &= [pq \mid sr], \\ J_3(pqrs) &= [ps \mid qr], & J_3'(pqrs) &= [pr \mid qs], \end{aligned} \tag{34}$$

where J_i and J_i' appear in the same matrix element. In the following we use the symbols J_i, J_i', $i = 1, 2, 3$, if we refer to an arbitrary integral belonging to the set of 4 identical ones, while $[pq \mid rs]$ denotes a specific integral.

A very important special case is when the orbitals are real and $h_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is a function of the electron coordinates. Then $J_1 = J_2'$, $J_2 = J_3'$ and $J_3 = J_1'$.

There are many distributions of the orbitals φ_p, φ_q, φ_r, φ_s in the configurations $\langle \boldsymbol{r} \mid \lambda\rangle$ and $\langle \boldsymbol{r} \mid \lambda'\rangle$ leading to a coupling of these configurations by a pair of $J_1(pqrs)$, $J_1'(pqrs)$ integrals. To choose one of the distributions we assume that $\langle \boldsymbol{r} \mid \lambda\rangle$ is the parent configuration for φ_p and for φ_r, and $\langle \boldsymbol{r} \mid \lambda'\rangle$ for φ_q and for φ_s. Moreover, let $n'(q) \leqslant n'(s)$, $n(p) \leqslant n(r)$ and let $\mathscr{P}_0$ line up φ_p with φ_q and φ_r with φ_s. It means that $\mathscr{P}_0$ places singles (doubles) of $\langle \boldsymbol{r} \mid \lambda\rangle$ at the positions occupied by singles (doubles) in $\langle \boldsymbol{r} \mid \lambda'\rangle$ whenever it is possible. Since all the orbitals, except φ_p, φ_q, φ_r, φ_s, are the same in both configurations, the occupation numbers fulfill the following equations:

$$\begin{aligned} &n(p) - n'(p) = n(r) - n'(r) = 1 \\ &n(q) - n'(q) = n(s) - n'(s) = -1. \end{aligned} \tag{35}$$

Finally we set $\langle \boldsymbol{r} \mid \lambda\rangle$ to be the configuration in which the number of singles is not greater than in $\langle \boldsymbol{r} \mid \lambda'\rangle$. It means that

$$n(p) + n(r) \leqslant n'(q) + n'(s). \tag{36}$$

The system of Eqs. (35) together with the conditions imposed upon n and n' gives 6 different sets of the occupation numbers of φ_p, φ_q, φ_r, φ_s in the configurations which may be coupled by the pair of $[pq \mid rs]$ and $[ps \mid rq]$ integrals, with $[pq \mid rs]$ being the one which in Eq. (24) is multiplied by $[U_S^N(\overline{\mathscr{P}}_0)]^{ff'}$. All these sets are collected in Table 1 (entries Nos. 1–6). There exists a simple correspondence between the sets of the occupation numbers and the configuration pair diagrams defined in [11] or the cases considered by Sarma and Rettrup [14]. The references are given in the last two columns in Table 1.

2. *Two of the indices are equal.* For a given set of the indices there are $4!/2 = 12$ integrals. Due to relations

$$\begin{aligned} J_1(pqps) &= J_1'(pqps) = [pq \mid ps] = [ps \mid pq] = [qp \mid sp] = [sp \mid qp] \\ J_2(pqps) &= J_3'(pqps) = [pp \mid qs] = [qs \mid pp] = [pp \mid sq] = [sq \mid pp] \\ J_3(pqps) &= J_2'(pqps) = [qp \mid ps] = [ps \mid qp] = [sp \mid pq] = [pq \mid sp] \end{aligned} \tag{37}$$

Table 1. Occupation numbers of φ_p, φ_q, φ_r and φ_s in the case of $\rho = 2$

No.	$n(p)$	$n(r)$	$n'(q)$	$n'(s)$	$n'(p)$	$n'(r)$	$n(q)$	$n(s)$	DNo.[a]	CNo.[b]
1	1	1	1	1	0	0	0	0	1	A9
2	1	1	1	2	0	0	0	1	7	A10
3	1	1	2	2	0	0	1	1	11	A12
4	1	2	1	2	0	1	0	1	3	A11
5	1	2	2	2	0	1	1	1	9	A13
6	2	2	2	2	1	1	1	1	6	A14
7	2	—	1	1	0	—	0	0	8	A8
8	2	—	1	2	0	—	0	1	4,5	A7
9	2	—	2	2	0	—	1	1	10	A6
10	2	—	2	—	0	—	0	—	2	A5

[a] Diagram number according to Ref. [11].

[b] Case number according to Ref. [14].

only 3 of them are different. The integral J_1 couples configurations differing by two orbitals, according to formula (27), while both J_2 and J_3 appear in the same matrix element (29), for configurations differing by one orbital.

Let us consider a pair of configurations coupled by a $[pq \mid ps]$ integral. Since $n(p) = 2$, $n'(p) = 0$ and we assume that $n(q) \leqslant n(s)$, only 3 different sets of the occupation numbers of φ_p, φ_q, and φ_s in $\langle r \mid \lambda\rangle$ and in $\langle r \mid \lambda'\rangle$ are possible. They are collected in Table 1, entries Nos. 7–9. The same occupation numbers of φ_q and φ_s are allowed in the case of $[pp \mid qs]$ and $[qp \mid ps]$ integrals. However $n(p) = n'(p) = 1, 2$ in this case.

3. Two pairs of equal indices. There are $4!/4 = 6$ integrals for a given set of indices:

$$\begin{aligned} J_1(pqpq) &= J_1'(pqpq) = [pq \mid pq] = [qp \mid qp] \\ J_2(pqpq) &= J_3'(pqpq) = [pp \mid qq] = [qq \mid pp] \\ J_3(pqpq) &= J_2'(pqpq) = [qp \mid pq] = [pq \mid qp]. \end{aligned} \tag{38}$$

The integrals $J_1(pqpq)$ couple configurations differing by two orbitals (28) with $n(p) = n'(q) = 2$, $n'(p) = n(q) = 0$ (Table 1, entry No. 10), while $J_2(pqpq)$ and $J_3(pqpq)$ may couple only two identical configurations (formula (32)) with $n(p) = n'(p) = 1, 2$ and $n(q) = n'(q) = 1, 2$.

4. Three indices are equal. For a given set of indices one may form four integrals:

$$[pq \mid qq] = [qp \mid qq] = [qq \mid pq] = [qq \mid qp]. \tag{39}$$

The $[pq \mid qq]$ integral couples two configurations differing by one orbital (according to formula (29)) if $n(q) = 1$, $n'(q) = 2$, $n(p) = 1, 2$, and $n'(p) = n(p) - 1$.

5. All the indices are equal. The integral $[pp \mid pp]$ appears only in diagonal elements of $\boldsymbol{H}$, coupling two identical configurations for which $n(p) = 2$.

6. The Coupling Constants

In order to evaluate the coupling constants, first of all the pairs of configurations which may be coupled by the $[pq \mid rs]$ integral must be determined. It means that we have to find the operators $\mathcal{R}_\lambda$ and $\mathcal{R}_{\lambda'}$ leading to the configurations λ and λ' in which the occupation numbers of φ_p, φ_q, φ_r, φ_s satisfy conditions derived in the previous section. In general, in a list of integrals, only one representative of a set of equivalent integrals $J_i(pqrs)$ is included. Therefore we shall extend the Table 1 in order to take into account all the configurations which may be coupled by any of the integrals belonging to the set.

Since the $\boldsymbol{H}$ matrix (7) is Hermitean, we assume that the configurations forming a pair coupled by $J_i(pqrs)$ integral are always put in a definite order. If $p_\lambda \neq p_{\lambda'}$, then in the matrix element $\boldsymbol{H}^{\lambda\lambda'}$, we set λ to be the configuration for which the number of singles is greater. If $p_\lambda = p_{\lambda'}$, but $n(p) \neq n'(p)$, then λ is the configuration for which the occupation number of φ_p is greater. If $p_\lambda = p_{\lambda'}$ and $n(p) = n'(p)$, but $n(q) \neq n'(q)$ then λ is the configuration, for which the occupation number of φ_q is greater.

It is convenient to introduce a permutation operator $\mathcal{P}_J$ acting on the orbital indices in an integral. In the case of all the indices p, q, r, s different, the relation (33) may be rewritten in the form:

$$J_1 = [12 \mid 34] = (13)(24)[12 \mid 34] = (12)(34)[12 \mid 34] = (14)(23)[12 \mid 34]$$

and similarily

$$J_1' = (24)J_1,\ J_2 = (234)J_1,\ J_2' = (34)J_1,\ J_3 = (432)J_1,\ J_3' = (23)J_1.$$

The indices 1, 2, 3, 4 are used here instead of p, q, r, s for simplicity of the notation and correspond to four arbitrary orbitals. Then, the occupation numbers of φ_1, φ_2, φ_3, φ_4 in the configurations coupled by, say, the $[34 \mid 12] = (13)(24)[12 \mid 34]$ integral may be obtained transposing the indices of the orbitals in Table 1. The distributions of the occupation numbers in configurations which may be coupled by the pair of integrals $J_1(pqrs)$ and $J_1'(pqrs)$, according to Eq. (24), are collected in Table 2. In the second column the permutation $\mathcal{P}_J$ defining the two-electron integral is given. The occupation numbers corresponding to the cases of $p_\lambda = p_{\lambda'}$ and $n(p) < n'(p)$ are given in parentheses. Now the coupling constants may be obtained according to formulae (24)–(26), if u, $\bar{\mathcal{P}}_0 = \mathcal{P}_\lambda \bar{\mathcal{P}}_R \mathcal{P}_{\lambda'}^+$, and $\bar{\mathcal{P}}_1 = \mathcal{P}_\lambda (k_x k_y) \bar{\mathcal{P}}_R \mathcal{P}_{\lambda'}^+$ are known. The permutations $\mathcal{P}_\lambda$, $\mathcal{P}_{\lambda'}$, and $\mathcal{P}_R$ are easy to derive from $\mathcal{R}_\lambda$ and $\mathcal{R}_{\lambda'}$. The transpositions $(k_x k_y)$ and the values of u are given in Table 2. In a similar way the sets of the occupation numbers which determine configurations coupled by the pairs of integrals $J_2(pqrs)$, $J_2'(pqrs)$ and $J_3(pqrs)$, $J_3'(pqrs)$ may be obtained.

In the case of integrals with one pair of equal indices, as a result of a similar consideration, we obtain 4 different sets of the occupation numbers if the configurations are coupled according to Eq. (27), i.e. by $J_1(pqps)$, and 8 sets if they are coupled according to Eq. (29) by the pairs of $J_2(pqps)$, $J_3(pqps)$ integrals. All these sets and $(k_x k_p)$ transpositions determining $\bar{\mathcal{P}}_2 = \mathcal{P}_\lambda (k_x k_p) \bar{\mathcal{P}}_R \mathcal{P}_{\lambda'}^+$ (compare (31)) as well as the values of u and t are collected in Table 3.

If there are two pairs of equal indices in an integral, then $J_1(pqpq)$ couples configurations according to (28), while $J_2(pqpq)$ and $J_3(pqpq)$ couple according to (32). The occupation numbers for these cases are displayed in Table 4. In the same table the

Table 2. Occupation numbers of φ_p, φ_q, φ_r and φ_s in configurations coupled by the integrals $J_1(pqrs)$ and $J_1'(pqrs)$

No.	$\mathscr{P}_J$	$n(p)$	$n(q)$	$n(r)$	$n(s)$	$n'(p)$	$n'(q)$	$n'(r)$	$n'(s)$	(k_xk_y)	u
1	$\mathscr{I}$, (13)(24)	1	0	1	0	0	1	0	1	(k_pk_r)	0
	(12)(34), (14)(23)	(0	1	0	1)	(1	0	1	0)		
2	$\mathscr{I}$	1	0	1	1	0	1	0	2	(k_pk_r)	1/2
	(12)(34)	0	1	1	1	1	0	2	0	(k_qk_s)	
	(13)(24)	1	1	1	0	0	2	0	1	(k_pk_r)	
	(14)(23)	1	1	0	1	2	0	1	0	(k_qk_s)	
3	$\mathscr{I}$, (13)(24)	1	1	1	1	0	2	0	2	(k_pk_r)	1
	(12)(34), (14)(23)	1	1	1	1	2	0	2	0	(k_qk_s)	
4	$\mathscr{I}$	1	0	2	1	0	1	1	2	(k_pk_r)	1
	(12)(34)	(0	1	1	2)	(1	0	2	1)		
	(13)(24)	2	1	1	0	1	2	0	1	(k_pk_r)	
	(14)(23)	(1	2	0	1)	(2	1	1	0)		
5	$\mathscr{I}$	1	1	2	1	0	2	1	2	(k_pk_r)	3/2
	(12)(34)	1	1	1	2	2	0	2	1	(k_qk_s)	
	(13)(24)	2	1	1	1	1	2	0	2	(k_pk_r)	
	(14)(23)	1	2	1	1	2	1	2	0	(k_qk_s)	
6	$\mathscr{I}$, (13)(24)	2	1	2	1	1	2	1	2	(k_pk_r)	2
	(12)(34), (14)(23)	(1	2	1	2)	(2	1	2	1)		

occupation numbers and the values of t for the case of three equal indices and for the case of coupling by one-electron integrals (Eq. (29)) are given. If all the indices are equal, then either $n(p) = n'(p) = 2$ (if the configurations are coupled by $[pp \mid pp]$) or $n(p) = n'(p) = 1, 2$ (if they are coupled by $[pp]$).

Now we have to find $\mathscr{R}_\lambda$ operators leading to configurations for which occupation numbers of certain orbitals are as given in Tables 2, 3 and 4. Let $n_0(p)$ be the occupation number of φ_p in $\langle r \mid 0\rangle$. Then the absolute value of

$$\Delta(p) = n(p) - n_0(p) \tag{40}$$

Table 3. Occupation numbers of φ_p, φ_q and φ_s in configurations coupled by $J_i(pqps)$, $i = 1, 2, 3$

$n(p)$	$n(q)$	$n(s)$	$n'(p)$	$n'(q)$	$n'(s)$	(k_xk_p)	i	u	t
0	1	1	2	0	0	—	1	1	
2	0	1	0	1	2	—		3/2	
2	1	0	0	2	1	—		3/2	
2	1	1	0	2	2	—		2	
1	1	0	1	0	1	(k_qk_p)	2,3		0
2	1	0	2	0	1				0
1	2	1	1	1	2				1
2	2	1	2	1	2				1
1	1	1	1	0	2				1/2
2	1	1	2	0	2				1/2
1	1	1	1	2	0	(k_sk_p)			1/2
2	1	1	2	2	0				1/2

Table 4. Occupation numbers of φ_p and φ_q in configurations coupled by $J_i(pqpq), J_i(pqqq)$, $i = 1, 2, 3$, and by $[pq]$

$n(p)$	$n(q)$	$n'(p)$	$n'(q)$	*integral*	t
2	0	0	2	$J_1(pqpq)$	
1	1	1	1	$J_2(pqpq), J_3(pqpq)$	
1	2	1	2		
2	1	2	1		
2	2	2	2		
1	1	0	2	$J_i(pqqq)$, $i = 1, 2, 3$	1/2
2	1	1	2		1
1	0	0	1	$[pq]$	0
1	1	0	2		1/2
1	1	2	0		1/2
2	1	1	2		1

is equal to the number of times the index p appears in $\mathscr{R}_\lambda$ – in the upper row if $\Delta(p) > 0$ and in the lower one if $\Delta(p) < 0$. Similar conditions are fulfilled for all the other orbitals involved in the integral under consideration. All the other symbols in $\mathscr{R}_\lambda$ may be arbitrary, limited only by the list of orbitals and by the maximum multiplicity of excitations taken into account. When both $\mathscr{R}_\lambda$ and $\mathscr{R}_{\lambda'}$ are determined, then we may easily obtain $\mathscr{P}_R$ and $\mathscr{P}_0$, $\mathscr{P}_1$, $\mathscr{P}_2$. In this way we have the complete information needed to evaluate the coupling constants and to assign them to appropriate pairs of configurations.

7. Remarks on an Implementation of the Method

The problems connected with an efficient programing of the CIMI method may be divided into two groups: searching for interacting configurations when a two-electron integral is given, and calculating the coupling constant for a given pair of configurations. Although an optimum solution of the problems depends on specific features of the available computer (size of the core store, cost of the CPU time vs. cost of the memory occupancy, efficiency and cost of using tapes, etc.), we can formulate some general remarks on an implementation of the presented algorithm.

7.1. Searching for Interacting Configurations

The configurations which may be coupled by a given two-electron integral are determined by the operators $\mathscr{R}_\lambda$ and $\mathscr{R}_{\lambda'}$. In the case of an m-fold excited configuration the operator is defined by $2m$ orbital indices. Some of the indices (at most 4) enter the two-electron integral and, for a given integral, are fixed. The remaining indices, being the same in both $\mathscr{R}_\lambda$ and $\mathscr{R}_{\lambda'}$, and determined by the conditions specified in Tables 1–4, are varied to accomplish the list of configurations. In the existing programs for the direct CI method (a review has recently been given by Roos [15]) only doubly excited configurations are allowed and, in consequence, at most two indices are varied. It means that in the program each integral is associated with at most one double loop over the orbital indices. An analogous procedure may also be applied in the present generalization, except that interactions of m-fold with m'-fold excited configurations lead, in the case of $\rho = 2$, to at most $(m + m' - 2)$-fold loops over the orbital indices. An example of the loop structure for the case No. 1, Table 2, and for doubly excited configurations was recently discussed by Roos [15].

7.2. Calculation of the Coupling Constants

In order to make the procedure of evaluation of the coupling constants very efficient, most of the representation matrices $[U_N^S(\mathscr{P})]^{ff'}$ should be kept in the core memory. If the maximum number of singles does not exceed 6, the representation matrices are at most 9×9 (for triplets). The required storage is then $9 \times 9 \times 6! = 58320$ double precision words, what seems rather unreasonable. However, all the elements of the representation matrices are square roots of simple fractions and one may keep all the different numbers met in the representation matrices in a small auxiliary array. Then, instead of the elements of U_N^S one may store their addresses in the auxiliary array as half-word integers. The necessary storage may be further reduced if symmetry properties of the matrices are taken into account. The simplest ones result from identities: $(kl)^\dagger = (kl)$, $((kl)(ln))^\dagger = (ln)(kl)$, etc., and reduce the necessary storage by factor 2. It gives a reasonable amount of 60 kbytes of the core store for triplets with at most 6 singles. In order to deal with cases involving a larger number of singles one may store only some matrices, e.g. the ones corresponding to single transpositions and to products of two transpositions. Since products of more than two transpositions are needed relatively seldom, the corresponding matrices may be generated by matrix multiplications.

Acknowledgements. The authors are indebted to Dr. Björn Roos for several helpful discussions concerning the direct CI method. The work has been sponsored by the Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Contract No. MR-9.

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Received May 31, 1978/October 16, 1978