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Matrix Elements of One- and Two-Electron Operators*

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A graphical representation of matrix elements of spin-free one- and two-electron operators is used for deriving a simple algorithm for the evaluation of their values. The method covers all the cases which may occur when wave functions are taken as mutually orthogonal antisymmetrized products of spinorbitals (which are assumed to form an orthonormal set) and are eigenfunctions of $\mathcal{S}^2$ and $\mathcal{S}_z$ operators. The resulting formulas are suitable as well for computer programming as for hand calculations.

Mit Hilfe einer graphischen Darstellung wird ein einfacher Algorithmus zur Bestimmung der Werte der Matrix-Elemente von spinfreien Ein- und Zweielektronenoperatoren abgeleitet. Durch diese Methode werden alle Fälle erfaßt, die auftreten, wenn die Wellenfunktionen wechselweise orthogonale, antisymmetrisierte Produkte von Spinorbitalen (von denen angenommen wird, daß sie einen orthogonalen Satz bilden) darstellen und Eigenfunktion der $\mathcal{S}^2$ und $\mathcal{S}_z$ Operatoren sind. Die erhaltenen Formeln eignen sich für Rechnungen mit und ohne Verwendung eines Computers.

1. Introduction

Although the multiexcited configurations were shown to be fundamentally important in the energy levels calculations, they are included rather exceptionally. One of the most important barriers for extension of configuration interaction expansions by inclusion of multiexcited configurations presents the problem of evaluation of matrix elements for open shell configurations. A simple method, originally formulated by Pauling [10], was further extended by numerous authors in spin-dependent [11] as well as in spin-free [8] formulation of quantum chemistry. However an applicability of the algorithms obtained is limited to the valence-bond wave functions. In the case of spin-projected wave functions the problem has been solved in its general form by Harris [2]. Evaluation of the matrix elements is considerably more troublesome when the wave functions (being antisymmetric eigenfunctions of $\mathcal{S}^2$ and $\mathcal{S}_z$ operators) are mutually orthogonal. Tables of formulas for different types of the matrix elements, published occasionally by various authors [9] are really convenient in some special cases, but are completely insufficient for an authomatic construction of configuration interaction matrices. The main source of difficulty lies in an enormous number of different types of formulas, which rapidly grows up with the number of singly occupied orbitals. The tables of Yamazaki [16], probably the most complete in this type, cover the configurations with at most six singly occupied orbitals and contain a few thousands of formulas. Another, signifficantly more condensed

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type of formulas, however limited to the singlet configurations being no more than doubly excited relatively to a closed shell ground-state, was derived by Čižek [1]. A very interesting algebraic approach making use of the permutational symmetry of the space part of the wave function was recently given by Kaplan [4]. The method enables to evaluate all the types of diagonal and some types of the off diagonal matrix elements. Recently, the second quantization formalism has been used for evaluation of the matrix elements by Kuprievich *et al.* [7][1].

A different and probably the most general is the Serber-Yamanouchi-Kotani approach [6] which may be easily applied in the case of an orthogonal set of antisymmetric configurations being eigenfunctions of $\mathcal{S}^2$ and $\mathcal{S}_z$ operators. The most important obstacle in its direct application is that the matrix elements, in the case of N-electron system, are expressed as sums over $N!$ terms. However when the wave functions are taken as linear combinations of antisymmetrized products of orthogonal one-electron spinorbitals, these sums contain only a few non-zero terms [2, 5, 12]. An efficient method enabling to select the nonvanishing terms and to determine the coefficients with which the appropriate integrals there appear was recently presented in two different versions by Ruedenberg, Salmon and Poshusta [12–14]. An alternative handling of the subject was independently proposed by the author [5]. In the present paper the Ruedenberg's formulas are rederived using a diagram technique[2] which is shown to be a very useful tool as well for general considerations as for practical calculations. An example of such calculation is given as an illustration of the method. Moreover a further simplification of these formulas, being particulary important from the point of view of an applicability of the method to computer-programming, is here performed.

2. Formulation of the Problem

We are concerned with one-electron operators

$$\mathcal{H}_1 = \sum_{i=1}^{N} h_1(\boldsymbol{r}_i) \tag{1}$$

and two-electron operators

$$\mathcal{H}_2 = \sum_{j=i+1}^{N} \sum_{i=1}^{N-1} h_2(\boldsymbol{r}_i, \boldsymbol{r}_j) \tag{2}$$

where $\boldsymbol{r}_i$ denote the spatial coordinates of electron i, N means number of the electrons and $h_2(\boldsymbol{r}_i, \boldsymbol{r}_j) = h_2(\boldsymbol{r}_j, \boldsymbol{r}_i)$. In particular, Hamiltonian of a system of N electrons can always be written in the form

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 \,. \tag{3}$$

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[1] A very complete review of literature concerning the subject is presented in an article of Ruedenberg and Poshusta [13] where the reader is referred to.

[2] This paper was completed before the Ruedenberg *et al.* results [12–14] have got to the author's knowledge. Therefore an approach of Kotani *et al.* [6] was taken as a starting point in this discussion and the notation used here is as close as it is possible to that of Kotani and rather different from the Ruedenberg's one.

Let us define a primitive function Ψ_λ^0 as a product of N one-electron orbitals chosen from an orthonormal set

$$\psi_1, \psi_2, \dots, \psi_K (K \geqq N/2)$$

$$\psi_\lambda^0(\boldsymbol{r}_1, \boldsymbol{r}_2, \dots, \boldsymbol{r}_N) = \prod_{i=1}^{N} \psi_{\lambda_i}(\boldsymbol{r}_i). \tag{4}$$

Every primitive function corresponds to an electronic configuration λ, described by the set of indices $[\lambda_1, \lambda_2, \dots, \lambda_N]$. Some orbitals can be doubly occupied. Then they appear twice in the product (4) and are there written after the singly occupied orbitals. Moreover, both kinds of orbitals are put in (4) in the growing order of their indices. It means that

$$\begin{gathered} \lambda_1 < \lambda_2 < \dots < \lambda_p \\ \lambda_{p+1} = \lambda_{p+2} < \lambda_{p+3} = \lambda_{p+4} < \dots < \lambda_{N-1} = \lambda_N \end{gathered} \tag{5}$$

where p denotes the number of singly occupied orbitals in configuration λ.

In order to construct a wave function with the proper spin and space symmetry properties, based on the orbital product (4), it is convenient to follow the work of Kotani *et al.* [6][3]. For this purpose we introduce an orthonormal set $\Theta_{SM,k}$ of all the linearly independent N-electron eigenfunctions of $\mathcal{S}^2$ and $\mathcal{S}_z$ operators corresponding to the eigenvalues $S(S+1)\hbar^2$ and $M\hbar$, which span a subspace of the whole 2^N dimensional N-spin space. This subspace is called the SM subspace. Its dimension f_S^N can be evaluated from the formula [6]:

$$f_S^N = \frac{(2S+1)\,N!}{(N/2+S+1)!\,(N/2-S)!}. \tag{6}$$

Index k numbers the basis functions of SM subspace and varies from 1 to f_S^N.

The SM subspace is invariant in respect to permutation operators $\mathcal{P}_\sigma$ acting on the spin coordinates of electrons

$$\mathcal{P}_\sigma \Theta_{SM,k} = \sum_{j=1}^{f_S^N} V_S^N(\mathcal{P})_{jk}\, \Theta_{SM,j}. \tag{7}$$

The $V_S^N(\mathcal{P})$ matrices form an irreducible representation of the N!th order permutation group $\mathfrak{S}_N$ [6]. The basis $\Theta_{SM,k}$ of SM subspace has been chosen as orthonormal. Then V_S^N matrices are unitary. As the basis $\Theta_{SM,k}$ is complete in the spin space, every normalized eigenfunction $\Phi_{SM}(\boldsymbol{r}, \boldsymbol{\sigma})$ of $\mathcal{S}^2$ and $\mathcal{S}_z$, depending on space $(\boldsymbol{r})$ and spin $(\boldsymbol{\sigma})$ coordinates of N electrons, can be expanded as

$$\Phi_{SM}(\boldsymbol{r}, \boldsymbol{\sigma}) = \frac{1}{\sqrt{f_S^N}} \sum_{k=1}^{f_S^N} \chi_{S,k}(\boldsymbol{r})\, \Theta_{SM,k}(\boldsymbol{\sigma}) \tag{8}$$

where $\chi_{S,k}(\boldsymbol{r})$ are normalized to unity and M-independent functions of the spatial coordinates of electrons. In the case when $\Phi_{SM}(\boldsymbol{r}, \boldsymbol{\sigma})$ satisfies the Pauli principle, and $\mathcal{P}$ is an operator of permutation of the space coordinates of electrons, then

$$\mathcal{P}\chi_{S,k} = \varepsilon_{\mathcal{P}} \sum_{j=1}^{f_S^N} V_S^N(\mathcal{P}^{-1})_{kj}\, \chi_{S,j} \equiv \sum_{j=1}^{f_S^N} U_S^N(\mathcal{P})_{jk} \chi_{S,j} \tag{9}$$

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[3] The most complete treatment of the problem is given in a recent paper of Salmon [15].

where $\varepsilon_{\mathscr{P}}$ is parity of the permutation $\mathscr{P}$ and $U^N_S(\mathscr{P})_{jk} = \varepsilon_{\mathscr{P}} V^N_S(\mathscr{P}^{-1})_{kj}$. As the $\boldsymbol{V}^N_S$ are unitary,

$$\boldsymbol{U}^N_S(\mathscr{P}) = \varepsilon_{\mathscr{P}} \boldsymbol{V}^N_S(\mathscr{P}) . \tag{10}$$

Hence the matrices $\boldsymbol{U}^N_S(\mathscr{P})$ form a dual representation of $\mathfrak{S}_N$. It is easy to observe, that $\chi_{S,k}(k = 1, 2, \ldots, f^N_S)$ are mutually orthogonal. Every normalizable function of space coordinates of electrons, when transforming according to (9), may be used as basis for construction of the wave function (8) which is an eigenfunction of $\mathscr{S}^2$ and $\mathscr{S}_z$ operators and satisfies the Pauli principle.

When some orbitals are doubly occupied in configuration λ, then there exists a subgroup $\mathfrak{H}_\lambda$ of $\mathfrak{S}_N$ for which Ψ^0_λ is invariant. Every permutation $\mathscr{Q} \in \mathfrak{H}_\lambda$ only inverts ordering within doubly occupied pairs. Since $\mathfrak{H}_\lambda$ is Abelian and $\mathscr{Q}^2 = \mathscr{I}$ ($\mathscr{I}$ means the identity operator) all $\boldsymbol{U}^N_S(\mathscr{Q})$ can be as follows:

$U^N_S(\mathscr{Q})_{ik} = \pm\delta_{ik}, (i, k = 1, 2, \ldots, f^N_S)$; and
$U^N_S(\mathscr{Q})_{kk} = +1$ when $k \leqq f$, while
$U^N_S(\mathscr{Q})_{kk} = -1$ for at least one $\mathscr{Q}$ when $k > f$.
It can be shown [6], that

$$f = f^p_S$$

and that the functions

$$\chi^{(m)}_{S,k} = \sqrt{f^N_S/(N!\,2^{(N-p)/2})} \sum_{\mathscr{P}} U^N_S(\mathscr{P})_{km} \mathscr{P} \Psi^0_\lambda \tag{11}$$

form an orthonormal set and fulfill relation (9) for $m \leqq f$, while for $m > f$ vanish identically. The sum is here extended over all $N!$ elements of $\mathfrak{S}_N$.

From (11) results, that for every configuration λ there exist f linearly independent functions

$$\Phi^{(\lambda)}_{SM,m}(\boldsymbol{r}, \boldsymbol{\sigma}) = 2^{(p-N)/4}/\sqrt{N!} \sum_{k=1}^{f^N_S} \sum_{\mathscr{P}} U^N_S(\mathscr{P})_{km}\, \Theta_{SM,k}(\boldsymbol{\sigma})\, \mathscr{P} \Psi^0_\lambda(\boldsymbol{r}) \tag{12}$$

$$m = 1, 2, \ldots, f;\ \mathscr{P} \in \mathfrak{S}_N ,$$

which fulfil the following conditions:

$$\mathscr{P}_\sigma \mathscr{P} \Phi^{(\lambda)}_{SM,m} = \varepsilon_{\mathscr{P}} \Phi^{(\lambda)}_{SM,m} , \tag{13}$$

$$\mathscr{S}^2 \Phi^{(\lambda)}_{SM,m} = \hbar^2 S(S+1)\, \Phi^{(\lambda)}_{SM,m} , \tag{14}$$

$$\mathscr{S}_z \Phi^{(\lambda)}_{SM,m} = \hbar M \Phi^{(\lambda)}_{SM,m} , \tag{15}$$

$$\langle \Phi^{(\lambda)}_{SM,m} | \Phi^{(\mu)}_{S'M',n} \rangle = \delta_{\lambda\mu} \delta_{SS'} \delta_{MM'} \delta_{mn} . \tag{16}$$

The matrix elements of an arbitrary Hermitean and spin-free operator $\mathscr{H}$ between the wave functions (12) can now be expressed as

$$\langle \Phi^{(\lambda)}_{SM,m} | \mathscr{H} | \Phi^{(\mu)}_{S'M',n} \rangle = \delta_{SS'} \delta_{MM'} H^{(\lambda\mu)}_{mn} \tag{17}$$

where [6]

$$H^{(\lambda\mu)}_{mn} = \sum_{\mathscr{P}}{}' \alpha_{\lambda\mu}(\mathscr{P})\, [U^N_S(\mathscr{P})]^{fg}_{nm} \langle \mathscr{P} \Psi^0_\lambda | \mathscr{H} | \Psi^0_\mu \rangle \tag{18}$$

$$m = 1, 2, \ldots, f; \quad n = 1, 2, \ldots, g;$$

$$f = f^p_S; \quad g = f^q_S; \quad f \geqq g;$$

p and q are the numbers of singly occupied orbitals in configurations λ and μ respectively ; $[\boldsymbol{U}^N_S(\mathscr{P})]^{fg}$ is the rectangular part of $\boldsymbol{U}^N_S(\mathscr{P})$ containing first f

rows and g columns;

$$\alpha_{\lambda\mu}(\mathscr{P}) = 2^{(p+q)/4-N/2}\,\mathrm{ord}\{\mathfrak{P}_{\lambda\mu}(\mathscr{P})\} \tag{19}$$

where $\mathrm{ord}\{\mathfrak{P}_{\lambda\mu}(\mathscr{P})\}$ is the order of a subset $\mathfrak{P}_{\lambda\mu}(\mathscr{P})$ of $\mathfrak{S}_N$ defined as follows: $\mathscr{R} \in \mathfrak{P}_{\lambda\mu}(\mathscr{P})$ if there exist $\mathscr{Q}_\lambda \in \mathfrak{H}_\lambda$ and $\mathscr{Q}_\mu \in \mathfrak{H}_\mu$, such that $\mathscr{R} = \mathscr{Q}_\lambda \mathscr{P} \mathscr{Q}_\mu$[4]; Σ' means that from each set $\mathfrak{P}_{\lambda\mu}(\mathscr{P})$ only one element should be included.

In the primitive function (4) there appear N orbitals ψ_{λ_i}, which are numbered from 1 to N by the index i. It is convenient to define, in paralell to the operators $\mathscr{P}$ which act on the space coordinates of electrons, also operators $\bar{\mathscr{P}}$ acting on the indices i numbering the orbitals. The operators $\mathscr{P}$ and $\bar{\mathscr{P}}$ are connected by a simple relation

$$\bar{\mathscr{P}} = \mathscr{P}^{-1} \tag{20}$$

when they act on Ψ_λ^0. For the representation matrices $U_S^N(\mathscr{P})$ it gives

$$\boldsymbol{U}_S^N(\bar{\mathscr{P}}) = \boldsymbol{U}_S^N(\mathscr{P})^+ \tag{21}$$

The formula (18) can be written involving $\bar{\mathscr{P}}$ operators:

$$H_{mn}^{(\lambda\mu)} = \sum_{\bar{\mathscr{P}}}{}' \alpha_{\lambda\mu}(\bar{\mathscr{P}})\,[U_S^N(\mathscr{P})]_{mn}^{fg}\,\langle \bar{\mathscr{P}}\Psi_\lambda^0 | \mathscr{H} | \Psi_\mu^0 \rangle \tag{22}$$

The formulas (18) and (22) are not satisfactory for application to many-electron systems, because the sums are extended over almost all $N!$ permutations of $\mathfrak{S}_N$. However only a few terms give nonvanishing contributions to the matrix elements. The problem to be solved is to choose these nonvanishing terms and to determine the coefficients with which they do appear. The corresponding formulas were recently derived by Ruedenberg, Salmon and Poshusta [12–14]. An alternative, and completely independently obtained, derivation (partly based on previous results of the author [5]) is outlined in the following.

3. Graphical Representation

In order to simplify the Eq. (22) we have found to be convenient to introduce a graphical representation of a pair of configurations. The orbitals appearing in the primitive functions corresponding to a pair of configurations are represented by asterisks (if singly occupied) and by circles (if doubly occupied). The symbol corresponding to ψ_{λ_i} (ψ_{μ_i}) orbital is labelled with the number $\lambda_i(\mu_i)$. The asterisks and circles are distributed in two rows and N columns. The symbols describing the configuration μ are placed in the first row and in the second one – the configuration λ. According to (18), always $f \geqq g$ (i.e. $p \geqq q$). The sequence of the symbols in both rows is the same as in the corresponding orbital products (4). The symbols corresponding to identical orbitals are joined by lines. If it is possible to join them in a few distinct ways, then the joining lines are drawn as short as possible. Such system circles, asterisks and joining lines is called *configuration-pair diagram* and denoted $D_{\lambda\mu}$. For example the pair of configurations:

$$\begin{aligned} \Psi_\mu^0 &= \psi_1(\boldsymbol{r}_1)\,\psi_3(\boldsymbol{r}_2)\,\psi_4(\boldsymbol{r}_3)\,\psi_4(\boldsymbol{r}_4)\,\psi_6(\boldsymbol{r}_5)\,\psi_6(\boldsymbol{r}_6) \\ \Psi_\lambda^0 &= \psi_3(\boldsymbol{r}_1)\,\psi_4(\boldsymbol{r}_2)\,\psi_6(\boldsymbol{r}_3)\,\psi_8(\boldsymbol{r}_4)\,\psi_1(\boldsymbol{r}_5)\,\psi_1(\boldsymbol{r}_6) \end{aligned} \tag{23}$$

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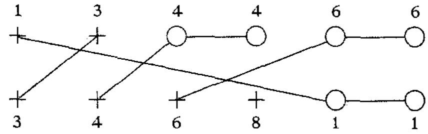
[4] Some useful properties of the double coset $\mathfrak{P}_{\lambda\mu}(\mathscr{P})$ are derived by Junker and Klein [3].

is represented by the diagram:

$D_{\lambda\mu} =$



. (24)

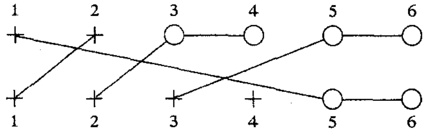
In such a way to every rectangular $\boldsymbol{H}^{(\lambda\mu)}$ matrix corresponds one $D_{\lambda\mu}$ diagram.

Every $D_{\lambda\mu}$ diagram generates a set of $N!$ diagrams $\mathscr{D}_{\lambda\mu}(\mathscr{P})$ called *numbered diagrams of a configuration pair.* The graphical representation of $\mathscr{D}_{\lambda\mu}(\mathscr{I})$ is the same as that of $D_{\lambda\mu}$, however the symbols representing the orbitals are now additionally provided with their consecutive numbers in the orbital product (4) (number i for ψ_{λ_i} orbital). In $\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}})$ diagram the order of orbitals in the first row is the same as in $\mathscr{D}_{\lambda\mu}(\mathscr{I})$ while in the second one it is changed in respect to $\mathscr{D}_{\lambda\mu}(\mathscr{I})$ and is the same as in $\bar{\mathscr{P}}\Psi_\lambda^0$. The joining lines are also properly changed. If we accept the convention that the operators $\bar{\mathscr{P}}$ may properly permute the orbitals in the second row of the numbered diagrams and do not affect the first row, then all $N!$ diagrams $\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}})$ can be expressed as

$$\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}}) = \bar{\mathscr{P}}\mathscr{D}_{\lambda\mu}(\mathscr{I}) . \tag{25}$$

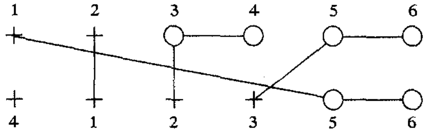
For example, for the diagram (24)

$\mathscr{D}_{\lambda\mu}(\mathscr{I}) =$



and

$(\overline{1432})\,\mathscr{D}_{\lambda\mu}(\mathscr{I}) =$



$= \mathscr{D}_{\lambda\mu}((\overline{1432}))$

In these diagrams the indices λ_i and μ_i are for simplicity sake omitted.

In the case when identical orbitals are on the same positions in Ψ_μ^0 and $\bar{\mathscr{P}}\Psi_\lambda^0$, the corresponding joining lines in the numbered diagram $\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}})$ are "vertical". The difference between number of electrons (N) and number of the vertical lines is called *rank* of the numbered diagram. The diagram $\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}})$ in which all the lines joining its rows are vertical is called the *ordered diagram.* Of course, there may be a few ordered diagrams for a given configuration-pair diagram. From among the permutations which transform $\mathscr{D}_{\lambda\mu}(\mathscr{I})$ into the ordered diagram we choose one and denote it $\bar{\mathscr{P}}_0$[5]. Then, this permutation is kept fixed for a given pair of configurations. In our example $\bar{\mathscr{P}}_0$ can be any permutation from the sets $\mathfrak{P}_{\lambda\mu}((\overline{1532}))$ or $\mathfrak{P}_{\lambda\mu}((\overline{46})(\overline{1532}))$. The rank of an ordered diagram is called rank of the configuration-pair diagram and equals the number of orbitals by which the two involved configurations differ. Where it is essential we write it as a superscript in the correspondent symbol: $D_{\lambda\mu}^r$.

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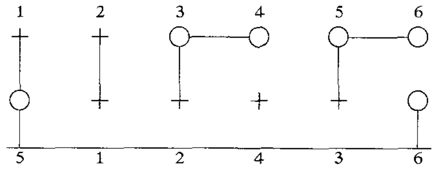
[5] The permutation $\bar{\mathscr{P}}_0$ is identical with the *line-up permutation* introduced by Ruedenberg [12].

The relation (22) states that the configuration-pair diagram $D_{\lambda\mu}$ is a superposition of the numbered diagrams $\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}})$

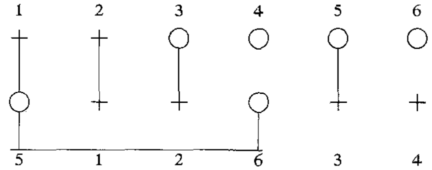
$$D_{\lambda\mu} = \sum_{\bar{\mathscr{P}}}{}' \alpha_{\lambda\mu}(\bar{\mathscr{P}})\,\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}})\,. \tag{26}$$

The prime in the sum means, that only one element from every set $\mathfrak{P}_{\lambda\mu}(\bar{\mathscr{P}})$ should be included. The orthogonality of the orbitals causes, that in the case of n-electron operators (we are interested in $n=1$ and $n=2$) only these diagrams will contribute to the sum (26) whose ranks do not exceed n. In our example $r=2$. Therefore nonzero contributions appear for two-electron operators and come from ordered diagrams only: one from the set $\mathfrak{P}_{\lambda\mu}((\overline{1532}))$ and one from $\mathfrak{P}_{\lambda\mu}((\overline{46})(\overline{1532}))$, say

$\mathscr{D}_{\lambda\mu}((\overline{1532})) =$



$\mathscr{D}_{\lambda\mu}((\overline{46})(\overline{1532})) =$



4. Classification of Configuration-Pair Diagrams

Every permutation $\bar{\mathscr{P}}$ may be expressed in the form

$$\bar{\mathscr{P}} = \bar{\mathscr{P}}^{sd}\bar{\mathscr{P}}^{s}\bar{\mathscr{P}}^{d} \tag{27}$$

where $\bar{\mathscr{P}}^{s}$ causes a mixing of singly occupied orbitals, $\bar{\mathscr{P}}^{d}$ – of doubly occupied ones, and $\bar{\mathscr{P}}^{sd}$ is a product of transpositions interchanging singly and doubly occupied orbitals. Decomposition (27) is always performed in such way, that $\bar{\mathscr{P}}^{sd}$ consists of the least possible number of transpositions.

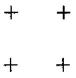
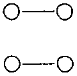
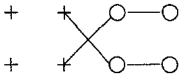
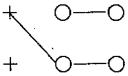
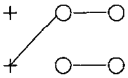
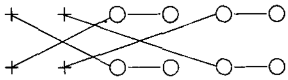
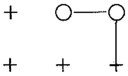
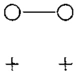
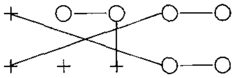
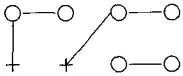
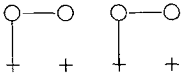
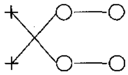
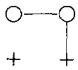
The decomposition (27) of $\bar{\mathscr{P}}_0$ permutation

$$\bar{\mathscr{P}}_0 = \bar{\mathscr{P}}_0^{sd}\bar{\mathscr{P}}_0^{s}\bar{\mathscr{P}}_0^{d} \tag{28}$$

can be used as a basis for an useful classification of configuration-pair diagrams. Namely, as will be seen, the type of formula for the matrix element (22), (26) is determined by this part of $\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}}_0^{s}\bar{\mathscr{P}}_0^{d})$ diagram, where non-identical orbitals are located on the same positions in the rows. Therefore it is convenient to classify the $D_{\lambda\mu}$ diagrams in such way, that to one class belong these diagrams for which $\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}}_0^{s}\bar{\mathscr{P}}_0^{d})$ has the same form.

All the distinct types of $\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}}_0^{s}\bar{\mathscr{P}}_0^{d})$ diagrams corresponding to $D_{\lambda\mu}^{r}$ diagrams with $r \leqq 2$ are collected in Table 1. These parts of the diagrams, where identical orbitals (when singly occupied) or identical pairs of orbitals (when doubly occupied) are located on the same positions in both rows, are there omitted. As

Table 1. Types of $\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}}_0^s\bar{\mathscr{P}}_0^d)$ diagrams

No.	$\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}}_0^s\bar{\mathscr{P}}_0^d)$	Rank of $D_{\lambda\mu}$	$\alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)$	$p-q$
1		2	1	0
2		2	1	0
3		2	2	0
4		2	2	0
5		2	2	0
6		2	4	0
7		2	$\sqrt{2}$	2
8		2	$\sqrt{2}$	2
9		2	$2\sqrt{2}$	2
10		2	$2\sqrt{2}$	2
11		2	2	4
12		1	1	0
13		1	2	0
14		1	$\sqrt{2}$	2
15		0	1	0

seen, all the $D^r_{\lambda\mu}$ diagrams ($r \leqq 2$) have been distributed into 15 classes. According to the rank r, there are 11 classes for $r=2$, 3 classes for $r=1$ and one class for $r=0$.

Let the number of orbitals being singly occupied in configuration $\lambda(\mu)$ and doubly occupied in configuration $\mu(\lambda)$ be denoted by $t_\lambda(t_\mu)$ and $\max(t_\lambda, t_\mu)$ be the bigger of these numbers. If $p=q$ then $\bar{\mathscr{P}}_0^{sd}$ consists of $t=\max(t_\lambda, t_\mu)$ transpositions. If $p \neq q$ then $(p-q)/2$ singly occupied orbitals of configuration λ may be brought into coincidence with the corresponding doubly occupied orbitals of configuration μ by means of $\bar{\mathscr{P}}_0^{s}$ (a pair of doubly occupied orbitals in μ may always be placed in a proper position as the representation matrix corresponding to a transposition of two doubly occupied pairs is unit). Hence, if $\max(t_\lambda, t_\mu) > (p-q)/2$ then $\bar{\mathscr{P}}_0^{sd}$ consists of

$$t=\max(t_\lambda, t_\mu)-(p-q)/2 \tag{29}$$

transpositions, and $\bar{\mathscr{P}}_0^{sd}=\mathscr{I}$ (i.e. $t=0$) in the opposite case.

5. Evaluation of $\alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)$

If $\mathfrak{P}_{\lambda\mu}(\bar{\mathscr{P}}_0)$ is decomposed after (28), then

$$\mathfrak{P}_{\lambda\mu}(\bar{\mathscr{P}}_0)=\{\mathfrak{H}_\mu \bar{\mathscr{P}}_0^{sd} \bar{\mathscr{P}}_0^{d} \mathfrak{H}_\lambda \bar{\mathscr{P}}_0^{s}\}\,. \tag{30}$$

$\bar{\mathscr{P}}_0^{d}$ may always be expressed as a product of operators transposing pairs of doubly occupied orbitals. Then $\{\bar{\mathscr{P}}_0^{d}\mathfrak{H}_\lambda\}=\{\mathfrak{H}_\lambda\bar{\mathscr{P}}_0^{d}\}$[6] and

$$\operatorname{ord}\{\mathfrak{P}_{\lambda\mu}(\bar{\mathscr{P}}_0)\}=\operatorname{ord}\{\mathfrak{H}_\mu \bar{\mathscr{P}}_0^{sd}\mathfrak{H}_\lambda\} \tag{31}$$

Now, if $\bar{\mathscr{P}}_0^{sd}=\mathscr{I}$, then $\operatorname{ord}\{\mathfrak{P}_{\lambda\mu}(\bar{\mathscr{P}}_0)\}=\operatorname{ord}\{\mathfrak{H}_\mu\mathfrak{H}_\lambda\}=2^{(N-q)/2}$ (because $\mathfrak{H}_\lambda$ is a subgroup of $\mathfrak{H}_\mu$ and $\mathfrak{H}_\mu\mathfrak{H}_\lambda=\mathfrak{H}_\mu$). Therefore, according to (19), in this case

$$\alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)=2^{(p-q)/4}\,. \tag{32}$$

If $\bar{\mathscr{P}}_0^{sd}$ consists of one transposition $(d's)$, where ψ_{λ_s} is a singly occupied orbital and $\psi_{\lambda_{d'}}=\psi_{\lambda_{d''}}$ is a doubly occupied one, then

$$\alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)=2^{(p-q)/4+1} \tag{33}$$

Indeed, if $\mathscr{Q}_\lambda \in \mathfrak{H}_\lambda$ then either $(d's)\,\mathscr{Q}_\lambda=\mathscr{Q}_\lambda(d's)$ (if $\mathscr{Q}_\lambda$ does not invert the $(d'd'')$ pair) or $(d's)\,\mathscr{Q}_\lambda=\mathscr{Q}_\lambda(d''s)$ (if $\mathscr{Q}_\lambda$ inverts $(d'd'')$). Hence the set $\{\mathfrak{H}_\mu\bar{\mathscr{P}}_0^{sd}\mathfrak{H}_\lambda\}$ consists of permutations $\mathfrak{H}_\mu(d's)$ and $\mathfrak{H}_\mu(d''s)$. Generally, if $\bar{\mathscr{P}}_0^{sd}$ involves t distinct doubly occupied orbitals then

$$\alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)=2^{(p-q)/4+t} \tag{34}$$

where t is determined by Eq. (29).

6. Representation Matrices

The appropriate rectangular parts of $U_S^N(\mathscr{P})$, necessary to evaluate the $H^{(\lambda\mu)}$ matrix (22) may be relatively easily obtained after the genealogical scheme [6] or using the SAAP formalism [14] (for the most important cases tables of $U_S^N(\mathscr{P})$

---

[6] It means that the sets $\{\bar{\mathscr{P}}_0^{d}\mathfrak{H}_\lambda\}$ and $\{\mathfrak{H}_\lambda\bar{\mathscr{P}}_0^{d}\}$ are identical. However the elements of $\mathfrak{H}_\lambda$ in general do not commute with $\bar{\mathscr{P}}_0^{d}$.

are available [6, 16]). As compromise between a time-consuming construction of every actually desired representation matrix and a storage-consuming keeping of the all $N!$ matrices in the machine core, it seems to be reasonable to store only the matrices of a few transpositions expressing the others, actually desired matrices, as their products. However in such case, to obtain the $f \times g$ part of $\boldsymbol{U}_S^N(\mathscr{P})$, full representation matrices for the component transpositions are needed, dimension (6) of whom violently grow up with the number of electrons. A considerable reduction of the necessary dimension is possible, basing on the following properties of $\boldsymbol{U}_S^N$ matrices [6]:

1. If in the primitive function (4) $\lambda_{d'} = \lambda_{d''}$ and $\lambda_r \neq \lambda_{d'}, \lambda_s \neq \lambda_{d'}$ then

$$[\boldsymbol{U}_S^N((d'd'')\,\mathscr{T})]^{ff} = [\boldsymbol{U}_S^N(\mathscr{T})]^{ff}\,, \tag{35}$$

$$[\boldsymbol{U}_S^N((d'r)\,\mathscr{T})]^{ff} = [\boldsymbol{U}_S^N((d''r)\,\mathscr{T})]^{ff} = -\tfrac{1}{2}[\boldsymbol{U}_S^N(\mathscr{T})]^{ff}\,, \tag{36}$$

$$[\boldsymbol{U}_S^N((d'r)\,(d''s)\,\mathscr{T})]^{ff} = \tfrac{1}{2}[\boldsymbol{U}_S^N(\mathscr{T})]^{ff} + \tfrac{1}{2}[\boldsymbol{U}_S^N((rs)\,\mathscr{T})]^{ff} \tag{37}$$

where $\mathscr{T}$ is an arbitrary permutation not containing d' nor d''.

2. Let $\mathfrak{S}_p$ be permutation group of the orbitals singly occupied in configuration λ. If $\mathscr{P} \in \mathfrak{S}_p$ then

$$[\boldsymbol{U}_S^N(\mathscr{P})]^{ff} = \boldsymbol{U}_S^p(\mathscr{P})\,. \tag{38}$$

Hence, only the representation matrices $\boldsymbol{U}_S^p$, corresponding to permutations $\mathscr{P} \in \mathfrak{S}_p$, are necessary for evaluating of all the matrix elements. This fact is of fundamental importance for application, as in general $p \ll N$.

7. The Matrix Elements

According to rank r of $D_{\lambda\mu}^r$ diagrams, four kinds of formulas are possible.

a) $r > 2$

As the orbitals are orthogonal, all the matrix elements of one- and two-electron operators are equal to zero in this case.

b) $r = 2$

In (26) there are at most two non-zero components, namely

$$D_{\lambda\mu}^2 = \alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)\,\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}}_0) + \alpha_{\lambda\mu}((ik)\,\bar{\mathscr{P}}_0)\,\mathscr{D}'_{\lambda\mu}((ik)\,\bar{\mathscr{P}}_0) \tag{39}$$

where i and k are the numbers of the orbitals of configuration λ which do not link to any orbital of μ. Prime in the second term means, that it appears only in the case when $(ik)\,\bar{\mathscr{P}}_0 \notin \mathfrak{P}_{\lambda\mu}(\bar{\mathscr{P}}_0)$. As can be easily verified, for all the diagrams with $r = 2$

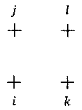
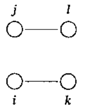
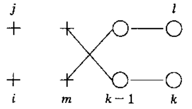
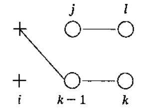
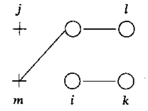
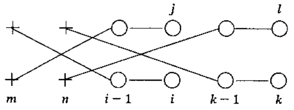
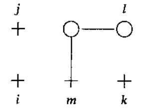
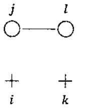
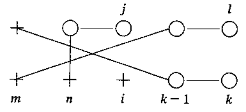
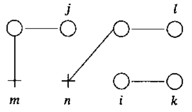
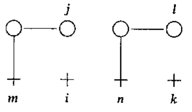
$$\alpha_{\lambda\mu}((ik)\,\bar{\mathscr{P}}_0) = \alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)\,. \tag{40}$$

Hence the relation (39) may be written as

$$\begin{aligned} \boldsymbol{H}^{(\lambda\mu)} = \alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)\,\{[\boldsymbol{U}_S^N(\bar{\mathscr{P}}_0)]^{fg}\,\langle\bar{\mathscr{P}}_0\Psi_\lambda^0|\mathscr{H}|\Psi_\mu^0\rangle \\ + [\boldsymbol{U}_S^N((ik)\,\bar{\mathscr{P}}_0)]^{fg}\,\langle(ik)\,\bar{\mathscr{P}}_0\Psi_\lambda^0|\mathscr{H}|\Psi_\mu^0\rangle'\}\,. \end{aligned} \tag{41}$$

Let ψ_{μ_j} and ψ_{μ_l} be the orbitals of configuration μ located in the diagram $\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}}_0)$ on the positions corresponding to ψ_{λ_i} and ψ_{λ_k} respectively. Then, after

Table 2. $a_{\lambda\mu}$ coefficients and $A_{\lambda\mu}$ matrices

No.	$\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}}_0^s\bar{\mathscr{P}}_0^d)$[a]	$a_{\lambda\mu}$	$A_{\lambda\mu}$
1		1	$\boldsymbol{U}_S^p((ik))$
2		1	0
3		−1	$\mathbf{1}+\boldsymbol{U}_S^p((im))$
4		−1	0
5		−1	0
6		1	$\boldsymbol{U}_S^p((mn))$
7		$\sqrt{2}$	$\sqrt{2}\,\boldsymbol{U}_S^p((ik))$
8		$\sqrt{2}$	0
9		$-\sqrt{2}$	$\sqrt{2}[\mathbf{1}+\boldsymbol{U}_S^p((im))]$
10		$-\sqrt{2}$	0
11		2	$2\,\boldsymbol{U}_S^p((ik))$

[a] Where essential, the orbitals are provided with their consecutive numbers in the orbital product (4) (i for ψ_{λ_i} (ψ_{μ_i}) orbital). The indices λ_i and μ_i are for simplicity sake omitted.

performing in (41) integration over all the variables but j-th and l-th, and making use of the orthogonality of orbitals, we get[7]

$$\boldsymbol{H}^{(\lambda\mu)} = \alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)\,[\{[\lambda_i\mu_j|\lambda_k\mu_l] + [\lambda_k\mu_j|\lambda_i\mu_l]\,\boldsymbol{U}_S^N((ik))\}\,\boldsymbol{U}_S^N(\bar{\mathscr{P}}_0)]^{fg} \tag{42}$$

where

$$[\lambda_i\mu_j|\lambda_k\mu_l] = \int \psi^*_{\lambda_i}(\boldsymbol{r}_1)\,\psi^*_{\lambda_k}(\boldsymbol{r}_2)\,\hbar_2(\boldsymbol{r}_1,\boldsymbol{r}_2)\,\psi_{\mu_j}(\boldsymbol{r}_1)\,\psi_{\mu_l}(\boldsymbol{r}_2)\,\mathrm{d}\tau_{12}\,. \tag{43}$$

Of course, the contributions from one-electron operators in this case vanish.

Formula (42) presents the most compact expression for the matrix elements in the case of $r=2$. However the representation matrices appearing in it are formed for the whole operators $\bar{\mathscr{P}}_0$ and $(ik)\,\bar{\mathscr{P}}_0$, including contributions from $\bar{\mathscr{P}}_0^d$ and from $\bar{\mathscr{P}}_0^{sd}$. As was previously explained, it is rather inconvenient in applications. Therefore we will perform a further simplification of (42). Making use of (28) we get

$$\boldsymbol{U}_S^N(\bar{\mathscr{P}}_0) = \boldsymbol{U}_S^N(\bar{\mathscr{P}}_0^{sd})\,\boldsymbol{U}_S^N(\bar{\mathscr{P}}_0^s)\,\boldsymbol{U}_S^N(\bar{\mathscr{P}}_0^d)\,. \tag{44}$$

From (35) and (37) it directly results that $[\boldsymbol{U}_S^N(\bar{\mathscr{P}}_0^d)]^{ff} = \mathbf{1}$ ($\mathbf{1}$ is $f \times f$ unit matrix). Using formulas (35)–(38) the matrices $[\boldsymbol{U}_S^N(\bar{\mathscr{P}}_0)]^{ff}$ and $[\boldsymbol{U}_S^N((ik)\,\bar{\mathscr{P}}_0)]^{ff}$ can be transformed as follows:

$$\alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)\,[\boldsymbol{U}_S^N(\bar{\mathscr{P}}_0)]^{ff} = a_{\lambda\mu}\,\boldsymbol{U}_S^p(\bar{\mathscr{P}}_0^s)\,, \tag{45}$$

$$\alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)\,[\boldsymbol{U}_S^N((ik)\,\bar{\mathscr{P}}_0)]^{ff} = \boldsymbol{A}_{\lambda\mu}\,\boldsymbol{U}_S^p(\bar{\mathscr{P}}_0^s) \tag{46}$$

where $a_{\lambda\mu}$ is a number and $\boldsymbol{A}_{\lambda\mu}$ – an $f \times f$ matrix. The values of $a_{\lambda\mu}$ and $\boldsymbol{A}_{\lambda\mu}$ depend on the specific form of the appropriate configuration-pair diagram. Coefficients $\alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)$ have been included into $a_{\lambda\mu}$ and $\boldsymbol{A}_{\lambda\mu}$ in order to simplify the notation. The $\boldsymbol{A}_{\lambda\mu}$ matrices can be constructed involving only $f \times f$ parts of the representation matrices corresponding to transpositions of singly occupied orbitals and are listed in Table 2. Also the values of $a_{\lambda\mu}$ are there given[8]. The formula (42) takes now the form:

$$\boldsymbol{H}^{(\lambda\mu)} = \{a_{\lambda\mu}[\lambda_i\mu_j|\lambda_k\mu_l] + \boldsymbol{A}_{\lambda\mu}[\lambda_k\mu_j|\lambda_i\mu_l]\}\,[\boldsymbol{U}_S^p(\bar{\mathscr{P}}_0^s)]^{fg}\,. \tag{47}$$

As an illustration of the method of treatment let us derive the $\boldsymbol{A}_{\lambda\mu}$ matrix and calculate the value of $a_{\lambda\mu}$ for diagram No. 6. Applying (36), (37) and (38) we get:

$$\begin{aligned}
[\boldsymbol{U}_S^N(\bar{\mathscr{P}}_0)]^{ff} &= [\boldsymbol{U}_S^N((i-1,m)\,(k-1,n)\,\bar{\mathscr{P}}_0^s)]^{ff} = \tfrac{1}{4}[\boldsymbol{U}_S^N(\bar{\mathscr{P}}_0^s)]^{ff} = \tfrac{1}{4}\boldsymbol{U}_S^p(\bar{\mathscr{P}}_0^s)\,,\\
[\boldsymbol{U}_S^N((ik)\,\bar{\mathscr{P}}_0)]^{ff} &= [\boldsymbol{U}_S^N((ik)\,(i-1,m)\,(k-1,n)\,\bar{\mathscr{P}}_0^s)]^{ff}\\
&= \tfrac{1}{2}[\boldsymbol{U}_S^N((k-1,n)\,\bar{\mathscr{P}}_0^s)]^{ff} + \tfrac{1}{2}[\boldsymbol{U}_S^N((km)\,(k-1,n)\,\bar{\mathscr{P}}_0^s)]^{ff}\\
&= \tfrac{1}{4}[\boldsymbol{U}_S^N((mn)\,\bar{\mathscr{P}}_0^s)]^{ff} = \tfrac{1}{4}\boldsymbol{U}_S^p((mn))\,\boldsymbol{U}_S^p(\bar{\mathscr{P}}_0^s)\,.
\end{aligned}$$

Hence $a_{\lambda\mu} = \alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)/4 = 1$, and $\boldsymbol{A}_{\lambda\mu} = \boldsymbol{U}_S^p((mn))$. Numbering of the orbitals after Table 2.

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[7] Note a difference between this formula and the corresponding one derived by Ruedenberg *et al.* [12–14]. In the Ruedenberg's formula the both terms do appear also when they are identical, while in (42) only in the case when they are essentially different. For this reason $\alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)$ differs in some cases from the Ruedenberg's $(N_{\alpha\beta}(U)\,N_{\gamma\delta}(V))^{1/2}$ coefficient by factor 2.

[8] Let us note that $a_{\lambda\mu} = \varepsilon 2^{(p-q)/4}$, where ε is parity of $\bar{\mathscr{P}}_0^{sd}$ permutation, and $\boldsymbol{A}_{\lambda\mu} \neq 0$ only if neither $\lambda_k = \lambda_i$ nor $\mu_j = \mu_l$.

c) $r=1$.

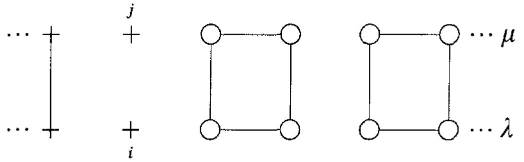
Retaining in (26) only nonvanishing terms,

$$D^1_{\lambda\mu}=\alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)\,\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}}_0)+\sum_{m=1}^{N}{}'\,\alpha_{\lambda\mu}((mi)\,\bar{\mathscr{P}}_0)\,\mathscr{D}_{\lambda\mu}((mi)\,\bar{\mathscr{P}}_0) \tag{48}$$

where ψ_{λ_i} does not link to any orbital of configuration μ. The prime over the sum means that from every set $\mathfrak{P}_{\lambda\mu}((mi)\,\bar{\mathscr{P}}_0)$ only one term is included.

As seen in Table 1, three distinct types of configuration-pair diagrams are possible (No. 12, 13 and 14). The correspondent formulas are as follows:

Diagram 12:



After simple manipulation we obtain

$$\alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)=1;\quad [\boldsymbol{U}^N_S(\bar{\mathscr{P}}_0)]^{ff}=\boldsymbol{U}^p_S(\bar{\mathscr{P}}^s_0);\quad \text{and}\quad (\text{if } m\neq i),$$

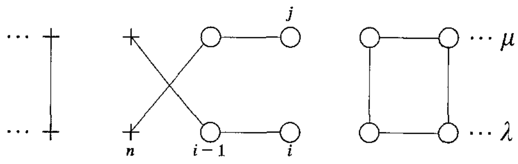
$$\alpha_{\lambda\mu}((im)\,\bar{\mathscr{P}}_0)=\begin{cases}1 & (\text{if } m\leqq p)\\ 2 & (\text{if } m>p),\end{cases}$$

$$[\boldsymbol{U}^N_S((im)\,\bar{\mathscr{P}}_0)]^{ff}=\begin{cases}\boldsymbol{U}^p_S((im))\,\boldsymbol{U}^p_S(\bar{\mathscr{P}}^s_0) & (\text{if } m\leqq p)\\ -\boldsymbol{U}^p_S(\bar{\mathscr{P}}^s_0)/2 & (\text{if } m>p).\end{cases}$$

Thus, Eq. (48) can be rewritten

$$\boldsymbol{H}^{(\lambda\mu)}=\left\{\langle\bar{\mathscr{P}}_0\Psi^0_\lambda|\mathscr{H}|\Psi^0_\mu\rangle+\sum_{\substack{m=1\\(m\neq i)}}^{p}[\lambda_i\lambda_m|\lambda_m\mu_j]\,\boldsymbol{U}^p_S((im))\right.$$
$$\left.-\sum_{m=1}^{(N-p)/2}[\lambda_i\lambda_{p+2m}|\lambda_{p+2m}\mu_j]\right\}\boldsymbol{U}^p_S(\bar{\mathscr{P}}^s_0)\,. \tag{49}$$

Diagramm 13:



Analogically,

$$\alpha_{\lambda\mu}(\bar{\mathscr{P}}_0)=2;\quad [\boldsymbol{U}^N_S(\bar{\mathscr{P}}_0)]^{ff}=-\boldsymbol{U}^p_S(\bar{\mathscr{P}}^s_0)/2;\quad \text{and } (\text{if } m\neq i,\, m\neq i-1)$$

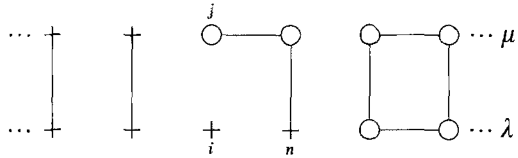
$$\alpha_{\lambda\mu}((im)\,\bar{\mathscr{P}}_0)=\begin{cases}2 & (\text{if } m\leqq p)\\ 4 & (\text{if } m>p),\end{cases}$$

$$[\boldsymbol{U}^N_S((im)\,\bar{\mathscr{P}}_0)]^{ff}=[\boldsymbol{U}^N_S((im)\,(i-1,n)\,\bar{\mathscr{P}}^s_0)]^{ff}$$
$$=\begin{cases}[1+\boldsymbol{U}^p_S((mn))]\,\boldsymbol{U}^p_S(\bar{\mathscr{P}}^s_0)/2 & (\text{if } m\leqq p)\\ \boldsymbol{U}^p_S(\bar{\mathscr{P}}^s_0)/4 & (\text{if } m>p).\end{cases}$$

Thus, in this case

$$\boldsymbol{H}^{(\lambda\mu)} = \left\{ -\langle \bar{\mathscr{P}}_0 \Psi^0_\lambda | \mathscr{H} | \Psi^0_\mu \rangle + \sum_{\substack{m=1 \\ (m \neq n)}}^{p} [\lambda_i \lambda_m | \lambda_m \mu_j] \left(\mathbf{1} + \boldsymbol{U}^p_S((mn))\right) + \sum_{\substack{m=1 \\ (m \neq (i-p)/2)}}^{(N-p)/2} [\lambda_i \lambda_{p+2m} | \lambda_{p+2m} \mu_j] \right\} \boldsymbol{U}^p_S(\bar{\mathscr{P}}^s_0) . \tag{50}$$

Diagram 14:



In the same way

$$\boldsymbol{H}^{(\lambda\mu)} = \sqrt{2} \left\{ \langle \bar{\mathscr{P}}_0 \Psi^0_\lambda | \mathscr{H} | \Psi^0_\mu \rangle + \sum_{\substack{m=1 \\ (m \neq i, m \neq n)}}^{p} [\lambda_i \lambda_m | \lambda_m \mu_j] \, \boldsymbol{U}^p_S((im)) - \sum_{m=1}^{(N-p)/2} [\lambda_i \lambda_{p+2m} | \lambda_{p+2m} \mu_j] \right\} [\boldsymbol{U}^p_S(\bar{\mathscr{P}}^s_0)]^{fg} . \tag{51}$$

Equations (49)–(51) present the final expressions for the matrix elements in the case of $r = 1$. Contributions from one-electron operators appear there only in integrals

$$\langle \bar{\mathscr{P}}_0 \Psi^0_\lambda | \mathscr{H} | \Psi^0_\mu \rangle = [\lambda_i \mu_j] + \sum_{\substack{m=1 \\ (m \neq i)}}^{N} [\lambda_i \mu_j | \lambda_m \lambda_m] \tag{52}$$

where

$$[\lambda_i \mu_j] = \int \psi^*_{\lambda_i}(\boldsymbol{r}_1) \, h_1(\boldsymbol{r}_1) \, \psi_{\mu_j}(\boldsymbol{r}_1) \, d\tau_1 . \tag{53}$$

Then, the $\boldsymbol{H}^{(\lambda\mu)}_1$ matrix of one-electron operator (1) in the case of $r = 1$ can be written in a condensed form

$$\boldsymbol{H}^{(\lambda\mu)}_1 = \varepsilon 2^{(p-q)/4} [\lambda_i \mu_j] \, [\boldsymbol{U}^p_S(\bar{\mathscr{P}}^s_0)]^{fg} \tag{54}$$

where ε is parity of $\bar{\mathscr{P}}^{sd}_0$ permutation

d) $r = 0$.

In this case $\boldsymbol{U}^N_S(\bar{\mathscr{P}}_0) = \mathbf{1}$, as $\bar{\mathscr{P}}_0$ is the identity operator. Thus

$$D^0_{\lambda\mu} = \mathscr{D}_{\lambda\mu}(\mathscr{I}) + \sum_{(ij)}{}' \alpha_{\lambda\mu}((ij)) \, \mathscr{D}_{\lambda\mu}((ij)) \tag{55}$$

where the sum is extended over the all distinct $\mathfrak{P}_{\lambda\mu}((ij))$ sets. The explicit expression for $\boldsymbol{H}^{(\lambda\mu)}$ is

$$\begin{aligned} \boldsymbol{H}^{(\lambda\mu)} = {} & \langle \Psi^0_\lambda | \mathscr{H} | \Psi^0_\mu \rangle + \sum_{i=j+1}^{p} \sum_{j=1}^{p-1} [\lambda_i \lambda_j | \lambda_j \lambda_i] \, \boldsymbol{U}^p_S((ij)) \\ & - \sum_{i=1}^{p} \sum_{j=1}^{(N-p)/2} [\lambda_i \lambda_{p+2j} | \lambda_{p+2j} \lambda_i] \\ & - 2 \sum_{i=j+1}^{(N-p)/2} \sum_{j=1}^{(N-p)/2-1} [\lambda_{p+2i} \lambda_{p+2j} | \lambda_{p+2j} \lambda_{p+2i}] \end{aligned} \tag{56}$$

where

$$\langle \Psi^0_\lambda | \mathscr{H} | \Psi^0_\mu \rangle = \sum_{i=1}^{N} [\lambda_i \lambda_i] + \sum_{i=j+1}^{N} \sum_{j=1}^{N-1} [\lambda_i \lambda_i | \lambda_j \lambda_j] \tag{57}$$

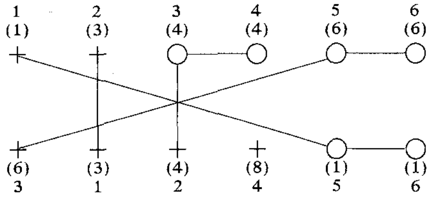
8. Example of Application

Let us evaluate the matrix elements of $\mathscr{H}$ operator (3) for the pair of configurations (23). In this case

$$\bar{\mathscr{P}}^s_0 = (23)(12); \quad \bar{\mathscr{P}}^d_0 = 1$$

and

$$\mathscr{D}_{\lambda\mu}(\bar{\mathscr{P}}^s_0 \bar{\mathscr{P}}^d_0) =$$



Names of the orbitals (the numbers $\lambda_i(\mu_i)$ for $\psi_{\lambda_i}(\psi_{\mu_i})$ orbitals) are given in parenthesis. As seen, the diagram corresponds to the case No. 9 (Tables 1 and 2). Making use of Table 2 and Eq. (47)

$$\boldsymbol{H}^{(\lambda\mu)} = \{-\sqrt{2}[84|16] + \sqrt{2}[14|86]\,[\mathbf{1} + \boldsymbol{U}^4_S((34))]\}\,[\boldsymbol{U}^4_S((23)(12))]^{fg}$$

For the singlet configurations[9] ($S=0$):

$$f = f^4_0 = 2; \quad g = f^2_0 = 1$$

$$\boldsymbol{U}^4_0((12)) = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}; \quad \boldsymbol{U}^4_0((23)) = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}; \quad \boldsymbol{U}^4_0((34)) = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

Thus

$$\boldsymbol{H}^{(\lambda\mu)} = \begin{bmatrix} 1/\sqrt{2} \\ \sqrt{3/2} \end{bmatrix} [84|16] - \begin{bmatrix} \sqrt{2} \\ 0 \end{bmatrix} [14|86].$$

For the triplet configurations ($S=1$):

$$f = f^4_1 = 3; \quad g = f^2_1 = 1$$

$$\boldsymbol{U}^4_1((12)) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1/3 & -2\sqrt{2}/3 \\ 0 & -2\sqrt{2}/3 & 1/3 \end{bmatrix}$$

$$\boldsymbol{U}^4_1((23)) = \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & -1 \end{bmatrix}; \quad \boldsymbol{U}^4_1((34)) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Thus

$$\boldsymbol{H}^{(\lambda\mu)} = \begin{bmatrix} -1/\sqrt{2} \\ -\sqrt{3/2} \\ 0 \end{bmatrix} [84|16] + \begin{bmatrix} \sqrt{2} \\ 0 \\ 0 \end{bmatrix} [14|86]$$

9. Numerical Procedure

Basing on the above presented method, an ALGOL procedure was written and run in a few programmes at GIER computer at the Department of Numerical

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[9] The representation matrices U^4_0 and U^4_1 are taken from [16].

Calculations, Warsaw University. The procedure evaluates the matrix elements for an arbitrary pair of configurations corresponding to a given spin multiplicity.

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