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Some Simplification in Spin-Free Configuration Interaction Studies

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A simplification has been attempted in the procedures for determining the matrix elements of the generators of the unitary group $U(n)$ over a tensor basis spanning the irreducible representation $\langle 2^{N/2-S}, 1^{2S}\rangle$ for an N-electron system. It has been shown that these matrix elements require, for their determination, only the corresponding representation matrices of cyclic permutations of the group S_N. A viable algorithm has been obtained for determining these representation matrices.

Key word: Spin-free configuration interaction.

1. Introduction

In a recent note Sarma and Rettrup [1] (referred to hereafter as I) suggested the use of a tensor basis spanning the irreducible representation (IR) $\langle 2^{N/2-S}, 1^{2S}\rangle$ of $U(n)$ for carrying out CI (Configuration Interaction) studies in molecules. The program based on this suggestion [2] proved to be considerably faster than the methods using spin-projected Slater determinants [2]. Basically the procedure in I involves the realization of the representation matrices for various orbital coordinate permutations $P \in S_N$. Though these permutations were explicitly spelt out, they were rather involved even for the matrix elements of single generators C_{st} of $U(n)$ different configurations. This was particularly true of the matrix element $(\rho'; \phi_{(i_{p+1}|s^2)}|C_{st}|\rho; \phi_{(i_p|sr_s,tr_t)})$ which required the matching permutation $P=(r_2r_3\cdots\tilde{r}_s)(r_1r_2\cdots r_t)$ (cf. Eq. (12) of I). This requirement leads to relatively complicated expressions for the CI matrix elements of the spin-free Hamiltonian listed in the Appendix of I.

It is the purpose of the present note to show that, as in the case of Eqs. (10) and (17) of I, it is possible to consider only a single cyclic permutation in determining

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the matrix element $(\rho'; \phi_{(i_{p+1}|s^2)}|C_{st}|\rho; \phi_{(i_p|sr_s,tr_t)})^{\langle\lambda\rangle}$. A simple programmable procedure will also be outlined to determine the representation matrices for cyclic permutations of S_N using the Young–Yamanouchi basis [4, 5]. The present method is outlined in Sect. 2 and a brief discussion is presented in Sect. 3.

2. Interconfigurational Matrix Elements for the Generators C_{st} of $U(n)$

Consider the set $\{\phi_i \mid i = 1, 2, \ldots, n\}$ of n orthonormal orbitals which form a basis for the fundamental representation of $U(n)$. We form the set of all tensorial products

$$\phi_{(i_p)} = \phi_{i_1}(1)\,\phi_{i_1}(2)\cdots\phi_{i_p}(2p-1)\,\phi_{i_p}(2p)\,\phi_{i_{p+1}}(2p+1)\ldots\phi_{i_{N-p}}(N),$$
$$i_1 < i_2 < \cdots < i_p;\ i_{p+1} < i_{p+2} < \cdots < i_{N-p},$$

p being the number of double occupied orbitals. No two $\phi_{(i_p)}$ and $\phi_{(j_p)}$ $((i_p) \neq (j_p))$ of the set are related to each other through a permutation of S_N. We further specify the occupancy of relevant orbitals, whenever required, by writing $\phi_{(i_p|s^2,r_s,r_s+1;\ldots;\,t,r_t;\ldots)}$ for the tensor product

$$\phi_{i_1}(1)\,\phi_{i_1}(2)\cdots\phi_s(r_s)\,\phi_s(r_s+1)\cdots\phi_{i_p}(2p)\cdots\phi_t(r_t)\cdots\phi_{i_{N-p}}(N).$$

For example, for $n = 8$, $N = 10$, $\phi_{(i_3|4^2,3,4;6,7;8,10)}$ represents

$$\phi_{i_1}(1)\,\phi_{i_1}(2)\,\phi_4(3)\,\phi_4(4)\,\phi_{i_3}(5)\,\phi_{i_3}(6)\,\phi_6(7)\,\phi_{i_8}(8)\,\phi_{i_9}(9)\,\phi_8(10).$$

The set of all non-zero projections $\omega^{\lambda}_{1\rho}\phi_{(i_p)} \equiv |\rho;\ \phi_{(i_p)})$, $\rho = 1, 2, \ldots, f^{\lambda}_N$; all $\phi_{(i_p)}$, then forms a basis for the IR $\langle\lambda\rangle \equiv \langle 2^{N/2-S}, 1^{2S}\rangle$ of $U(n)$ in I. We now consider the effect of the generators $C_{st}(s, t = 1, 2, \ldots, n)$ of $U(n)$ on the configuration $|\rho;\ \phi_{(i_p|s,r_s;t,r_t)})$. Using the arguments of I, we obtain,

$$C_{st}|\rho;\ \phi_{(i_p|sr_s,tr_t)})^{\langle\lambda\rangle} = \sqrt{2}|\rho;\ \phi_{(i_{p+1}|sr_s,sr_t)})^{\langle\lambda\rangle}. \tag{1}$$

We now define a cyclic permutation $P = (r_s + 1, r_s + 2, \ldots, r_t)$ which leads to the result,

$$C_{st}|\rho;\ \phi_{(i_p|sr_s,tr_t)})^{\langle\lambda\rangle} = \sqrt{2}\sum_{\rho'}\Gamma^{\lambda}_{\rho',\rho}(P)|\rho';\ \phi_{(i_{p+1}|s^2,r_s,r_s+1)})^{\langle\lambda\rangle}, \tag{2}$$

where the notation used is the same as in I and,

$$\phi_{(i_{p+1}|s^2,r_s,r_s+1)} = \phi^2_{i_1}\cdots\phi^2_{i_p}\phi_{i_{p+1}}(r_1)\cdots\phi_s(r_s)\phi_s(r_s+1)\cdots\phi_{i_{N-p}}(r_N-2p). \tag{3}$$

The procedure outlined in I requires that the right side of Eq. (2) be further transformed so that we obtain the state $|\rho'';\ \phi_{(i_{p+1}|s^2,r_1,r_2)})^{\langle\lambda\rangle}$ before being matched with $|\rho';\ \phi_{(i_{p+1}|s^2)})^{\langle\lambda\rangle}$. This essentially implies that for this case we need a product of overlapping cyclic permutations $(r_2 r_3 \cdots \bar{r}_s)(r_1 r_2 \cdots r_t)$ for the matching. Determining the representation matrices, $\Gamma^{\lambda}_{\rho',\rho}[(r_2 r_3 \cdots \bar{r}_s)(r_1 r_2 \cdots r_t)]$, of S_N for such permutations is a relatively difficult task involving summation over intermediate states.

However, it was shown in a recent note [6] that a state $|\rho'; \phi_{(i_{p+1}|s^2,r_1,r_2)})^{\langle\lambda\rangle}$ can be readily transformed into a linear combination of the states $|\rho'_{(\pm)}; \phi_{(i_{p+1}|s^2,r_s,r_s+1)})^{\langle\lambda\rangle}$ as,

$$|\rho'; \phi_{(i_{p+1}|s^2,r_1,r_2)})^{\langle\lambda\rangle} = \epsilon_s \left\{ \left(\frac{d^{\rho'_+}_{ss+1} + 1}{2d^{\rho'_+}_{ss+1}} \right)^{1/2} |\rho'_+; \phi_{(i_{p+1}|s^2,r_s,r_s+1)})^{\langle\lambda\rangle} + \left(\frac{d^{\rho'_-}_{ss+1} - 1}{2d^{\rho'_-}_{ss+1}} \right)^{1/2} |\rho'_-; \phi_{(i_{p+1}|s^2,r_s,r_s+1)})^{\langle\lambda\rangle} \right\}, \tag{4}$$

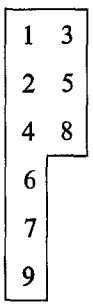
where $\epsilon_s = +1\,(-1)$ if r_s is the orbital coordinate of the odd (even) electron; ρ'_+ (ρ'_-) is the standard tableau obtained from ρ' by decreasing all entries from r_1 to $r_s + 1$ by 2, moving them one row up in the same column and putting r_s ($r_s + 1$) in the second column followed by $r_s + 1$ (r_s) in the first column leaving all entries beyond $r_s + 1$ unchanged; $d^{\rho'_+}_{ss+1}(d^{\rho'_-}_{ss+1})$ is the axial distance between r_s and $r_s + 1$ in ρ'_+ (ρ'_-). As an illustration, consider

$$-\left|\begin{matrix}12\\36;\ \phi_4^2\,\phi_1\phi_2\phi_3\phi_6\\4\\5\end{matrix}\right\rangle^{\langle 2^2,1^2\rangle} = (\tfrac{5}{8})^{1/2}\left|\begin{matrix}15\\26;\ \phi_1\phi_2\phi_3\phi_4^2\,\phi_6\\3\\4\end{matrix}\right\rangle^{\langle 2^2,1^2\rangle} + (\tfrac{3}{8})^{1/2}\left|\begin{matrix}14\\26;\ \phi_1\phi_2\phi_3\phi_4^2\,\phi_6\\3\\5\end{matrix}\right\rangle^{\langle 2^2,1^2\rangle}. \tag{5}$$

This transformation implies that we need only consider the matching permutation of Eq. (2) in determining the matrix element $(\rho'; \phi_{(i_{p+1}|s^2)}|C_{st}|\rho; \phi_{(i_p|sr_s,tr_t)})^{\langle\lambda\rangle}$ where $\lambda = \langle 2^{N/2-S}, 1^{2S}\rangle$. Thus we find that the determination of the matrix elements of C_{st} of $U(n)$ requires simple cyclic permutations only (cf. Eq. (2) and Eqs. (9), (16) of I.

We will now outline a simple programmable method for determining the matrix representation of the IR $\langle 2^{N/2-S}, 1^{2S}\rangle$ for the cyclic permutation $(r_s r_s \pm 1 \cdots r_i \pm 1\ r_t)$. We shall obtain these representation matrices using Young–Yamanouchi basis. The IR $\langle 2^{N/2-S}, 1^{2S}\rangle$ is characterized by standard Young tableaux which have at most two columns. In view of this we will consider an alternative to the Yamanouchi notation [4] which is more convenient for programming on a computer. All entries in the first column of the Young tableau (of length $N/2 + S$) are identified by the box number in which they occur as measured from the top. For each entry in the second column we add $N/2 + S$ to the box number in which it occurs again as measured from the top. If we arrange these box number associations in a row read increasingly in electron entries from left to right we obtain a unique

identification of each standard Young tableau [4] with the corresponding symbol. As an illustration consider the following identification:



$\Leftrightarrow [127384596].$ (6)

The main advantage of the new notation is that axial distances between consecutive entries are readily measurable in this representation. Consider a pair of entries $(k, k+1)$ which are associated with the entries $\bar{k}, \bar{k}'$ in the new notation. Then it is simple to verify that the axial distance is given by

$$d_{k\,k+1} = \begin{cases} -|\bar{k} - \bar{k}'| + N/2 + S + 1, \\ \qquad \text{if } \bar{k}(\bar{k}') > N/2 + S \quad \text{and} \quad \bar{k}'(\bar{k}) \leqslant N/2 + S \\ -1, \quad \text{if both } \bar{k}, \bar{k}' \leqslant N/2 + S \quad \text{or both} \quad \bar{k}, \bar{k}' > N/2 + S. \end{cases} \tag{7}$$

Using the tableau given in Eq. (6) we find, for example, that $d_{8\,9} = -(9-6) + 6 + 1 = 4$, $d_{7\,8} = -4 + 7 = 3$ etc.

Since the row symbol for the standard Young tableau is read as increasing in electron entries from left to right, the location of a pair of consecutive entries and the determination of axial distances becomes trivial. Using the rules for the matrix elements of elementary transpositions between Y–Y bases we

$$(k, k+1)[\cdots \bar{k}\,\bar{k}' \cdots] = \pm \frac{1}{d_{k\,k+1}} [\cdots \bar{k}\,\bar{k}' \cdots] + \frac{(d_{k\,k+1}^2 - 1)^{1/2}}{d_{k\,k+1}} [\cdots \bar{k}'\,\bar{k} \cdots] \tag{8}$$

if $\bar{k}$ (or $\bar{k}'$) $\leqslant N/2 + S$ and $\bar{k}'$ (or $\bar{k}$) $> N/2 + S$, and

$$(k, k+1)[\cdots \bar{k}\,\bar{k}' \cdots] = -[\cdots \bar{k}\,\bar{k}' \cdots] \tag{9}$$

if both $\bar{k}$ and $\bar{k}' \leqslant N/2 + S$ or $> N/2 + S$. In Eq. (8), $d_{k\,k+1}$ is as defined by Eq. (7) and $+$ $(-)$ sign is to be used if $\bar{k} < \bar{k}'$ $(\bar{k} > \bar{k}')$.

We now use Eqs. (7), (8) and (9) to determine the matrix elements of the cyclic permutation $(r_s, r_s + 1, \ldots, r_t - 1, r_t)$. Expressing this permutation as $(r_s, r_s + 1)$ $(r_s + 1, r_s + 2) \cdots (r_t - 1, r_t)$ we consider its effect on the basis state $[\cdots \bar{t}'\,\bar{t} \cdots]$, where $\bar{t}'$ and $\bar{t}$ are the entries corresponding to $r_t - 1$ and r_t respectively. Since the cyclic permutation does not affect the entries corresponding to $r_q < r_s$ or $> r_t$, it is obvious that

$$\langle [\cdots \bar{s}_1\,\bar{s}_1' \cdots \bar{t}_1'\,\bar{t}_1 \cdots] | (r_s, r_s + 1, \ldots, r_t - 1, r_t) | [\cdots \bar{s}\,\bar{s}' \cdots \bar{t}'\,\bar{t} \cdots] \rangle^{\langle \Lambda \rangle} = 0$$

unless all entries corresponding to $r_q < r_s$ or $> r_t$ match in the initial and final tableau-states. For the non-zero case, omitting entries beyond those corresponding to r_m, we have

$$\langle[\cdots \bar{\imath}'_1\ \bar{\imath}_1]|(r_s, r_s+1, \ldots, r_t-1)(r_t-1, r_t)|[\cdots \bar{\imath}'\ \bar{\imath}]\rangle^{\langle\lambda\rangle}$$

$$= \begin{cases} -\delta_{\bar{\imath}\bar{\imath}_1}\langle[\cdots \bar{\imath}'_1]|(r_s, r_s+1, \ldots, r_t-1)|[\cdots \bar{\imath}']\rangle^{\langle\lambda\rangle}, \\ \text{if } \bar{\imath}', \bar{\imath} > N/2+S \quad \text{or} \quad \bar{\imath}', \bar{\imath} \leqslant N/2+S \\ \pm \dfrac{\delta_{\bar{\imath}\bar{\imath}_1}}{d_{r_t-1r_t}}\langle[\cdots \bar{\imath}'_1]|(r_s, r_s+1, \ldots, r_t-1)|[\cdots \bar{\imath}']\rangle^{\langle\lambda\rangle} \\ + \delta_{\bar{\imath},\bar{\imath}'_1}\dfrac{(d^2_{r_t-1r_t}-1)}{d_{r_t-1r_t}}\langle[\cdots \bar{\imath}'_1]|(r_s, r_s+1, \ldots, r_t-1)|[\cdots \bar{\imath}]\rangle^{\langle\lambda\rangle} \\ \text{if } \bar{\imath}(\bar{\imath}') \leqslant N/2+S \quad \text{and} \quad \bar{\imath}'(\bar{\imath}) > N/2+S. \end{cases} \tag{10}$$

Thus the non-zero matrix elements result from contributions from two possible choices for every elementary transposition in the cyclic permutation. For the transposition $(r_p - 1, r_p)$ the choice to be made is clear from an inspection of r_pth entry in the final state symbol. Since the residual cyclic permutation does not involve r_p we can omit this entry from the symbol and proceed to the next transposition. As an illustration consider the matrix element,

$$\langle[172384569]|(123456789)|[123748569]\rangle^{\langle 2^3,1^3\rangle}.$$

Here $N/2 + S + 1 = 7$ and we can successively use Eqs. (7) and (10) to obtain,

$$\begin{aligned} &\langle[172384569]|(12345678)(89)|[123748569]\rangle \\ &\quad = \tfrac{1}{4}\langle[17238456]|(1234567)(78)|[12374856]\rangle \\ &\quad = -\tfrac{1}{4}\langle[1723845]|(123456)(67)|[1237485]\rangle \\ &\quad = \tfrac{1}{16}\langle[172384]|(12345)(56)|[123748]\rangle \\ &\quad = \frac{1}{16}\times\frac{2\sqrt{2}}{3}\langle[17238]|(1234)(45)|[12378]\rangle \\ &\quad = \frac{1}{12\sqrt{2}}(-1)\langle[1723]|(123)(34)|[1237]\rangle \\ &\quad = -\frac{1}{12\sqrt{2}}\times\frac{2\sqrt{2}}{3}\langle[172]|(12)(23)|[127]\rangle \\ &\quad = -\frac{1}{18}\times\frac{\sqrt{3}}{2}\langle[17]|(12)|[17]\rangle \\ &\quad = -\frac{\sqrt{3}}{36}, \end{aligned} \tag{11}$$

where, at each stage, the matched entries not affected by the residual fragment of the cycle have been omitted for notational convenience.

3. Discussion

We have demonstrated that the matrix elements of generators C_{st} of $U(n)$ require only cyclic permutations for their determination. This is a considerable simplification over the procedure presented in I. We have further shown that the Young–Yamanouchi representation matrices for cyclic permutation can be directly determined without recourse to Rumer basis as was done in I. This leads to a considerable reduction of storage requirements and permits the scope of CI calculations to be enlarged to include more open shells. The notation of Eq. (6) is extremely useful for programming for the matrix elements of cyclic permutations.

The combined use of unitary and permutation group approaches, in which the projected Young basis (PYB)[1, 2, 6] is used to realize the basis states of IR $\langle 2^{N/2-S}, 1^{2S}\rangle$ of $U(n)$, therefore reduces the problem of evaluation of the matrix elements of generators of $U(n)$ to that of determining single open-shell cyclic permutation matrix elements. Similar conclusions have been reached by Ruttink [7] in recent publications. He realizes the basis states of $U(n)$ by application of creation operators on the vacuum state. The cyclic permutation matrix elements are evaluated by him by comparison of spin diagrams (spin coupling schemes for open-shell orbitals). Our approach, however, is spin-free and the basis states $|\rho; \phi_{(i_\rho)}\rangle$ are realized by use of the Wigner operators for S_N.

Paldus [8] and Shavitt [9] have given methods of evaluating the generator matrix elements through a graphical procedure (Graphical Unitary Group Approach, GUGA). In their procedure, the contributions of an integral (or a block of integrals) are given by certain loops on the graphs. This procedure is useful for full CI calculations. However the GUGA procedure is inefficient for carrying out limited CI calculations [9]. No such limitation exists for our procedure. Another advantage of the present approach is that it can be very easily extended to the case of non-orthogonal orbitals. Once the overlap matrix is evaluated, a slight modification of the computer program developed in I will give the matrix elements of the Hamiltonian between non-orthogonal configurations [10].

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