Application of the $U(3)$ Symmetric Matrices Algebra to Molecular Problems

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The application of some properties of the $U(3)$ basis algebra to the calculation of the SC π bond matrix order is shown, for certain states of 6-electron molecular systems possessing a twofold symmetry axis not passing through any π center. Pyridazine is used as a numerical example.

Key words: Bond order – $U(3)$ algebra – π excited states

1. Introduction

We are interested in applying more general algebras to molecular calculations. We have already employed the $U(2)$ algebra to 4-electron cases [1]; we shall now use the $U(3)$ algebra for 6-electron molecules, in order to calculate the π bond order matrix P for certain states. These obey $n_l + n_h = I$ [2], where n_l is a diagonal matrix with half the occupation numbers of the lowest energy levels, n_h a diagonal matrix with half the occupation numbers of the associated highest energy levels, and I the unit matrix. The even π system must possess a binary symmetry axis not passing through any π center. The SC bond orders are obtained without calculating the MO's. The basis functions split into two groups, one symmetric and the other antisymmetric with respect to the axis. The variational principle is thus applied separately for each of the two groups. Electron interaction is considered through a compromise Hamiltonian [1] between the ground state and the excited states considered, on the same footing [3].

Recently, the Clebsch–Gordan coefficients have been utilized for setting up symmetry-adapted linear combinations of atomic orbitals [4], revealing an increasing interest in this kind of problems.

For the moment, the consequences of these applications are not easy to predict. In the meantime, let us quote Feynman's opinion: "...The formulation is mathematically equivalent to the more usual formulations. There are, therefore, no

fundamentally new results. However, there is a pleasure in recognizing old things from a new point of view." [5]

2. Formalism

The splitting of the basis functions leads to the two matrix equations [1]:

$$JP^+ = \text{symmetric}; \quad KP^- = \text{symmetric} \tag{1}$$

where

$$J_{\mu\nu} = H_{\mu\nu} + H_{\mu,N+1-\nu}; \quad K_{\mu\nu} = H_{\mu\nu} - H_{\mu,N+1-\nu}; \quad P_{\mu\nu}^\pm = \sum_{i\pm} n_\mu^{i\pm} \chi_\mu^i \pm \chi_\nu^{i\pm}. \tag{2}$$

H is the effective Hamiltonian, there are N electrons, χ_μ^i is the coefficient of atomic orbital μ whose occupation number is $(2n^i)$, and the $+$ or $-$ signs label respectively the symmetric or antisymmetric levels.

Bond orders are determined through Q matrices defined by $Q^\pm = 2P^\pm - I$. These are $N/2$-dimensional, for $P_{\mu\nu} = P_{\mu\nu}^+ + P_{\mu\nu}^-$ and $P_{\mu,N+1-\nu} = P_{\mu\nu}^+ - P_{\mu\nu}^-$ ($\mu, \nu = 1 \cdots N/2$), and satisfy

$$JQ^+ = \text{symmetric}; \quad KQ^- = \text{symmetric} \tag{3}$$

$$(Q^+)^3 = Q^+; \quad (Q^-)^3 = Q^-. \tag{4}$$

With electronic interaction, Eqs. (3) take the form [1]:

$$[2J + (C^+I) + (C^-I) + (C^+Q^+) + (C^-Q^-)]Q^+ = \text{symmetric}$$
$$[2K + (C^-I) + (C^+I) + (C^-Q^+) + (C^+Q^-)]Q^- = \text{symmetric}. \tag{5}$$

The basic matrices of the $U(3)$ group, through which any 3×3 real symmetric matrix may be expressed, are the unit matrix and [6]:

$$F_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}; \quad F_2 = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}; \quad F_3 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix};$$

$$\tag{6}$$

$$F_4 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}; \quad F_5 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

We shall follow the Einstein convention in our formulae, avoiding the summation sign. The F matrices satisfy the anticommutation relations

$$\{F_i, F_j\} = d_{ijk}F_k + \tfrac{4}{3}\delta_{ij} \tag{7}$$

where d_{ijk} are totally symmetric coefficients, with values

$$d_{112} = 2/\sqrt{3}; \quad d_{144} = 1; \quad d_{155} = -1; \quad d_{345} = 1; \quad d_{222} = -2/\sqrt{3}$$

$$d_{233} = 2/\sqrt{3}; \quad d_{244} = -1/\sqrt{3}; \quad d_{255} = -1/\sqrt{3} \tag{8}$$

Aside from those obtained by symmetry, these are the only non-zero coefficients. Let us now define

$$d_{ij} = d_{ijk}q_k; \qquad d_i = d_{ij}q_j; \qquad d = d_iq_i; \qquad q^2 = q_iq_i. \tag{9}$$

It is verified identically that

$$d_{ij}d_j = \tfrac{4}{3}q^2q_i \tag{10}$$

and

$$d_id_jd_{ijk} = \tfrac{8}{3}dq_k - \tfrac{4}{3}q^2d_k. \tag{11}$$

Let us now write our $\boldsymbol{Q}^{\pm}$ matrices (we shall write just $\boldsymbol{Q}$ for shortness) under the form

$$\boldsymbol{Q} = q_0 + q_i\boldsymbol{F}_i = q_0 + \boldsymbol{q}\cdot\boldsymbol{F}. \tag{12}$$

In this case

$$\Delta = \det(\boldsymbol{Q}) = q_0^3 - q_0q^2 + \tfrac{1}{3}d. \tag{13}$$

It is easily verified that

$$(\boldsymbol{q}\cdot\boldsymbol{F})^2 = q_iF_iq_jF_j = \tfrac{1}{2}q_iq_j\{F_i, F_j\} = \tfrac{1}{2}q_iq_j(d_{ijk}F_k + \tfrac{4}{3}\delta_{ij})$$
$$= \tfrac{2}{3}q^2 + \tfrac{1}{2}d_iF_i \tag{14}$$

and $(\boldsymbol{q}\cdot\boldsymbol{F})^3 = (\boldsymbol{q}\cdot\boldsymbol{F})^2\boldsymbol{q}\cdot\boldsymbol{F} = \tfrac{2}{3}q^2\boldsymbol{q}\cdot\boldsymbol{F} + \tfrac{1}{2}\boldsymbol{d}\cdot\boldsymbol{F}\boldsymbol{q}\cdot\boldsymbol{F} = \tfrac{2}{3}q^2\boldsymbol{q}\cdot\boldsymbol{F} + \tfrac{1}{4}d_iq_j\{F_i, F_j\} = \tfrac{2}{3}q^2\boldsymbol{q}\cdot\boldsymbol{F} + \tfrac{1}{4}d_iq_j(d_{ijk}F_k + \tfrac{4}{3}\delta_{ij}) = \tfrac{2}{3}q^2\boldsymbol{q}\cdot\boldsymbol{F} + \tfrac{1}{4}d_id_{ij}F_j + \tfrac{1}{3}d$ and by (10)

$$(\boldsymbol{q}\cdot\boldsymbol{F})^3 = \tfrac{1}{3}d + (\tfrac{2}{3}q^2 + \tfrac{1}{3}q^2)\boldsymbol{q}\cdot\boldsymbol{F} = \tfrac{1}{3}d + q^2\boldsymbol{q}\cdot\boldsymbol{F} \tag{15}$$

so that

$$\boldsymbol{Q}^3 = (q_0 + \boldsymbol{q}\cdot\boldsymbol{F})^3 = q_0^3 + 3q_0^2\boldsymbol{q}\cdot\boldsymbol{F} + 3q_0(\boldsymbol{q}\cdot\boldsymbol{F})^2 + (\boldsymbol{q}\cdot\boldsymbol{F})^3$$
$$= q_0^3 + 3q_0^2\boldsymbol{q}\cdot\boldsymbol{F} + 3q_0(\tfrac{2}{3}q^2 + \tfrac{1}{2}\boldsymbol{d}\cdot\boldsymbol{F}) + \tfrac{1}{3}d + q^2\boldsymbol{q}\cdot\boldsymbol{F} \tag{16}$$

and if $\boldsymbol{Q}^3 = \boldsymbol{Q}$, the coefficients in (16) must be equal to those of (12), which leads to

$$q_0 = q_0^3 + 2q_0q^2 + \tfrac{1}{3}d; \qquad q_i = 3q_0^2q_i + \tfrac{3}{2}q_0d_i + q^2q_i. \tag{17}$$

We have, therefore, the two equations

$$d = 3q_0(1 - q_0^2 - 2q^2), \tag{18}$$

$$q_0d_i = \tfrac{2}{3}(1 - 3q_0^2 - q^2)q_i. \tag{19}$$

We are faced with three cases:

I – The trivial solutions [7] are $q_i = 0$, $q_0 = 0$, ± 1($\boldsymbol{Q} = 0$, $\pm\boldsymbol{I}$)

II – If $q_0 = 0$, it must be $\boxed{d = 0}$ and $\boxed{q^2 = 1}$ (it turns out that $\Delta = 0$) (20)

III – If $q_0 \neq 0$, by (19) we may write $d_i = Aq_i$ (21)

It is clear that, by (10), if we multiply (21) by d_{ij}, we obtain

$$\tfrac{4}{3}q^2q_j = Ad_j = AAq_j = A^2q_j \qquad A^2 = \tfrac{4}{3}q^2. \tag{22}$$

In order for (21) to satisfy (18) and (19), the following equations must hold:

$$Aq^2 = 3q_0(1 - q_0^2 - 2q^2),\tag{23}$$

$$Aq_0 = \tfrac{2}{3}(1 - 3q_0^2 - q^2).\tag{24}$$

From (24) we obtain

$$q_0 = -\frac{A}{4} \pm \sqrt{\tfrac{1}{3} - \tfrac{1}{4}q^2}.$$

Replacing in (23) and simplifying, the possible solutions are:

$$q^2 = \begin{cases} \tfrac{1}{3}; & A^2 = \tfrac{4}{9}(A = \pm\tfrac{2}{3}); & q_0 = -\dfrac{A}{4} \pm \dfrac{1}{2} \begin{cases} A = \tfrac{2}{3} \to q_0 = \tfrac{1}{3} & \text{or} \quad -\tfrac{2}{3} \\ A = -\tfrac{2}{3} \to q_0 = -\tfrac{1}{3} & \text{or} \quad +\tfrac{2}{3} \end{cases} \\[4mm] \tfrac{4}{3}; & A^2 = \tfrac{16}{9}; & A = \pm\tfrac{4}{3}; \qquad q_0 = -\dfrac{A}{4} \begin{cases} A = 4/3 \to q_0 = -1/3 \\ A = -4/3 \to q_0 = +1/3 \end{cases} \end{cases} \tag{25}$$

Equation (21) takes the form

$$\boxed{d_i = \tfrac{2}{3}q_i; \qquad q^2 = \tfrac{1}{3}} \qquad q_0 = \tfrac{1}{3}; \qquad -\tfrac{2}{3}(\Delta = 0) \tag{26}$$

or $d_i = -\tfrac{2}{3}q_i$ and the former solution changed in sign or also:

$$\boxed{d_i = \tfrac{4}{3}q_i; \qquad q^2 = \tfrac{4}{3}} \; ; \qquad q_0 = -\tfrac{1}{3}(\Delta = 1) \tag{27}$$

obtained putting $q_i = 2q_i'$.

We also have

$$\boxed{d_i = -\tfrac{4}{3}q_i; \qquad q^2 = \tfrac{4}{3}},$$

which is the last one with q_i changing sign, and having $\Delta = -1$.

Due to the identities in the d_{ijk} coefficients, these equations do not determine q_i, aside from Case I, which is known "*a priori*". Physically, this is due to the fact that we have not yet introduced the system's Hamiltonian. This is what we do next, leading to the missing mathematical conditions.

We shall write all the equations for J, considering that there will be exactly similar equations for K. The matrix J being symmetric, it may be written in the form

$$J = j_0 + j_i F_i.\tag{28}$$

In order to find the numbers j_0, j_i, we shall use the following properties

$$\text{Tr}\,(F_i) = 0; \qquad \text{Tr}\,(F_iF_j) = \tfrac{1}{2}\text{Tr}\,(\{F_i, F_j\}) = \tfrac{1}{2}\text{Tr}\,(d_{ijk}F_k + \tfrac{4}{3}\delta_{ij})$$

$$= \tfrac{1}{2}\cdot\tfrac{4}{3}\delta_{ij}\,\text{Tr}\,(I) = 2\delta_{ij}.\tag{29}$$

Therefore

$$j_0 = \tfrac{1}{3}\text{Tr}\,(J); \qquad j_i = \tfrac{1}{2}\text{Tr}\,(F_i J).\tag{30}$$

As $[\overline{Q}, J] = 0[1]$, $[q \cdot F, j \cdot F] = 0$. This in general implies that $q \cdot F$ is a function of $j \cdot F$

$$q \cdot F = \sum_{n=0}^{\infty} a_n (j \cdot F)^n. \tag{31}$$

We shall now define $D_{ij} = d_{ijk} j_k$, $D_i = D_{il} j_l$; $D = D_i j_i$. In $(j \cdot F)^n$, for $n = 1$ F_i appears with j_i; for $n = 2$ (see (14) with j instead of q) F_i is associated to D_i; for $n = 3$ (see (15)) F_i appears again with j_i, etc. Hence, in the summation of (31), F_i appears only associated to j_i or to D_i. We may then write $q \cdot F = \lambda_1 j \cdot F + \lambda_2 D \cdot F$, or

$$q_i = \lambda_1 j_i + \lambda_2 D_i, \tag{32}$$

λ_1, λ_2 being functions of j. Therefore,

$$d_{ij} = d_{ijk} q_k = d_{ijk} (\lambda_1 j_k + \lambda_2 D_k) = \lambda_1 D_{ij} + \lambda_2 d_{ijk} D_k,$$

$$d_i = d_{il} q_l = (\lambda_1 D_{il} + \lambda_2 d_{ilk} D_k)(\lambda_1 j_i + \lambda_2 D_i)$$

$$= \lambda_1^2 D_{il} j_l + 2\lambda_1 \lambda_2 D_{il} D_l + \lambda_2^2 d_{ilk} D_l D_k,$$

$$d_i = \lambda_1^2 D_i + 2\lambda_1 \lambda_2 \tfrac{4}{3} j^2 j_i + \lambda_2^2 (\tfrac{8}{3} D j_i - \tfrac{4}{3} j^2 D_i),$$

using (10) and (11) with j instead of q

$$d_i = (\lambda_1^2 - \tfrac{4}{3} j^2 \lambda_2^2) D_i + \tfrac{8}{3} (\lambda_1 \lambda_2 j^2 + D\lambda_2^2) j_i. \tag{33}$$

Finally, $d = d_i q_i = d_i (\lambda_1 j_i + \lambda_2 D_i)$, therefore,

$$d = (\lambda_1^2 - \tfrac{4}{3} j^2 \lambda_2^2)(\lambda_1 D + \lambda_2 D \cdot D) + \tfrac{8}{3}(\lambda_1 \lambda_2 j^2 + D\lambda_2^2)(\lambda_1 j^2 + \lambda_2 D). \tag{34}$$

Besides

$$q^2 = (\lambda_1 j_i + \lambda_2 D_i)(\lambda_1 j_i + \lambda_2 D_i) = \lambda_1^2 j^2 + 2\lambda_1 \lambda_2 D + \lambda_2^2 D \cdot D. \tag{35}$$

In (33), (34) and (35), λ_1 and λ_2 are unknown, but the coefficients are functions of j, all easily calculated through the corresponding definitions. Let us remark that, by (10), $D \cdot D = D_i D_i = \tfrac{4}{3}(j^2)^2$.

3. Solving the Equations

I. The three trivial solutions always exist, and are independent from the Hamiltonian [7].

II. The equation $d = 0$ (Eq. (34)) is a homogeneous, cubic equation in λ_1, λ_2, with known coefficients. It may hence only determine the quotient $r_a = \lambda_1^{(a)}/\lambda_2^{(a)}$ ($a = 1, 2, 3$), r_a being the three solutions of the cubic equation (34). For each solution r_a, the substitution $\lambda_1^{(a)} = r_a \lambda_2^{(a)}$ in (35) equalized to one, gives a simple quadratic equation with two values for λ_2, $\pm \lambda_2^{(a)}$. Therefore, $\lambda_1 = \pm r_a \lambda_2^{(a)}$. These are then six solutions.

III. The equation $d_i = \tfrac{2}{3} q_i$ is solved through (32) and (33)

$$\tfrac{2}{3}\lambda_1 = \tfrac{8}{3}(\lambda_1 \lambda_2 j^2 + \lambda_2^2 D), \tag{36}$$

$$\tfrac{2}{3}\lambda_2 = \lambda_1^2 - \tfrac{4}{3}\lambda_2^2 j^2. \tag{37}$$

From (36) we get:

$$\lambda_1 = \frac{4D\lambda_2^2}{1 - 4j^2\lambda_2}. \tag{38}$$

Replacing (38) in (37), a cubic equation with known coefficients in λ_2 is obtained. The three corresponding solutions introduced in (38), together with $q = \frac{1}{3}$ or $-\frac{2}{3}$, and Eq. (32), give six solutions. Changing signs in λ_1, λ_2 and q_0, we get six more solutions.

III′. If in the first three λ_1, λ_2 of III we make the substitution $\lambda_{1,2} \rightarrow 2\lambda_{1,2}$, a q_i is obtained which corresponds to $d_i = \frac{4}{3}q_i$. This must be associated with $q_0 = -\frac{1}{3}$ (three solutions). Changing the signs of q_i and q_0 gives additional three solutions. Both in III and III′ all solutions are automatically normalized, to $q^2 = \frac{1}{2}$(III) and $q^2 = \frac{4}{3}$ (III′).

We have altogether 27 solutions. Actually, in general there will be 27 for Q^+ and 27 for Q^- (or for P^+ and P^-). As explained in [1], the coupling is limited within the same case.

In the 6-electron case, a direct solution of the SC bond orders is no more possible when electron interaction is introduced through the compromise Hamiltonian [1]. But we may iterate using the Q matrices, not needing the calculation of MO's.

A further condition must be introduced, however, so as to preserve the *non-crossing rule* between levels belonging to the same symmetry. Those of different symmetry, of course, are completely free to mix in any way. As we do not calculate the MO's, we must ensure that on iterating we choose, among the cubic equations solutions, those which reproduce the same case. This is not hard to fix, keeping in mind that $n^{i\pm}$ are the eigenvalues of $P^\pm$.

We know, from (14) applied to j, that

$$D \cdot F = 2(j \cdot F)^2 - \tfrac{4}{3}j^2 \tag{39}$$

and as $(j \cdot F)^2 = (J - j_0)(J - j_0)$ and $q \cdot F = Q - q_0$, $q \cdot F = \lambda_1 j \cdot F + \lambda_2 D \cdot F$ becomes:

$$Q - q_0 = \lambda_1(J - j_0) + 2\lambda_2(J^2 - 2j_0 J + j_0^2) - \tfrac{4}{3}\lambda_2 j^2. \tag{40}$$

Bearing in mind that $p_0^\pm = \frac{1}{6}\mathrm{Tr}\, P^+ = N^+/6$, applying this operator to x^{i+} gives

$$2P^+ - I - 2p_0^+ + 1]x^{i+} = \{(\lambda_1 - 4j_0\lambda_2)J + 2\lambda_2 J^2 + 2\lambda_2(j_0^2 - \tfrac{2}{3}j^2) - \lambda_1 j_0\}x^{i+}$$

$$\left[2n^{i+} - 1 - \frac{N^+}{3} + 1\right]x^{i+} = \{(\lambda_1 - 4j_0\lambda_2)E^{i+} + 2\lambda_2(E^{i+})^2$$
$$+ 2\lambda_2(j_0^2 - \tfrac{2}{3}j^2) - \lambda_1 j_0\}x^{i+}$$

$$2n^{i+} - \frac{N^+}{3} = (\lambda_1 - 4j_0\lambda_2)E^{i+} + 2\lambda_2(E^{i+})^2 + 2\lambda_2(j_0^2 - \tfrac{2}{3}j^2) - \lambda_1 j_0 \tag{41}$$

E^{i+} being the eigenvalues of J.

The iteration is carried out in the following way:

1) The solutions without interaction are first found as starting points. This is straightforward.

2) The equations are set again, replacing *J* and *K* by the expressions between square brackets of (5), and working with them in the same way as before. Of the possible solutions arising from the cubic equations in each case, and the alternatives in the λ's signs, only one will verify Eqs. (41) or their analogues for the antisymmetric basis. This is not difficult to program.

The serious trouble in some of these superexcited states (superexcited meaning excitations usually greater than the first ionization potential [8]) is the well-known convergence problem. This deserves much more attention, and we deal with it elsewhere [9]. As far as it concerns this paper, we shall just mention that we overcome it by introducing a convergence parameter ξ in the compromise Hamiltonian:

$$H_{\mu\nu} = H_{\mu\nu}^0 + \xi P_{\mu\nu} C_{\mu\nu}. \tag{42}$$

This seems a neater approach than the damping procedures or energy-shift methods which appear in the literature for somewhat limited applications [9–11].

4. Example

We apply the above formalism to the pyridazine molecule, with the atom labelling of Fig. 1. The Hückel starting parameters are

$$\alpha_C = 0; \quad \beta_{CC} = 1; \quad \alpha_N = 1.5; \quad \beta_{CN} = 1.1; \quad \beta_{NN} = 1.2$$

which (see Table 1) give in the ground state a π contribution of 1.69D to the dipole moment, in agreement with the 1.79D value obtained by Pukanic *et al.* [12] with a modified PPP treatment. The Coulomb integrals between μ and ν atoms appearing in $C_{\mu\nu}$ are picked from the Pariser–Parr table [13]. For shortness, instead of using spectroscopic notation, we shall refer to the symmetric eigenvalues as S_1, S_2, S_3 and to the antisymmetric ones as A_1, A_2, A_3.

We are dealing with the open-shell cases in the same way as the closed-shell ones, that is we are using the half-electron approximation [14, 15]. For the moment, our goal is simply the obtention of SC bond orders avoiding the MO calculation, but we shall return in detail elsewhere to this problem [9].

The table shows the SC $P_{\mu\nu}$ results for neighboring atoms (those for non-neighboring atoms are available under request), and the ξ parameter.
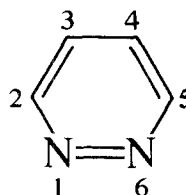

Fig. 1

Table 1. SC bond orders $P_{\mu\nu}$ between atoms μ and ν for the 27 solutions of pyridazine, following the atom labelling of Fig. 1. Bond orders are shown only for neighboring atoms. ξ is the convergence parameter

State	P_{11}	P_{22}	P_{33}	P_{12}	P_{23}	P_{34}	P_{16}	ξ
Case I. Particular solutions								
$(S_1)^2(S_2)^2(S_3)^2$	1	1	1	0	0	1	1	
$S_1 A_1 S_2 A_2 S_3 A_3$	1	1	1	0	0	0	0	
$(A_1)^2(A_2)^2(A_3)^2$	1	1	1	0	0	-1	-1	
Case II. $N^+ = N^-$								
$(S_1)^2(A_1)^2 S_2 A_2$	1.138	0.936	0.925	0.732	0.597	0.035	0.261	1
$S_1(A_1)^2(S_2)^2 A_3$	0.970	0.939	1.091	0.405	0.350	0.354	0.115	0.8
$(S_1)^2 A_1(A_2)^2 S_3$	1.191	0.921	0.888	0.470	0.110	-0.522	0.222	0.8
$A_1(S_2)^2 S_3(A_3)^2$	0.720	1.114	1.166	-0.441	-0.122	0.505	-0.215	-0.8
$S_1(A_2)^2(S_3)^2 A_3$	0.977	1.099	0.924	-0.428	-0.341	-0.317	-0.048	-1
$S_2 A_2(S_3)^2(A_3)^2$	0.774	1.104	1.122	-0.724	-0.592	-0.043	-0.255	-1
Case III. $N^+ \neq N^-$								
$(S_1)^2(S_2)^2 A_1 S_3$	1.065	0.961	0.974	0.325	0.316	0.856	0.839	1
$(S_1)^2 S_2 A_1 A_2 S_3$	1.131	0.947	0.922	0.383	0.238	0.189	0.507	1
$(S_1)^2 S_2(S_3)^2 A_2$	1.143	0.972	0.885	0.040	-0.100	0.333	0.696	0.8
$S_1(A_1)^2 S_2 A_2 A_3$	1.082	0.955	0.963	0.350	0.323	-0.169	-0.209	1
$S_1(S_2)^2 A_1 S_3 A_3$	0.804	0.964	1.232	0.127	0.085	0.413	0.278	1
$(A_1)^2 S_1(A_2)^2 A_3$	1.124	0.948	0.928	0.381	0.290	-0.782	-0.606	1
$S_1(S_2)^2 A_3(S_3)^2$	0.800	1.085	1.115	-0.365	-0.280	0.783	0.589	-1
$S_1 A_1 S_3(A_2)^2 A_3$	1.156	1.072	0.772	-0.137	-0.084	-0.392	-0.220	-1
$S_1 S_2 A_2(A_3)^2 S_3$	0.862	1.078	1.060	-0.353	-0.309	0.162	0.239	-1
$S_2(A_1)^2 A_2(A_3)^2$	0.806	1.031	1.163	0.000	0.081	-0.347	-0.700	-0.8
$S_2 A_1 A_2 S_3(A_3)^2$	0.789	1.085	1.126	-0.360	-0.241	-0.203	-0.500	-1
$A_1 S_3(A_2)^2(A_3)^2$	0.889	1.068	1.043	-0.333	-0.303	-0.861	-0.811	-1
Case III'. $N^+ \neq N^-$ and $n_i = 1$ or 0								
$(S_1)^2(S_2)^2(A_1)^2$	1.103	0.943	0.954	0.674	0.647	0.685	0.649	1
$(S_1)^2(A_1)^2(A_2)^2$	1.154	0.928	0.918	0.825	0.491	-0.674	-0.070	1
$(S_1)^2(A_2)^2(S_3)^2$	1.301	0.944	0.755	0.044	-0.158	-0.284	0.355	0.4
$(S_2)^2(A_1)^2(A_3)^2$	0.655	1.058	1.287	-0.005	0.147	0.280	-0.379	-0.4
$(S_2)^2(S_3)^2(A_3)^2$	0.749	1.117	1.134	-0.807	-0.494	0.663	0.072	-1
$(A_2)^2(S_3)^2(A_3)^2$	0.829	1.096	1.075	-0.684	-0.630	-0.694	-0.616	-1

Case I does not depend on the ξ value [7]; the three solutions correspond respectively to: $N^+ = N$, $N^- = 0$; every $n_i = \frac{1}{2}$ (Hall's standard reference state [16]); $N^- = N$, $N^+ = 0$.

Case II implies $N^+ = N^-$, that is $n^i = 1$, $\frac{1}{2}$ or 0.

In Case III, $N^+ \neq N^-$. The half-occupational numbers n^i may be 1, $\frac{1}{2}$ or 0, being limited to 1 and 0 for Case III'.

In short, the application of general group algebra permits a different approach to the problem of the direct calculation of the SC π bond order matrix.

Finally, let us remark that when passing from the 4-electron to the 6-electron case, the condition $n_l + n_h = I$ makes the 9 solutions become 27 solutions. The $U(4)$

development leads to $3^{N/2} = 3^4 = 81$ solutions. A two π electron system has thus as unique solutions the three particular ones.

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