

APPLICATION OF THE U(3) SYMMETRIC MATRICES ALGEBRA TO
MOLECULAR PROBLEMS

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The application of 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 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) one, in 6-electron molecules, in order to calculate the π bond order matrix P for certain states. These obey $n_\ell + n_h = I$ [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 both 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]:

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

where

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

H being 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 as $Q^{\pm} = 2P^{\pm} - I$. These are N/2-dimensional, for $P_{\mu\nu} = P_{\mu\nu}^+ - P_{\mu\nu}^-$ and $P_{\mu, N+1-\nu} = P_{\mu\nu}^+ + P_{\mu\nu}^-$ ($\mu, \nu = 1 \dots N/2$), and satisfy

$$JQ^+ = \text{sym.} \quad KQ^- = \text{sym.} \quad (3)$$

$$(Q^+)^3 = Q^+ \quad (Q^-)^3 = Q^- \quad (4)$$

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

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

$$[2K + (C^-I) + (C^+I) + (C^-Q^+) + (C^+Q^-)]Q^- = \text{sym.}$$

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]:

$$F_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}; F_2 = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}; F_3 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}; F_4 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}; F_5 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \quad (6)$$

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

$$\{F_i, F_j\} = d_{ijk} F_k + \frac{4}{3} \delta_{ij} \quad (7)$$

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

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

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

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

Let us now define

$$d_{ij} = d_{ijk} q_k ; d_i = d_{ij} q_j ; d = d_i q_i ; q^2 = q_i q_i \quad (9)$$

It is verified identically that

$$d_{ij} d_j = \frac{4}{3} q^2 q_i \quad (10)$$

and

$$d_i d_j d_{ijk} = \frac{8}{3} d q_k - \frac{4}{3} q^2 d_k \quad (11)$$

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

$$Q = q_0 + q_i F_i = q_0 + q \cdot F \quad (12)$$

In this case $\Delta = \det(Q) = q_0^3 - q_0 q^2 + \frac{1}{3} d$ (13)

It is easily verified that

$$\begin{aligned} (q \cdot F)^2 &= q_i F_i q_j F_j = \frac{1}{2} q_i q_j \{F_i, F_j\} = \frac{1}{2} q_i q_j (d_{ijk} F_k + \frac{4}{3} \delta_{ij}) = \\ &= \frac{2}{3} q^2 + \frac{1}{2} d_i F_i \end{aligned} \quad (14)$$

$$\begin{aligned} \text{and } (q \cdot F)^3 &= (q \cdot F)^2 q \cdot F = \frac{2}{3} q^2 q \cdot F + \frac{1}{2} d \cdot F q \cdot F = \frac{2}{3} q^2 q \cdot F + \\ &+ \frac{1}{4} d_i q_j \{F_i, F_j\} = \frac{2}{3} q^2 q \cdot F + \frac{1}{4} d_i q_j (d_{ijk} F_k + \frac{4}{3} \delta_{ij}) = \\ &= \frac{2}{3} q^2 q \cdot F + \frac{1}{4} d_i d_{ij} F_j + \frac{1}{3} d \end{aligned}$$

and by (10)

$$(q \cdot F)^3 = \frac{1}{3} d + \left(\frac{2}{3} q^2 + \frac{1}{3} q^2\right) q \cdot F = \frac{1}{3} d + q^2 q \cdot F \quad (15)$$

So that

$$\begin{aligned} Q^3 &= (q_0 + q \cdot F)^3 = q_0^3 + 3q_0^2 q \cdot F + 3q_0 (q \cdot F)^2 + (q \cdot F)^3 = \\ &= q_0^3 + 3q_0^2 q \cdot F + 3q_0 \left(\frac{2}{3} q^2 + \frac{1}{2} d \cdot F\right) + \frac{1}{3} d + q^2 q \cdot F \quad (16) \end{aligned}$$

And if $Q^3 = Q$, the coefficients in (16) must be equal to those of (12), which leads to

$$q_0 = q_0^3 + 2q_0 q^2 + \frac{1}{3} d \quad ; \quad q_i = 3q_0^2 q_i + \frac{3}{2} q_0 d_i + q^2 q_i \quad (17)$$

We have therefore the two equations

$$d = 3q_0 (1 - q_0^2 - 2q^2) \quad (18)$$

$$q_0 d_i = \frac{2}{3} (1 - 3q_0^2 - q^2) q_i \quad (19)$$

We are faced with three cases.

- I - The trivial solutions $\boxed{7}$ are $q_i = 0, q_0 = 0, \pm 1$ ($Q=0, \pm I$)
- 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 $d_i = A q_i$ (21)

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

we obtain

$$\frac{4}{3} q^2 q_j = A d_j = AA q_j = A^2 q_j \quad A^2 = \frac{4}{3} q^2 \quad (22)$$

In order for (21) to satisfy (18) and (19), it must be:

$$Aq^2 = 3q_0 (1 - q_0^2 - 2q^2) \quad (23)$$

$$Aq_0 = \frac{2}{3} (1 - 3q_0^2 - q^2) \quad (24)$$

From (24) we obtain

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

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

$$q^2 = \begin{cases} \frac{1}{3} ; A^2 = \frac{4}{9} (A = \pm \frac{2}{3}) ; q_0 = -\frac{A}{4} \pm \frac{1}{2} \begin{cases} A = \frac{2}{3} \rightarrow q_0 = \frac{1}{3} \text{ or } -\frac{2}{3} \\ A = -\frac{2}{3} \rightarrow q_0 = -\frac{1}{3} \text{ or } +\frac{2}{3} \end{cases} \\ \frac{4}{3} ; A^2 = \frac{16}{9} ; A = \pm \frac{4}{3} ; q_0 = -\frac{A}{4} \begin{cases} A = 4/3 \rightarrow q_0 = -1/3 \\ A = -4/3 \rightarrow q_0 = +1/3 \end{cases} \end{cases}$$

Equation (21) takes the form

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

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

or also:

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

obtained putting $q_i = 2q'_i$.

There is too $\boxed{d_i = -\frac{4}{3} q_i ; q^2 = \frac{4}{3}}$, which is the last one with q_i changing sign, and has $\Delta = -1$.

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, being understood that there will be exactly similar equations for K. The matrix J being symmetric, it may be written under the form

$$J = j_0 + j_i F_i \quad (28)$$

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

$$\begin{aligned} \text{Tr}(F_i) = 0 ; \text{Tr}(F_i F_j) &= \frac{1}{2} \text{Tr}(\{F_i, F_j\}) = \frac{1}{2} \text{Tr}(d_{ijk} F_k + \frac{4}{3} \delta_{ij}) = \\ &= \frac{1}{2} \cdot \frac{4}{3} \delta_{ij} \text{Tr}(I) = 2\delta_{ij} \end{aligned} \quad (29)$$

Therefore

$$j_0 = \frac{1}{3} \text{Tr}(J) \quad ; \quad j_i = \frac{1}{2} \text{Tr}(F_i J) \quad (30)$$

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

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

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

$$q_i = \lambda_1 j_i + \lambda_2 D_i \quad (32)$$

λ_1, λ_2 being functions of j . Therefore

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

$$d_i = d_{il} q_l = (\lambda_1 d_{il} j_l + \lambda_2 d_{ilk} D_k) (\lambda_1 j_l + \lambda_2 D_l)$$

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

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

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

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

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

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

Besides

$$q^2 = (\lambda_1 j_i + \lambda_2 D_i) (\lambda_1 j_i + \lambda_2 D_i) = \lambda_1^2 j^2 + 2 \lambda_1 \lambda_2 D + \lambda_2^2 D \cdot D \quad (35)$$

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), $D \cdot D = D_i D_i = \frac{4}{3} (j^2)^2$.

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 $r_a = \frac{\lambda_1^{(a)}}{\lambda_2^{(a)}}$. ($a = 1, 2, 3$), 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 $\lambda_2, \pm \lambda_2^{(a)}$. Therefore, $\lambda_1 = \pm r_a \lambda_2^{(a)}$. These are then six solutions.

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

$$\frac{2}{3} \lambda_1 = \frac{8}{3} (\lambda_1 \lambda_2 j^2 + \lambda_2^2 D) \quad (36)$$

$$\frac{2}{3} \lambda_2 = \lambda_1^2 - \frac{4}{3} \lambda_2^2 j^2 \quad (37)$$

From (36):

$$\lambda_1 = \frac{4D\lambda_2^2}{1-4j^2\lambda_2} \quad (38)$$

Replacing (38) in (37), a cubic equation with known coefficients in λ_2 is obtained. The three corresponding solutions introduced in (38), together with $q_0 = \frac{1}{3}$ 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 signs of q_i and q_0 give other 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 in all 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.

It is no more possible, in the 6-electron case, a direct solution of the SC bond orders 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^{\pm} are the eigenvalues of P^{\pm} .

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

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

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:

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

Bearing in mind that $p_0^{\pm} = \frac{1}{3} \text{Tr } P^{\pm} = N^{\pm}/6$, applying this operator to x^{\pm} gives

$$\begin{aligned} [2P^+ - I - 2p_0^+ + I] x^{\pm} &= \{(\lambda_1 - 4j_0 \lambda_2) J + 2\lambda_2 J^2 + 2\lambda_2 (j_0^2 - \frac{2}{3} j^2) - \lambda_1 j_0\} x^{\pm} \\ [2n^{\pm} - 1 - \frac{N^{\pm}}{3} + I] x^{\pm} &= \{(\lambda_1 - 4j_0 \lambda_2) E^{\pm} + 2\lambda_2 (E^{\pm})^2 + 2\lambda_2 (j_0^2 - \frac{2}{3} j^2) - \lambda_1 j_0\} x^{\pm} \\ 2n^{\pm} - \frac{N^{\pm}}{3} &= (\lambda_1 - 4j_0 \lambda_2) E^{\pm} + 2\lambda_2 (E^{\pm})^2 + 2\lambda_2 (j_0^2 - \frac{2}{3} j^2) - \lambda_1 j_0 \quad (41) \end{aligned}$$

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 analogous 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:

$$H_{\mu\nu} = H_{\mu\nu}^0 + \xi P_{\mu\nu} C_{\mu\nu} \quad (42)$$

This seems a neater approach than the damping procedures or energy-shift methods which appear in the literature for somewhat limited applications [9,10,11].

4. Example

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

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

which (see table 1) give in the ground state a π contribution of 1.69 D to the dipole moment, in agreement with the 1.79 D 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 neighbouring atoms (those for non-neighbouring atoms are available under request), and the ξ parameter.

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 the III' case.

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

Finally, let us remark than when passing from the 4-electron to the 6-electron case, the condition $n_\ell + n_h = 1$ 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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State	P_{11}	P_{22}	P_{33}	P_{12}	P_{23}	P_{34}	P_{16}	ξ
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Case I. Particular Solutions

$(S_1)^2(S_2)^2(S_3)^2$	1	1	1	0	0	1	1	
$S_1A_1S_2A_2S_3A_3$	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. $N^+ = N^-$

$(S_1)^2(A_1)^2S_2A_2$	1.138	0.936	0.925	0.732	0.597	0.035	0.261	1
$S_1(A_1)^2(S_2)^2A_3$	0.970	0.939	1.091	0.405	0.350	0.354	0.115	0.8
$(S_1)^2A_1(A_2)^2S_3$	1.191	0.921	0.888	0.470	0.110	-0.522	0.222	0.8
$A_1(S_2)^2S_3(A_3)^2$	0.720	1.114	1.166	-0.441	-0.122	0.505	-0.215	-0.8
$S_1(A_2)^2(S_3)^2A_3$	0.977	1.099	0.924	-0.428	-0.341	-0.317	-0.048	-1
$S_2A_2(S_3)^2(A_3)^2$	0.774	1.104	1.122	-0.724	-0.592	-0.043	-0.255	-1

Case III. $N^+ \neq N^-$

$(S_1)^2(S_2)^2A_1S_3$	1.065	0.961	0.974	0.325	0.316	0.856	0.839	1
$(S_1)^2S_2A_1A_2S_3$	1.131	0.947	0.922	0.383	0.238	0.189	0.507	1
$(S_1)^2S_2(S_3)^2A_2$	1.143	0.972	0.885	0.040	-0.100	0.333	0.696	0.8
$S_1(A_1)^2S_2A_2A_3$	1.082	0.955	0.963	0.350	0.323	-0.169	-0.209	1
$S_1(S_2)^2A_1S_3A_3$	0.804	0.964	1.232	0.127	0.085	0.413	0.278	1
$(A_1)^2S_1(A_2)^2A_3$	1.124	0.948	0.928	0.381	0.290	-0.782	-0.606	1
$S_1(S_2)^2A_3(S_3)^2$	0.800	1.085	1.115	-0.365	-0.280	0.783	0.589	-1
$S_1A_1S_3(A_2)^2A_3$	1.156	1.072	0.772	-0.137	-0.084	-0.392	-0.220	-1
$S_1S_2A_2(A_3)^2S_3$	0.862	1.078	1.060	-0.353	-0.309	0.162	0.239	-1
$S_2(A_1)^2A_2(A_3)^2$	0.806	1.031	1.163	0.000	0.081	-0.347	-0.700	-0.8
$S_2A_1A_2S_3(A_3)^2$	0.789	1.085	1.126	-0.360	-0.241	-0.203	-0.500	-1
$A_1S_3(A_2)^2(A_3)^2$	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

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 neighbouring atoms. ξ is the convergence parameter.

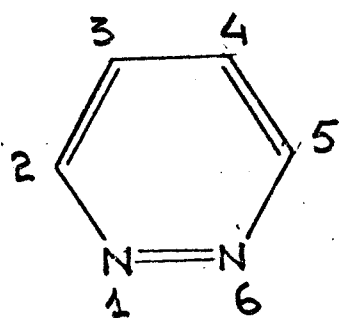


FIGURE 1