Some Features of Excited States Density Matrix Calculation and Their Pairing Relations in Conjugated Systems

Myriam Segre de Giambiagi and Mario Giambiagi

Centro Brasileiro de Pesquisas Físicas, CBPF/CNPq, Rio de Janeiro, RJ-Brasil

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Direct PPP-type calculations of self-consistent (SC) density matrices for excited states are described and the corresponding "thawn" molecular orbitals (MO) are discussed. Special attention is addressed to particular solutions arising in conjugated systems of a certain symmetry, and to their chemical implications. The $U(2)$ and $U(3)$ algebras are applied, respectively, to the 4-electron and 6-electron cases; a natural separation of excited states in different cases follows. A simple approach to the convergence problem for excited states is given. The complementarity relations, an alternative formulation of the pairing theorem valid for heteromolecules and non-alternant systems, allow some fruitful experimental applications. Together with the extended pairing relations shown here, they may help to rationalize general trends.

1. Introduction

SCF methods confront substantial difficulties when dealing rigorously with excited states [1 – 3], and much interesting work was done with the simpler methods ([4], p. 106). Methods involving different degrees of sophistication have been proposed in order to overcome the problem that the excited state functions are usually not orthogonal to the ground state functions [5 – 7].

Years ago, Hall studied the problem of direct determination of SC bond orders for even AH [8, 9], having not received then the due attention; his reference standard state [10] has pointed at a way which recently was rediscovered. In the last years considerable effort has been devoted to approaches that do not favour the ground state regarding the excited states. McWeeny [11] minimizes the average of the states associated with a given orbital configuration, using this term in a wider sense than usual. He remembers that a single effective Hamiltonian, whose eigenvectors determine the corresponding optimum orbitals for both the closed and open shells, is not unique and its eigenvalues have no physical meaning, for any member of a three-parameter family of Hamiltonians will possess the same egenvectors [12].

Indeed, the physical meaning of individual energy levels becomes obscured on exciting a molecule, as soon as the "frozen" scheme is loosened [13, 14], for they are functions of the specific state. On the other hand, Mehrotra and Hoffmann [15] have set forth an attractive way of recovering the primitive significance of the Mulliken-Walsh diagrams. They propose an "average state" (resembling Hall's reference state) as a compromise between all the electronic states of a molecule taken "in a democratic fashion", their tempered orbital energies being quite appealing.

McLachlan first pointed out a pairing property for π electronic states in alternant hydrocarbons (AH) within the PPP approximation [16]. Soon after Löwdin [17] indicated a paring theorem in the different orbitals for different spins (DODS) approximation. A formal theory of effective π-electron Hamiltonian was recently proposed [18]. The PPP theory has been reformulated by Koutecký [19], offering a well-defined model Hamiltonian and transcribing it into second quantized formalism; the McLachlan pairing theorem may be seen under this form [4].

It has been shown that the pairing theorem may be extended to non-orthogonal basis and is valid for *any* alternant and non-alternant conjugated systems. This, stated as the complementarity relations [20], has further been extended to anions and cations [21].

In this report a PPP density matrix formulation for excited states is expounded, with emphasis on pairing relations between particular solutions arising in π systems of a certain symmetry.

Reprint requests to M. S. de Giambiagi and M. Giambiagi, Centro Brasileiro de Pesquisas Fisicas, Rua Xavier Sigaud 150, 22290 Rio de Janeiro-RJ, Brasil.

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2. SC Bond Orders and the Related MO's

Hall proposed a method for calculating the SC P bond order matrix between atoms of different sets in even AH [8]. In the case of N electrons, this amounts to determining an $N/2$ matrix Π. Let us define n_l as a diagonal matrix with half the occupation numbers n_i of the lowest energy levels, and n_h a diagonal matrix with half the occupation numbers of the associated highest energy levels [22]. The whole discussion is restricted to the cases where $n_l + n_h = I$ (I, unit matrix), thus ruling out some of the states considered by Nesbet [23]. Hall restricts himself to the states where $n_i = 2$ or 0, involving $\det \Pi = 0$. This is easily extended so as to include $n_i = 1$, and to odd AH [22]. the basic equations are:

$$F' \Pi = \text{symmetric} \quad \text{and} \quad \Pi \Pi' \Pi = \Pi \,, \tag{1}$$

where F' is the adjoint of a suitable effective Hamiltonian including electron interaction. If H^0 is the Hamiltonian without interaction, the electronic π energy is known to be [24]

$$E_\pi = \mathrm{Tr}(F' \Pi) + \mathrm{Tr}(H^0 \Pi) \,, \tag{2}$$

Hall [9] represents Π as a rotation matrix, which is not the most general representation for a unitary matrix, for it does not include inversion. For the states with all symmetric (antisymmetric) levels doubly occupied in butadiene, he writes two matrices which are not solutions of the problem [9]. It has been shown [25] that these states have particular solutions of the form

$$P^{\pm} = \begin{pmatrix} 1 & & & \pm 1 \\ & \ddots & \iddots & \\ & \iddots & \ddots & \\ \pm 1 & & & 1 \end{pmatrix} , \tag{3}$$

The P's being now $N \times N$ matrices, and the elements outside the diagonals being zero.

These peculiar solutions are *internally self-consistent* in the sense of Mehrotra and Hoffmann [15], who overlooked them. Together with Hall's reference state, they arise whenever a π system has a twofold symmetry axis not passing through any of the N π-electron centers. In the corresponding states, any molecule shall have *unitary charges*, regardless of the nature of its atoms. It is as if in these states the electrons activity differences cancelled out.

The increasing difficulty in obtaining new simple but generally valid rules for conjugated systems has been remarked [26]. For systems where a twofold symmetry axis crosses two π centers, it may be easily shown [27] that the particular solutions do not lead to states of the neutral molecule, but of the corresponding double ions, having electronic π charges of 2(0) for the atoms on the axis, and unitary charges for the other atoms.

Equations (1), when applied to butadiene, give the bond orders of Table 1, numbered according to the increasing total energy; a_u and b_g correspond to the MO's

$$\begin{aligned} 1\,a_u &= a(\varphi_1 + \varphi_4) + b(\varphi_2 + \varphi_3) \,, \\ 1\,b_g &= b(\varphi_1 - \varphi_4) + a(\varphi_2 - \varphi_3) \,, \\ 2\,a_u &= b(\varphi_1 + \varphi_4) - a(\varphi_2 + \varphi_3) \,, \\ 2\,b_g &= a(\varphi_1 - \varphi_4) - b(\varphi_2 - \varphi_3) \,. \end{aligned} \tag{4}$$

Now, one may wonder which are the wave function coefficients reproducing these bond orders. They appear in Table 2, together with the increasing order in the energy levels obtained in the PPP calculation [13].

The table makes clear the effect of "thawing", that is of performing self-consistency for each state. Parr and Mulliken [28] firstly raised the question of the validity of calculating excited states from "frozen" ground state MO's, in their classical treatment of trans-butadiene. Calculations of states 3) and 5) with their method confirm the behaviour described in Table 2, whilst state 8) does not converge whatever the starting coefficients may be [13]. In thawing, the order of nodal planes usually does not coincide with the order of the orbital energies. In Table 2 it is seen that, as the energy levels change with occupation numbers, they may cross one another. But they may not cross as in state 8), which infringes the non-crossing rule between levels of the same symmetry. This would explain the

Table 1. Trans-butadiene bond orders from (1).

State	P_{12}	P_{23}	P_{14}
1) $(1a_u)^2(1b_g)^2$	0.9771	0.2127	−0.2127
2) $(1a_u)^2(1b_g)^1(2a_u)^1$	0.4680	0.6758	0.3241
3) $(1a_u)^2(2a_u)^2$	0	1	1
4) $(1a_u)^1(1b_g)^2(2b_g)^1$	0.4963	−0.4396	−0.5604
5) $(1b_g)^2(2b_g)^2$	0	−1	−1
6) $(1a_u)^1(2a_u)^2(2b_g)^1$	−0.4457	0.2734	0.7266
7) $(1b_g)^1(2a_u)^1(2b_g)^2$	−0.4930	−0.5834	−0.4166
8) $(2a_u)^2(2b_g)^2$	−0.9239	−0.3826	0.3826

Table 2. MO coefficients for trans-butadiene.

State	*a*	*b*	Increasing order of energy levels
1)	0.4437	0.5506	$1a_u, 1b_g, 2a_u, 2b_g$
2)	0.4026	0.5813	$1a_u, 1b_g, 2a_u, 2b_g$
3)	0.3530	0.6127	$1a_u, 2a_u, 1b_g, 2b_g$
4)	0.4688	0.5293	$1b_g, 1a_u, 2b_g, 2a_u$
5)	0.5011	0.4989	$1b_g, 1a_u, 2b_g, 2a_u$
6)	0.3698	0.6027	$1a_u, 2a_u, 1b_g, 2b_g$
7)	0.4564	0.5401	$1b_g, 1a_u, 2b_g, 2a_u$
8)	0.3936	0.5875	$2a_u, 2b_g, 1a_u, 1b_g$

lack of convergence of the Parr-Mulliken calculation for this state, and therefore indicates that at least the most excited states must be handled otherwise.

3. Applications of the $U(2)$ and $U(3)$ Symmetric Matrices Algebra

The equations which led to the particular solutions suggest a way of treating conjugated systems with a twofold symmetry axis not passing through any of the N π centers. The secular equations split in two sets according to the basis functions, which are either symmetric (+) or antisymmetric (−) with respect to the symmetry axis. The problem may be set up in terms of two $N/2$-dimensional matrices Π^+ and Π^- [29]. The separation of the basis set in two sets facilitates speculating about the eigenvalue stability (minimum, maximum or saddle point) [30]. Mestechkin [31, 32] has studied restricted Hartree-Fock instability under a form closely related with this one.

For excited states, a Hamiltonian is proposed which involves a compromise between the fundamental and excited states [29]:

$$H_{\mu\nu} = H^0_{\mu\nu} + P_{\mu\nu} C_{\mu\nu} . \tag{5}$$

By introducing the matrices

$$Q^{\pm} = 2\Pi^{\pm} - I \tag{6}$$

two sets of equations equivalent to (1) are obtained:

$$\begin{aligned} &[J' + (C^+ Q^+) + (C^- Q^-)]\, Q^{\pm} = \text{sym}; \\ &[K' + (C^- Q^+) + (C^+ Q^-)]\, Q^{-} = \text{sym}; \\ &(Q^{\pm})^3 = Q^{\pm} . \end{aligned} \tag{7}$$

(CQ) are not products of C and Q, but must be understood as $(CQ)_{\mu\nu} = C_{\mu\nu} Q_{\mu\nu}$. We have

$$\begin{aligned} J' &= 2J + (C^+ I) + (C^- I); \\ K' &= 2K + (C^- I) + (C^+ I); \end{aligned} \tag{8}$$

$$\begin{aligned} J_{\mu\nu} &= H^0_{\mu\nu} + H^0_{\mu, N+1-\nu}; \\ K_{\mu\nu} &= H^0_{\mu\nu} - H^0_{\mu, N+1-\nu}; \end{aligned} \tag{9}$$

$$C^{\pm}_{\mu\nu} = C_{\mu\nu} \pm C_{\mu, N+1-\nu}, \tag{10}$$

and the $C_{\mu\nu}$ are proportional to the Coulomb integrals between atomic orbitals on atoms μ and ν.

Now, the 4-electron and 6-electron cases may be calculated applying more general algebras in a different approach for the direct calculation of the SC P matrix. In the 4-electron case, both Q^+ and Q^- (referred to as Q for shortness) may be written as sums of a scalar part and a vectorial part:

$$Q = q_0 + q \cdot \sigma , \tag{11}$$

where σ designates the Pauli matrices.

Similarly, for the 6-electron case

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

Any 3×3 real symmetric matrix can be expressed through the basic matrices of the $U(3)$ group, which are the unit matrix and the five F matrices [33, 34].

Three cases follow [29, 33]:

I. Three trivial solutions, $q_i = 0$, $q_0 = 0, \pm 1$ ($Q = 0, \pm I$), corresponding to the two particular solutions and Hall's reference state.

II. $q_0 = 0$, $q^2 = 1$.

III. $q_0 \neq 0$, $q_i \neq 0$.

The coupling of Q^+ and Q^- (and accordingly of Π^+ and Π^-) in (7) is limited within the same case. We have found no modulo 4 type [35] relations, establishing some qualitative difference between $U(2)$ and $U(3)$.

In the 4-electron case [29], systems of transcendental equations are obtained, which may be solved by a generalization of the *regula falsi* [36]. The 6-electron case must be solved iteratively, and a further condition is introduced, in order to preserve the non-crossing rule [33].

There are $3^{N/2}$ solutions obeying $n_l + n_h = I$*, that is the 9 states for $N = 4$ become 27 for $N = 6$. A two

* Obviously, $n_l + n_h = I$ is intended for AH, but we keep it for heteromolecules where the MO's follow with reasonable closeness the association scheme.

π electron system has thus as unique solutions the three particular ones, and the $U(4)$ development (a bit cumbersome but feasible) yields 81 solutions. The ground state appears in case II for the $U(2)$ calculation, and in a sub-case III′ of III in $U(3)$. Diazoethane is used as an example in $U(2)$ and pyridazine in $U(3)$.

4. Simplified Approach to the Convergence Problem

The convergence problem for excited states is overcomed by inserting a single convergence parameter ξ for each state in the compromise Hamiltonian [30, 33]:

$$H_{\mu\nu} = H^0_{\mu\nu} + \xi P_{\mu\nu} C_{\mu\nu} . \tag{13}$$

The energy is calculated from

$$\mathrm{Tr}(J^* \Pi^+) + \mathrm{Tr}(J \Pi^+) + \mathrm{Tr}(K^* \Pi^-) + \mathrm{Tr}(K \Pi^-) , \tag{14}$$

where

$$\begin{aligned} J^* &= J + (C^+ \Pi^+) + (C^- \Pi^-) ; \\ K^* &= K + (C^- \Pi^+) + (C^+ \Pi^-) \end{aligned} \tag{15}$$

and the due correction for the spurious repulsion of the half-electron approximation [37, 14, 30] is taken into account. As long as the excited states obey the aufbau principle, a convergence parameter is not needed. There is certainly trouble when the order of the occupation numbers is *completely* inverted, and difficulties are expected even for partial inversion [30] (see Figure 2).

When the inversion is complete, changing ξ from 1 to -1 restores a situation where the variation method may be applied, the highest Π^+ eigenvalue corresponding thus to the highest J^* eigenvalue [34]. This is as if we built these states with the aufbau principle occupying the energy levels "downwards" from the "top", instead of "upwards" from the "bottom". We have called it the *anti-aufbau* construction; it is associated with the intrinsic divergence problem faced in [38]. Taking a single convergence parameter for each state involves a maximum simplicity criterion. All factors not taken explicity into account are ascribed to ξ, which physically may be thought as playing a role similar to the additional potential introduced in the Fock operator by Beebe [39] in order to modify the virtual orbitals.

When solving Hartree-Fock density matrix equations [40], iterations usually do not preserve the symmetry of the density matrix, although it is idempotent and normalized. Symmetry must be forced at each iteration; this in turn generally destroys the idempotency, which is recovered through the McWeeny purification process [40]. In a thorough Hartree-Fock density matrix treatment of localized electronic interactions in molecules and solids, the orbitals of the local subspace are demanded to factor into two distinct orthonormal sets, one completely occupied and the other completely unoccupied [41]. In general this requirement is imposible to fulfill. Again, one must give up either the idempotency or the localization of the density matrix. The present PPP calculation does not seem to encounter the mentioned drawbacks, maybe due to oversimplification.

As a starting matrix P in (13) for the desired state we can use one built with the eigenfunctions (i.e. some virtual orbitals also) of another state. It is expected [30] that the solution may depend on the starting matrix, as uses to happen in more sophisticated treatments [41]; being, or not, near the solution could not only accelerate convergence but decisive. Nevertheless, it is found [42] that given ξ, whatever the wavefunctions used to build the initial P, *it converges to the same solution.*

5. Pairing Relations

Michl [43] has called attention to compounds with heteroatoms at least approximately paired in the PPP sense, a concept that is best grasped with an example: "benzene with one heteroatom whose effective electronegativity deviates from that of carbon, and benzene with another heteroatom whose effective electronegativity deviates from that of carbon by the same amount in the opposite direction are paired if electron repulsion integrals satisfy certain conditions." He, together with other authors, has published a long series of papers where these ideas are applied to magnetic circular dichroism (MCD) of cyclic π systems. However, mirror images from the viewpoint of the complementarity relation admit a broader inference than the one sought. The monocyclic azines offer an instance of these pairs of images, clearly revealed by their complementary π charges [44]: pyridine-pentazine, pyridazine-v-tetra-

zine, pyrimidine-as-tetrazine, pyrazine-s-tetrazine and the self-complementary s-triazine.

The choice of parameters must be such as not to cause too large deviations from perfect pairing [45], so as to relate the HOMO's and LUMO's of a pair to those of the parent hydrocarbon [46]. It should be stressed that two species only approximately paired have opposite sign MCD spectra [47], and this experimental result emphasizes the importance of pairing properties. It is also predicted that two such molecules should have opposite π magnetic anisotropy, one being diamagnetic and the other paramagnetic [48].

From the complementarity relation [20], provided tow complementary states (Fig. 1) are calculated with the same Hamiltonian, we have

$$P^{(\mathrm{I})} + P^{(\mathrm{II})} = 2I\,. \tag{16}$$

If the Hamiltonian are different, let us say by a perturbation ΔH [42],

$$H^{(\mathrm{I})} = H^{(\mathrm{II})} + \Delta H\,, \tag{17}$$

it will be

$$P^{(\mathrm{I})} + P^{(\mathrm{II})} = 2I + \varepsilon(\Delta H)\,, \tag{18}$$

where ε must be a functional of ΔH.

Other pairing relations involving the particular solutions may be found, deriving for example from the $U(3)$ algebra application, for the 12 states where $N^+ \neq N^-$ (number of electrons respectively in symmetric and antisymmetriy levels) and singly occupied levels are allowed [33, 42] (Figure 2). The three particular solutions are the $P^{\pm}$ matrices from (3) and the reference state one $P^0 = I$. If these 12 states are calculated with the same Hamiltonian, they may be paired off, satisfying either

$$P^{(\mathrm{i})} + P^{(\mathrm{ii})} = P^+ + P^0$$

or

$$P^{(\mathrm{i})} + P^{(\mathrm{ii})} = P^- + P^0\,. \tag{19}$$

Again, if the Hamiltonian is not the same, we shall have

$$P^{(\mathrm{i})} + P^{(\mathrm{ii})} = P^+ + P^0 + \varepsilon(\Delta H)$$

or

$$P^{(\mathrm{i})} + P^{(\mathrm{ii})} = P^- + P^0 + \varepsilon(\Delta H)\,. \tag{20}$$

Equation (16) may also be written under the form

$$P^{(\mathrm{I})} + P^{(\mathrm{II})} = P^+ + P^-$$

or else

$$P^{(\mathrm{I})} + P^{(\mathrm{II})} = 2P^0\,, \tag{21}$$

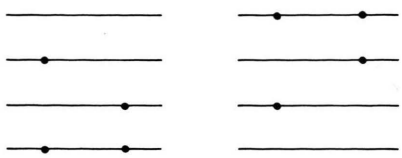

Fig. 1. Two complementary states.

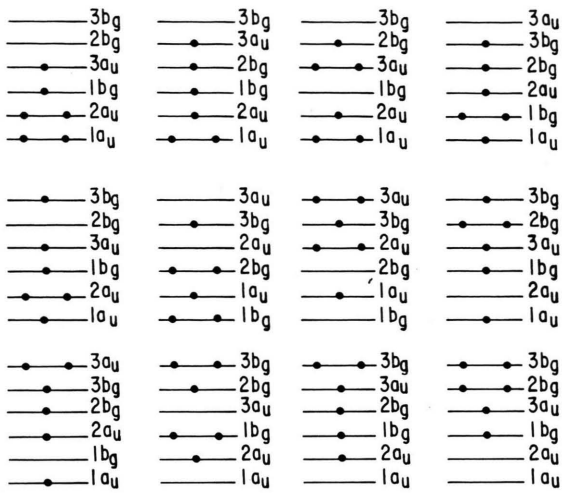

Fig. 2. The 12 states obeying the pairing relations (19) in the $U(3)$ development.

which discloses the analogy between relations (16) and (19), and the self-complementarity of the reference state.

Amos and Hall [49] have found that the single determinant wavefunction written under the DODS assumption may be forced to be an eigenfunction of S^2 under certain conditions. They mention that this may occur if there are sufficient MO's of one spin and one irreducible representation to span completely the space of all functions of that symmetry; the molecular orbitals of the opposite spin and the same symmetry can then be expressed in terms of them.

This is just the case of the 12 states which pair following (19). Let us ascribe to these states the maximum multiplicity and suppose that the α orbitals are those which span for example the three-dimensional space of symmetrical orbitals. The one (two) electron of symmetrical orbitals may be transformed so as to give one doubly occupied and two singly occupied (two doubly occupied and one singly occupied) symmetrical orbitals. The determinant becomes thus an eigenfunction of S^2, which in the mentioned example represents either a quin-

tuplet or a triplet. For this case, hence, the adapted DODS method and the half-electron method are two possible alternatives that reduce the unrestricted calculation to a restricted one.

As has recently been demonstrated [50], the complex MO's (CMO) in the natural orbital (NO) representation may be brought into the pairing form in which each CMO has only two NO components. These NO appear in pairs with complementary occupation numbers, a condition tantamount to $n_l + n_h = I$.

It may be claimed that we are too unrealistic in contemplating states probably not comparable with experiment. Nevertheless, even if some states have purely academic character, their pairing properties with lower lying states deserve both speculative and applied consideration. Despite its inherent simplicity, this PPP approach may provide useful hints to much more accurate and sophisticated methods based on pairing schemes, such as alternant molecular orbitals [51] or antisymmetrized geminal power functions [52].

[1] M. Rossi, J. Chem. Phys. **46,** 989 (1967).
[2] N. Ohmichi, J. Chem. Phys. **67,** 1669 (1977).
[3] A. Golebiewski, J. Hinze, and E. Yurtsever, J. Chem. Phys. **70,** 1101 (1979).
[4] G. Del Re, G. Berthier, and J. Serre, Electronic States of Molecules and Atom Clusters, Lecture Notes in Chemistry No. 13, Springer-Verlag, Berlin 1980, p. 30.
[5] T. M. Bustard and H. H. Jaffé, J. Chem. Phys. **53,** 534 (1970).
[6] R. Colle, R. Montagnani, P. Riani, and O. Salvetti, Theoret. Chim. Acta **48,** 257 (1978).
[7] S. P. Battarayya and D. Mukherjee, Int. J. Quantum Chem. **20,** 1165 (1981).
[8] G. G. Hall, Proc. Roy. Soc. London **A 229,** 251 (1955).
[9] G. G. Hall, J. Chem. Phys. **33,** 953 (1960).
[10] G. G. Hall, Proc. Roy. Soc. London **A 213,** 102 (1952).
[11] R. McWeeny, Mol. Phys. **28,** 1273 (1974).
[12] R. McWeeny in Molecular Orbitals in Chemistry, Physics and Biology, edited by P. O. Löwdin and B. Pullman, Academic Press, New York 1964, p. 305.
[13] M. Giambiagi, M. S. de Giambiagi, R. Ferreira, and S. Blanck, Chem. Phys. Lett. **38,** 65 (1976).
[14] M. S. de Giambiagi, M. Giambiagi, and R. Ferreira, Chem. Phys. Lett. **52,** 80 (1977).
[15] P. K. Mehrotra and R. Hoffmann, Theor. Chim. Acta **48,** 301 (1978).
[16] A. D. McLachlan, Mol. Phys. **2,** 271 (1959).
[17] P. O. Löwdin, J. Appl. Phys. **33** (Suppl.), 251 (1962).
[18] B. H. Brandow, Int. J. Quantum Chem. **25,** 207 (1979).
[19] J. Koutecký, Chem. Phys. Lett. **1,** 249 (1967).
[20] M. S. de Giambiagi and M. Giambiagi, Chem. Phys. Lett. **1,** 563 (1968).
[21] R. Carbó, M. S. de Giambiagi, and M. Giambiagi, Nuovo. Cim. **59 B,** 204 (1969).
[22] C. G. Bollini, J. J. Giambiagi, M. Giambiagi, and M. S. de Giambiagi, Theor. Chim. Acta **18,** 394 (1970).
[23] R. K. Nesbet, Proc. Roy. Soc. London **A 230,** 322 (1955).
[24] R. McWeeny, Proc. Roy. Soc. London **A 235,** 496 (1956).
[25] C. G. Bollini, J. J. Giambiagi, M. Giambiagi, and M. S. de Giambiagi, Theor. Chim. Acta **22,** 234 (1971).
[26] I. Gutman, Chem. Phys. Lett. **58,** 137 (1978).
[27] M. S. de Giambiagi and M. Giambiagi, Lett. Nuovo. Cim. **25,** 459 (1979).
[28] R. G. Parr and R. S. Mulliken, J. Chem. Phys. **18,** 1338 (1950).
[29] C. G. Bollini, J. J. Giambiagi, M. Giambiagi, and M. S. de Giambiagi, Theor. Chim. Acta **43,** 89 (1976).
[30] M. S. de Giambiagi, M. Giambiagi, and H. G. P. Lins de Barros, Z. Naturforsch. **35 a,** 1006 (1980).
[31] M. M. Mestechkin, Int. J. Quantum Chem. **13,** 469 (1978).
[32] M. M. Mestechkin, Int. J. Quantum Chem. **15,** 601 (1979).
[33] C. G. Bollini, J. J. Giambiagi, M. Giambiagi, and M. S. de Giambiagi, Theor. Chim. Acta **52,** 27 (1979).
[34] D. B. Lichtenberg, Unitary Symmetry and Elementary Particles, Academic Press, New York 1970, Chapter 6.
[35] I. Gutman and O. E. Polansky, Theor. Chim. Acta **60,** 203 (1981).
[36] J. Gordon, private communication.
[37] M. J. S. Dewar, J. A. Marshall, and C. G. Venier, J. Amer. Chem. Soc. **90,** 1953 (1968).
[38] R. E. Stanton, J. Chem. Phys. **75,** 3426 (1981).
[39] N. H. F. Beebe, Int. J. Quantum Chem. **15,** 589 (1979).
[40] L. Cohen and C. Frishberg, J. Chem. Phys. **65,** 4234 (1976).
[41] B. Kirtman and C. de Melo, J. Chem. Phys. **75,** 4592 (1981).
[42] M. S. de Giambiagi, M. Giambiagi, and A. F. Castro, Lett. Nuovo. Cim. **33,** 327 (1982).
[43] J. Michl, J. Chem. Phys. **61,** 4270 (1974).
[44] M. S. de Giambiagi and M. Giambiagi, J. Chim. Phys. **64,** 880 (1967).
[45] N. H. Jorgensen, P. B. Petersen, E. W. Thulstrup, and J. Michl, Int. J. Quantum Chem. Symp. **12,** 419 (1978).
[46] J. W. Waluk, E. Vogel, and J. Michl, J. Org. Chem. **46,** 3306 (1981).
[47] J. Michl, Chem. Phys. Lett. **39,** 386 (1976).
[48] D. M. S. Esquivel, M. S. de Giambiagi, and M. Giambiagi, Chem. Phys. Lett. **64,** 131 (1979).
[49] A. T. Amos and C. G. Hall, Proc. Roy. Soc. London **A 263,** 483 (1961).
[50] J. Hendeković, Chem. Phys. Lett. **76,** 593 (1980).
[51] R. Pauncz, Alternant Molecular Orbital Method, Saunders, Philadelphia 1967.
[52] O. Goscinski, Horizons of Quantum Chemsitry, Eds. K. Fukui and B. Pullman, Reidel, Massachusetts 1980, p. 17.

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