J. Am. Chem. Soc. 1982, 104, 3029-3034

transfer states which never appear explicitly. For equal bond lengths, the second-order level introduces a single parameter and allows a topologically determined Heisenberg Hamiltonian. This effective exchange term simply reproduces the coupling through singly ionic adjacent charge-transfer states. As will be shown in the following paper, this crude model is able to reproduce the exact ordering of lowest singlet–triplet states for a large series of hydrocarbons, even in nearly degenerate situations. It offers a rationalization of the prefered multiplicity in cyclobutadiene and of the $m^* = m^0 + 2$ rule.

The recurrence equations (eq 9) allow one to go to higher orders. The convergence of this QDMBPT approach for the proposed partition of the VB matrix has been assumed throughout and will be discussed in view of the numberical results in the following paper. Despite the bielectronic nature of the zeroth-order Hamiltonian, the unlinked contributions vanish and the perturbation expansion produces some effective operators characterizing (i) connected fragments of the molecule, (ii) an S_z value on the considered fragment, and (iii) a definite spin exchange on this fragment. If the Hamiltonian of the problem is simplified to the Hubbard scheme, these high order contributions simply introduce a second parameter, namely, the ratio $\lambda = F/\Delta E$.

The fourth-order analysis exhibits as the largest effect a four-body operator performing a cyclic double-spin permutations on four-membered rings. Analogous six-body cyclic exchange operators for benzene-type rings dominate the sixth-order contributions. The fourth- and sixth-order contributions may be expressed in terms of products of integers by λ^4 or λ^6 (in g units). The model proposed in this paper appears as a very attractive tool since it produces VBCI-types matrices of reasonable size, using two parameters only, which are directly determined by the topology. Its numerical and interpretative power will be illustrated in the following paper. It may be generalized in two directions: (i) to ionic excited states of hydrocarbons and to their positive and negative ions; (ii) to clusters of metal atoms where each atom contributes only one s electron, as relevant, for instance, in clusters of alkaline atoms.

IV. Appendix. Sixth-Order Cyclic Operators

The cyclic sixth-order operators may be written in a compact form through a matrix formulation for th various S_z values (Table II).

A Valence Bond Effective Hamiltonian for Neutral States of π Systems. 2. Results

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Abstract: The previously defined VB effective Hamiltonian has been applied to a series of conjugated hydrocarbons. The second-order Heisenberg-type Hamiltonian is sufficient to predict the spin multiplicity preference of biradicals and furnishes a rationalization of the $m^* = m^0 + 2$ rule. After inclusion of fourth- and sixth-order corrections, the results obtained from this very simple two-parameter Hamiltonian compare accurately with the *full* π CI-PPP results, not only for the singlet–triplet separation but also for the total π energy. The analysis of the wave function shows the dominant role of spin alternation. For ($N = 4n$, $4n + 2$) cyclic molecules the Nth-order effective cyclic spin exchange plays the main role in the specific ground-state stabilization; it represents collective circular movements of the electrons, i.e., ring currents, and allows a direct demonstration of the $4n/4n + 2$ determinism of the antiaromaticity–aromaticity character in a highly correlated model.

In the preceding paper,[1] a π valence bond effective Hamiltonian formalism has been defined. In this approach, the neutral determinants of the VB basis set are the only ones to appear explicitly, the others (i.e., the ionic ones) being taken into account by a quasi-degenerate many-body perturbation technique.[2] A recurrence equation gives the expression of the effective Hamiltonian $\bar{H}_n$ at nth order. The unlinked cluster cancellations allow a very important shortcut in the calculation of the operator $\bar{H}_n$, since a given molecule may be constructed as a "kit" from primitive fragments. For these fragments f with a total $S_z = s$, the effective operators $\bar{h}_{n_{f_s}}$ are calculated once for all, and the most important ones have been given.

This paper proposes to apply this formalism to some typical problems. It shows that second-order perturbation is sufficient to determine the spin multiplicity preference, while quantitative agreement with full CI is obtained for the lowest state energies as soon as higher order terms are introduced. Surprisingly enough the model reproduces the total energies, despite the use of only two parameters. Part 3 presents some simple theoretical applications of this model: it gives a demonstration of the aromaticity rule for cyclic compounds and makes evident the existence and the importance of the role of ring currents. The convergence problem is discussed. The resulting description of the electronic assembly as governed by partial spin ordering and collective movements is exemplified.

I. Second-Order Results and Qualitative Implications. The Spin Multiplicity Preference

As previously noted, our effective Hamiltonian is a magnetic or Heisenberg-type Hamiltonian, and it should essentially predict the spin multiplicity of the lowest states. Döhnert and Koutecky[3] recently calculated the lowest eigenvalues of the full π CI matrix for a series of conjugated hydrocarbons, assuming a Pariser–Parr–Pople Hamiltonian. Table I reproduces their calculated values (column 1) for 20 significant molecules, which may be compared with our second-order values (column 2). The zero energy is different in both methods (our zero is the highest multiplicity eigenstate of the molecule; it corresponds to a situation in which each atom bears a frozen electron of α spin while the PPP energy is taken from separated atoms), and the most relevant comparison is concerned with the singlet–triplet separation. One may notice that our second-order Hamiltonian always gives the correct singlet–triplet ordering, even when these states are nearly

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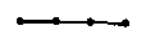
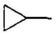
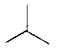
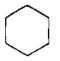
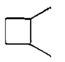
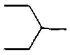
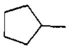
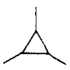
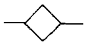
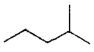
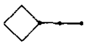
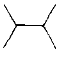
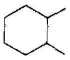
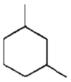
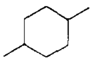
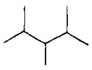
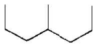
(1) J. P. Malrieu and D. Maynau, preceding paper in this issue.

(2) J. H. Van Vleck, *Phys. Rev.*, **33**, 467 (1929); J. des Cloiseaux, *Nucl. Phys.*, **20**, 321 (1960); B. H. Brandow, *Rev. Mod. Phys.*, **39**, 771 (1967); G. Hose and U. Kaldor, *J. Phys. B*, **12**, 3827 (1979); I. Shavitt and T. Redmon, *J. Chem. Phys.*, **73**, 5711 (1980).

(3) D. Döhnert and J. Koutecky, *J. Am. Chem. Soc.*, **102**, 1789 (1980).

0002-7863/82/1504-3029$01.25/0

Table I. The Two Lowest States of a Series of π Systems[a]

molecules	Döhnert and Koutecký[3] (in eV)	EVB model	
		second order	higher orders
 **1**	(a) r_0 = 1.35 Å r_1 = 1.45 Å S, −9.34 T, −6.14 (b) $r_0 = r_1$ = 1.4 Å $E_T - E_S$ = 2.5	S, −4.73 g T, −3.41 g	S, −8.13 T, −5.87
 **2**	S, −8.04 T, −7.75	S, −6 g T, −4 g	S, −8.19 T, −7.80
 **3**		S, −5 g T, −4 g	S, −8.81 T, −7.09
 **4**	S, −5.84 T, −6.72	S, −3 g T, −4 g	S, −5.32 T, −6.86
 **5**	S, −15.66 T, −11.74	S, −8.61 g T, −7.24 g	S, −16.05 T, −12.21
 **6**	S, −13.75 T, −11.63	S, −8.33 g T, −7.51 g	S, −13.83 T, −11.86
 **7**	S, −13.05 T, −11.03	S, −7.45 g T, −6.31 g	S, −12.85 T, −10.88
 **8**	S, −14.17 T, −12.67	S, −8 g T, −7.27 g	S, −13.86 T, −12.58
 **9**	S, −13.91 T, −11.69	S, −8 g T, −6.53 g	S, −13.96 T, −11.51
 **10**	S, −11.84 T, −12.55	S, −7.23 g T, −7.90 g	S, −11.47 T, −12.89
 **11**	S, −11.29 T, −11.79	S, −6.29 g T, −6.88 g	S, −10.92 T, −11.82
 **12**	S, −12.91 T, −12.66	S, −8.70 g T, −7.25 g	S, −13.10 T, −12.71
 **13**	S, −11.50 T, −11.41	S, −6.83 g T, −6.63 g	S, −11.72 T, −11.45
 **14**	S, −18.34 T, −17.37	S, −11.03 g T, −10.29 g	S, −19.79 T, −18.68
 **15**	S, −17.25 T, −17.64	S, −9.92 g T, −10.64 g	S, −18.33 T, −19.17
 **16**	S, −18.25 T, −17.32	S, −11.00 g T, −10.28 g	S, −19.70 T, −18.70
 **17**	S, −16.07 T, −16.09	S, −9.32 g T, −9.44 g	S, −16.13 T, −16.26
 **18**	S, −16.49 T, −16.89	S, −9.26 g T, −9.74 g	S, −16.01 T, −16.75

[a] Comparison between the EVB model and the Pariser–Parr results (full CI, taken from ref 3). The second-order results are given in *g* units and the higher orders in eV.

degenerate, as occurs for compounds **13** and **17**.

This very simple effective exchange Hamiltonian seems therefore to be able to predict the preferred multiplicity through a diagonalization of a rather small matrix. It also confirms some qualitative rationalizations. Actually, as mentioned by Döhnert and Koutecky, triplet ground states only appear for alternant compounds where

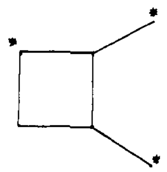
$$m^* = m^0 \pm 2$$

if m^* (m^0) are the number of starred (unstarred) atoms. Among our examples, the compounds **4**, **10**, **11**, **15**, **17**, and **18** belong to this category. The general statement that the ground-state multiplicity is given by $S = (m^* - m^0)/2$ has been given by Ovchinnikov[4] using an Heisenberg spin Hamiltonian, where

$$K_{12}^{\mathrm{eff}} = \tfrac{1}{2}\left(\sqrt{(\Delta E)^2 + 16F^2} - \Delta E\right) \qquad (1)$$

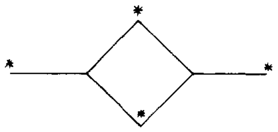
(where F is a resonance integral between adjacent atoms and ΔE is the transition energy to the ionic states), is taken from the ethylene S.T. splitting problem.

The ($m^* = m^0 \pm 2$) rule may be easily understood in this model by referring to the *diagonal* matrix elements of our effective Hamiltonian. The triplets may be analyzed through their S_z = 1 components, i.e., by attributing an excess of two α spins (i.e., two stars). Let us recall now (cf. part 1) that the diagonal stabilization of each determinant is proportional to the number $n_P{}^I$ of spin alternating chemical bonds. The maximal value of a diagonal element will be obtained when spin alternations occur on *all* chemical bonds, i.e., when the determinant corresponds to an alternant graph. For instance



$S_z = 0$

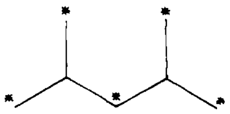
has a diagonal term equal to −6g as well as



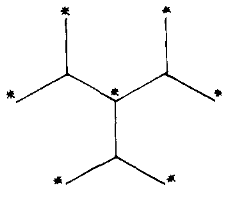
$S_z = 1$

Now it is clear that for the $m^* = m^0$ alternant hydrocarbons, the largest stabilization of diagonal elements occurs in the S_z = 0 matrix, while for the $m^* = m^0 + 2$ alternant hydrocarbons the lowest diagonal element occurs in the $S_z = \pm 1$ matrix, i.e., for the *triplets*; for these molecules the diagonal of the $|S_z| = 1$ Hamiltonian matrix involves lower energy terms than the S_z = 0 matrix. This gives a strong presumption for the lowest eigenvalue to correspond to a triplet state.

This simple interpretation may be extended to more complex cases; for odd number of electrons, for instance



is a ground-state quadruplet since $m^* = m^0 + 3$ ($E_{S^2=4} = -7.95g$, $E_{S^2=2} = -7.72g$). On similar grounds



has a quintuplet ground state since $m^* = m^0 + 4$, as confirmed by the numerical calculation ($E_{S^2=5} = -11.90g$, $E_{S^2=3} = -11.71g$).

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(4) A. O. Ovchinnikov, *Theor. Chim. Acta*, **47**, 297 (1978).

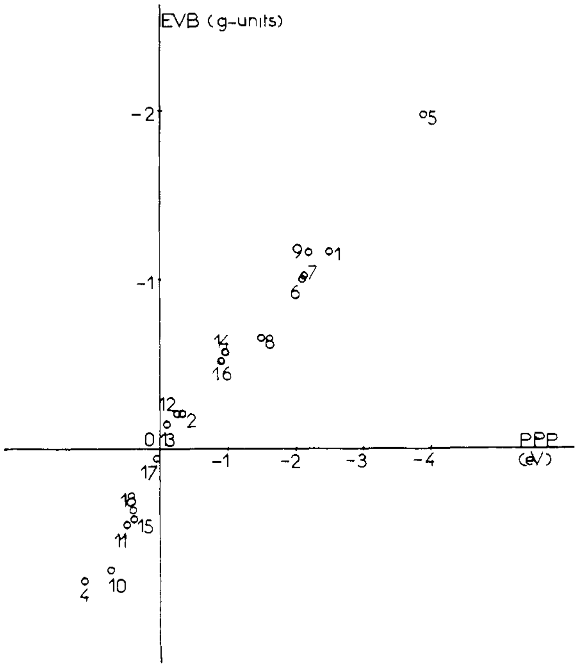

Figure 1. The singlet–triplet separation of a series of conjugated hydrocarbons: correlation between EVB and full CI PPP results (taken from ref 3) (labels of compounds in Table I).

This argument dealing with the lowest diagonal element offers a rationale for the ground-state multiplicity rule, but it *cannot* be considered as a *demonstration* since the off-diagonal interaction between determinants has not been considered. Compounds **13** and **17** in Table I are already almost degenerate at the second-order level, which can only be understood by the role of the off-diagonal elements, since the difference between the lowest $S_z = 0$ and $S_z = 1$ diagonal elements is equal to $\pm g$.

One may notice that the existence of a Kekule formula warrants the existence of singlet ground state (shown clearly by perturbing the localized determinant as done in the PCILO[5] scheme). However, this condition is not necessary since $m^* = m^0$ non Kekule compounds such as compound **13** are not triplet, despite their biradical nature and Hund's rule. This violation of Hund's rule seems normal in our model since the $S_z = 1$ matrix has much higher diagonal elements than the $S_z = 0$ matrix (in this peculiar example the lowest diagonal elements are $-4g$ for $S_z = 1$ and $-5g$ for $S_z = 0$).

For the same reason, cyclobutadiene appears as a natural singlet, as it should, a result which is rather difficult to establish when demonstrated in the MO CI approach.[6] However one may notice that our second-order values sometimes are very far from the exact ones; the cyclobutadiene singlet–triplet separation for instance is overestimated ($2g$ instead of 0.29 eV) and reversely the ST separation is underestimated for benzene ($1.37g$ instead of 3.92 eV). This remark points out the limits of the low-order model, especially for cyclic compounds, and suggests an improvement of the model by including higher order corrections.

II. Higher Order Numerical Results

(1) Choice of the Parameters. The fourth (respectively sixth) order terms are expressed as multiple of $(g/2)\lambda^2$ (respectively $(g/2)\lambda^4$) where

$$g/2 = F^2/\Delta E \tag{2}$$

$$\lambda = -F/\Delta E \tag{3}$$

F being the off-diagonal Fock matrix element between adjacent π AO's and ΔE being the energy difference between a neutral and an ionic pair

$$\Delta E \simeq (\text{aa,aa}) - (\text{aa,bb})$$

or the effective one-center bielectronic repulsion integral in the Hubbard[7] model. The most widely used value of F (equal to β in the PPP Hamiltonian) is −2.35 eV; a reasonable value of ΔE (5.5 eV) leads to $g \simeq 2$ eV. (The value $g = 1.95$ eV, taken in Table I, results from Figures 1 and 2). A fit for the cyclobutadiene ST separation suggests that $\lambda = 0.17$ which is much lower than the theoretical estimate; this apparent contradiction will be discussed in the Conclusion.

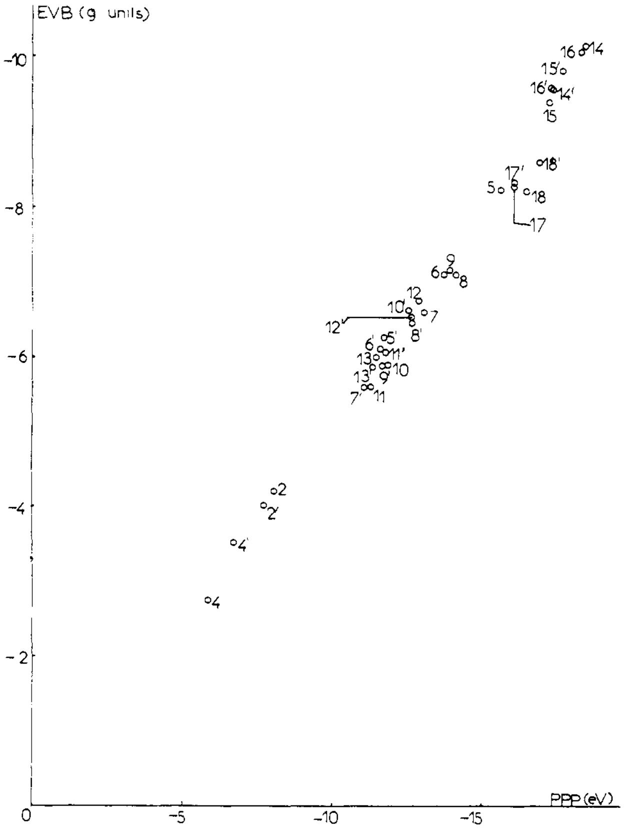

Figure 2. Correlation between EVB and full CI PPP results for a series of conjugated hydrocarbons. Full CI results are taken from ref 3 (labels of compounds in Table I). Primed indexes are concerned with triplet states.

(2) Singlet–Triplet Separation. With regard to the separation between the lowest singlet and triplet of the previously studied series of hydrocarbons, the numerical agreement (cf. Figure 1) with the results of the full π CI has been significantly improved. As expected, the high orders improve particularly the compounds involving four (labeled **2**, **6**, **10**, **12**) or six (labeled **5**, **14**, **15**, **16**) membered rings, which illustrates the importance of cyclic contributions. The much smaller fourth-order one-bond and two-bond corrections also improve the results for noncyclic compounds.

(3) Total Energies. As mentioned in Section I, the zero energy of our VB model is the energy of the highest multiplet and therefore is different from the zero energy of the PPP model. The almost perfect agreement between the fourth and the cyclic sixth-order results with the PPP full CI result of Dönhert and Koutecky,[3] as exemplified in Figure 2, seems almost incredible, since only two parameters have to be used and the size of the diagonalized matrices never exceeded 70, while the PPP Hamiltonian handles several hundred values of the basic parameters for so many different geometries and the full CI result is concerned with a very large number of determinants. This agreement supports two separate conclusions: (i) the efficiency of a Hubbard Hamiltonian (which has been assumed in our derivation for the

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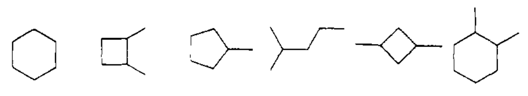
(5) S. Diner, J. P. Malrieu and P. Claverie, *Theor. Chim. Acta*, **13**, 1 (1969); J. P. Malrieu, P. Claverie, and S. Diner, *ibid.*, **13**, 18 (1969); for a review see J. P. Malrieu, in G. Segal "Modern Theoretical Chemistry", Vol. 7, Plenum Press, New York, 1977, p 69.

(6) W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, **99**, 4587 (1977); H. Kolmar and V. Staemmler, *Theor. Chim. Acta*, **48**, 223 (1978).

(7) J. Hubbard, *Proc. R. Soc. London, Ser.* **1976**, 283 (1963).

Table II. Weight of the Different Types of Spin Distributions in the Ground-State Wave Function of Six Molecules[a]



			$p = 0$			
q	0.457	0.399	0.833	0.509	0.529	0.316
m	2	2	6	1	1	2
q/m	0.229	0.200	0.139	0.509	0.529	0.158
			$p = 2^b$			
q	0.521	0.503	0.020	0.159	0.266	0.489
m	12	8	4	1	3	16
q/m	0.043	0.063	0.005	0.159	0.089	0.031
			$p = 3^c$			
q	0.022	0.093	0.126	0.263	0.177	
m	6	8	6	6	8	
q/m	0.004	0.012	0.021	0.044	0.022	

[a] p = deviation of the number of spin alternation (n_i) from its maximum value, m = number of determinants with n_i spin alternations, q = weight of these determinants, and q/m = mean weight of these determinants. [b] Except for the fourth compound, for which $p = 1$. [c] Except for the fourth compound, for which $p = 2$.

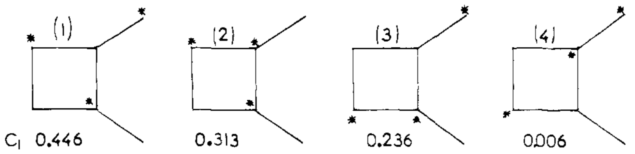
sake of simplicity), which gives results almost identical with those of the more complex PPP Hamiltonian, as already noticed several times (the basic effective parameters of a π calculation are the hopping integral between adjacent bonds and the effective repulsion of an electron pair on the same center; the other parameters play a minor role); (ii) the efficiency of our effective valence bond model to reach the full π CI results.

(4) A Few Other Examples. Comparison could be made for the neutral singlet excited states such as the ^1A_g "forbidden" state of linear polyenes; for instance the model predicts a $^1A_g \rightarrow {}^1A_g$ transition energy of 3.52 eV for octatetraene, for which the experimental (0–0) transition is observed at 3.46 eV.[8]

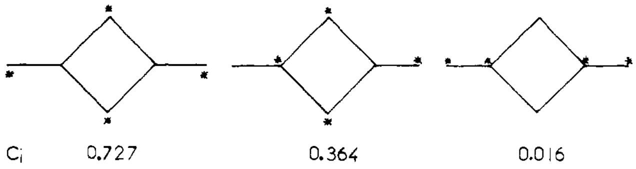
One may compare higher excited states for benzene for which the neutral singlets are calculated in the EVB model to be 5.56 ($^1B_{2u}$) and 8.70 eV ($^1E_{2g}$) above the ground state, which compares fairly well with the π CI ab initio result using a minimal basis set[9] (respectively 5.2 and 8.4 eV) or with the full π CI semiempirical results of Čížek et al.[10] The neutral triplets ($^3B_{1u}$, $^3E_{1u}$, and $^3E_{2g}$) are calculated to be 3.82, 5.85, and 7.23 eV above the ground state, while ref 9 gives them at 3.9, 5.3, and 7.2 eV (experimental values being 3.95, 4.75, and 6.6 eV).

One should notice that the formalism equally applies to the odd numbers of electrons, i.e., to neutral free radicals, without any special difficulty. For instance, the lowest excited state of the benzyl radical are calculated to lie 3.6 and 4.1 eV above the ground state, the experimental value being 2.7 and 4.0 eV. One may notice that the EVB model is in good accord with the CI or experimental results, especially for benzene. A more sophisticated model, which should not consider all bond lengths equal, would certainly give better results for the other compounds.

(5) Domination of the Spin Alternation in the Wave Function. Spin alternating configurations are only possible on alternant hydrocarbons; in that case (and if $m^* = m^0$), there are only two, differing by a full spin exchange. As noted previously the spin alternating configurations have the lowest diagonal energy in the second-order Hamiltonian and play a major role in the lowest eigenstates. Table II gives the weights of these alternating configurations in the ground state of a series of molecules, compared with those of more numerous less ordered configurations where only n_i (lower than the number of bonds n_b) spin alternations occur. The preference for spin alternation may be measured by comparing the normalized weight $(q/m)n_i$ of the configurations with n_i spin alternations $p_i = n_b - n_i$ (p_i is the departure from the maximum spin alternation), $q^{p_i} = \sum c_i^2(n_i)$, m^{p_i} = number of determinants with n_i spin alternations, and $(q/m)^{p_i} = q^{p_i}/m^{p_i}$ = average weight of the determinants with n_i spin alternations. As appears from Table II the molecule may be viewed as a preferentially spin-ordered assembly (look, for instance, at the small weight of the configurations strongly departing from spin alternation); the spin exchanges may be viewed by introducing some moderate disorder around the perfect spin alternations considered as basic structures. The various determinants having equal numbers of spin alternations, i.e., equal second-order diagonal energies, may have very different weights, according to their proximity to the fully alternant determinant(s); as an example, one may quote the dimethylenecyclobutene for which



The weak coefficient of structure **4** with respect to structures **2** and **3** may be understood by the fact that it can only be reached from **1** through two spin exchanges instead of one. The same phenomenon can be observed for the 1.3 dimethylenecyclobutadiene, for which $m^* = m^0 + 2$

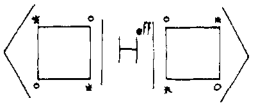


In view of the dominance of spin alternant structures, one might be tempted to use the exponential transformation recently proposed by Klein et al.[11] which introduces the local spin disorder in a way analogous to the coupled cluster expansions for the correlation problem.

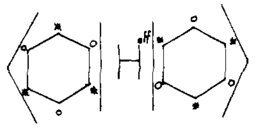
III. Aromaticity and Ring Currents

(1) Dominant Role of Cyclic Spin Exchange. The $4n$-membered circles are supposed to have ground-state singlets less stable than the $4n$ open chain (antiaromaticity), while the $(4n + 2)$ circles should exhibit a ground-state stabilization with respect to the corresponding linear molecules. Comparing the values for $N = 4$ and $N = 6$, one gets equal energies for butadiene (−8.13 eV) and cyclobutadiene (−8.19 eV) while benzene (−16.eV) is greatly stabilized with respect to hexatriene (−12.9 eV). It is worthwhile to analyze the origin of this effect in some detail. The singlet cyclobutadiene energy at the second-order level is greatly overestimated (by 3.5 eV) while benzene singlet energy is underestimated (by 1.2 eV) when treated at the fourth-order level. When fourth-order cyclic corrections are omitted in cyclobutadiene, the discrepancy remains. Cyclic nth-order corrections therefore appear to play the main role in the departure of energy from linearity.

Among the cyclic terms, the largest one has been shown to be the circular spin exchange (and the diagonal associate term of opposite sign).



$$= 40F^4/\Delta E^3 = 20g\lambda^2 \simeq 1.2 \text{ eV}$$



$$= 504F^6/\Delta E^5 = 252\, g\lambda^4 \simeq 0.46 \text{ eV}$$

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(8) M. F. Granville, G. R. Holton, B. E. Kohler, *J. Chem. Phys.*, **72**, 4671 (1980).

(9) P. Rancurel, B. Huron, L. Praud, J. P. Malrieu, and G. Berthier, *J. Mol. Spectrosc.*, **60**, 259 (1976).

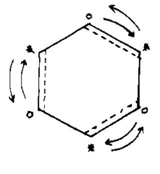
(10) J. Čížek, A. Pellégatti, and J. Paldus, *Int. J. Quantum Chem.*, 9, 987 (1975).

(11) D. J. Klein and M. A. Garcia-Bach, *Phys. Rev.*, 3, **19**, 877 (1979).

Its dominant role is illustrated by removing it from the matrix Hamiltonian; this leads to a 0.48-eV energy loss for benzene.

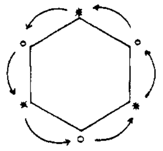
The (anti) aromatic specific energy corrections seems therefore to be due to a circular spin-exchange N-body operator coupling the two spin alternant determinants. One must remember that this off-diagonal term corresponds with equal diagonal terms of opposite signs on the spin alternant determinant, which stabilizes them if the off-diagonal term is positive.

(2) The Physical Content of the Cyclic Spin Exchange: A Ring Current. Let us examine the possible perturbative travel, i.e., the electron jumps, which may be allowed to reach one of the spin alternant determinants in a circle of its full spin-exchanged associate. As a limit case one might imagine processes which permute the electrons on each double bond of a Kekuke graph

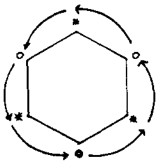


this corresponds to unlinked contributions involving only $N/2$ bonds and disappears in the perturbation development. No segment can be used in both directions at the nth order since this would necessarily imply that two adjacent bonds are not concerned at the nth step, resulting in an unchanged spin on one carbon.

The only linked process to perform the whole spin permutation



is a circular clockwise or anticlockwise movement of the electrons. Each bond is involved once, and all the electrons are involved. This matrix element (and its diagonal counterpart) represents the perturbative transcription of a collective circular movement of electrons along the circle, i.e., a ring current. (One should notice that the diagonal corrections do *not* necessarily involve *all* electrons: for instance, the process



only involves α-spin electrons.) These ring currents are therefore responsible for the specific cyclic energy.

The concept of ring currents plays an important role in the interpretation of the magnetic properties of aromatic compounds[12] although its necessity has been questioned.[13] Their role in the ground-state stabilization, sometimes called strobilism,[14] was not clear. A perturbative approach had been proposed by one of us[15] starting from localized MO's, i.e., from a Kekule graph as zeroth-order wave function and using diagrammatic expansion, but this demonstration did not include correlation effects.

(3) The Parity Rule of (Anti) Aromaticity. In order to establish the general $(4n)/4n + 2$ rule of (anti) aromaticity one must demonstrate (i) that the cyclic exchange term between the two spin alternant determinants ($\phi_1 = |1\bar{2}3...\bar{N}\rangle$ and $\phi_2 = |\bar{1}2\bar{3}...N\rangle$) has a constant positive sign $\langle\phi_1|H^{\text{eff}}|\phi_2\rangle > 0$ and (ii) that the singlet ground state involves an out-of-phase combination of these determinants in $4n + 2$ cycles and an in-phase combination in $4n$ cycles

$$\psi_{\text{GS}}{}^1 = \frac{1}{\sqrt{2}}\left[\left|1\bar{2}3...\bar{N}\right| - \left|\bar{1}2\bar{3}...N\right|\right] + \text{others for } N = 4n + 2$$

$$\psi_{\text{GS}}{}^1 = \frac{1}{\sqrt{2}}\left[\left|1\bar{2}3...\bar{N}\right| + \left|\bar{1}2\bar{3}...N\right|\right] + \text{others for } N = 4n$$

The second result is evident since the ground state is always ^1A_g in character; considering the symmetry $\mathcal{R}$ with respect to a plane bisecting two opposite bonds of the ring, this symmetry operation changes all the spins and transforms ϕ_1 into $\pm\phi_2$. The parity of $N/2$ determines the symmetry of the ground-state eigenvector since

$$\mathcal{R}\phi_1 = \phi_2 \text{ for } N = 4n$$

$$\mathcal{R}\phi_1 = -\phi_2 \text{ for } N = 4n + 2$$

The $\langle\psi_{\text{GS}}{}^1|\bar{H}^n|\psi_{\text{GS}}{}^1\rangle$ necessarily involves

$$+\langle\phi_1|H|\phi_2\rangle \text{ if } N = 4n$$

$$-\langle\phi_1|H|\phi_2\rangle \text{ if N} = 4n + 2$$

and the aromaticity rule is demonstrated if $\langle\phi_1|H|\phi_2\rangle$ is actually positive. The proof is given in Appendix.

This matrix element allows a significant resonance energy (antiresonance for $4n$ ring singlets) between the two spin alternant formulas, and the resulting picture of benzene-like molecules is a turning spin wave. A time-dependent perturbation theory would allow for some time scale to this collective exchange process. One may notice that in $4n + 2$ rings the extradiagonal correction must be added to the attractive diagonal cyclic correction, resulting in a strong aromatic stabilization, while a cancellation occurs between the diagonal and off-diagonal corrections for the $4n$ rings, leading to a nonaromaticity rather than an antiaromaticity, as numerically observed in Table I for cyclobutadiene, which has the same π energy as the butadiene.

We have not been able to derive the algebraic N dependence of the resonance $\langle\phi_1|H|\phi_2\rangle$ integral, i.e., the N dependence of the (anti) aromatic correction.

IV. Conclusion

The numerical accuracy of the EVB Hamiltonian proposed in part 1 appears from a numerical comparison with full π CI results of ref 3, for a wide series of chemical graphs. This agreement is somewhat surprising in view of (i) the use of two parameters only (i.e., a Hubbard Hamiltonian), instead of several hundreds of different values for the bielectronic integrals and (ii) the crudeness of the definition of the zeroth-order subspace (on the neutral determinants) and the strength of the coupling with adjacent ionic determinants. The perturbation actually would diverge for reasonable values of parameters F and ΔE (cf. the sixth-order term $504F^6/\Delta E^5$), and we were led to use as independent basic parameters the second-order parameter g $(=2F^2/\Delta E)$ and the higher order ratio λ $(=F/\Delta E)$. One may notice that by using a PPP model instead of a Hubbard Hamiltonian would introduce larger $\Delta E'$ $(>\Delta E)$ denominators for nonadjacent monoionic intermediate determinants and the reduction of λ may partly take this factor into account. The decoupling of these two parameters ($g = 2$ eV, $\lambda = -0.17$) essentially reflects, in our opinion, the divergent behavior of the QDMBPT when applied to the problem with usual values of the integrals. The QDMBPT should converge for a low λ ratio, i.e., small hopping integrals (large interatomic distances) and/or large ΔE values (i.e., large self-repulsion integrals). The two-body (ethylene) problem suggests a radius of convergence equal to $\lambda = -{}^1/_4$, i.e., $4|F| < |\Delta E|$, as appears clearly from eq 1. In an ab initio VB calculation, Norbeck and Gallup[13] noticed that for benzene their symmetrized ionic structures had lower energies than the symmetrized neutral states. This surprising statement is no longer valid in the case of ZDO Hamiltonians in which the monoionic structures do not interact.[13] But is is sure that for all types of Hamiltonians the lowest ionic eigenstates of such molecules are embedded in the upper part of the neutral

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(12) E. Hückel, in "Grundzüge der Theorie ungessätigter und aromatischer Verbindungen", Verlag Chemie, Berlin 1938. M. J. S. Dewar, "Aromaticity", Special Publication n°21, p. 177, London Chemical Society (1967).

(13) J. M. Norbeck and G. A. Gallup, *J. Am. Chem. Soc.*, **95**, 4460 (1973); *96*, 3386 (1974).

(14) I. Nebot-Gil and J. P. Malrieu, *J. Am. Chem. Soc.*, in press.

(15) J. P. Malrieu, (O. Chalvet, R. Daudel, S. Diner, and J. P. Malrieu (eds)), in "Localization and Delocalization in Quantum Chemistry", D. Reidel Pub. Co, Dordrecht-Holland (1975) p. 335.

spectrum and this situation may result in a nonconvergent behavior of the perturbation expansion. However, the success of the model proves the ability of the QDMBPT to derive the logic and structure of an effective Hamiltonian which remains efficient beside the radius of convergence of the QDMBPT used to establish it, provided that the high orders are tempered through a diminution of $|\lambda|$.

Anyway the EVB Hamiltonian seems a very promising tool. It gives accurate results at a very low cost; diagonalization of moderate matrices (up to 12 atoms), built according to a very simple logic, gives results very close to the full π CI result. The model has been used elsewhere[14] to predict the evolution of the $^1A_g \rightarrow {}^1A_g$ forbidden transition in the series of linear polyenes and the N dependence of the lowest allowed transition energy in odd polyenes.

The demonstration of the aromaticity rule for cyclic polyenes has been achieved in a highly correlated model, and its physical content as a collective circular movement of electrons supports the interpretation of aromaticity that is due to ring currents. This example illustrates the power of the QDMBPT applied to the VB problem.

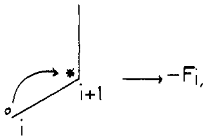
The analysis of the resulting wave function (i.e., the component of the exact wave function on the neutral subspace of the VB theory) shows the importance of spin alternation (assumed and verified by the ASMO method[16]). The picture of the electronic structure of the molecule, as it arises from our EVB model, is somewhat different from the usual MO description, in terms of filling canonical delocalized MO's or coupled electron pairs in localized bond MO's. The "faithful couple" of the electron pair[17] is replaced by a dance of electrons of opposite spins, permuting their positions through instantaneous ionic pairs; that dance is far from being disordered since some basic figures (regular spin alternation) are dominant (at least locally) and since some collective movements such as the ring currents along the circles appear to play a prominent role.

IV. Appendix. Sign of the Full Spin Permutation Matrix Element of Order $N = 2n$ for an N-Membered Ring

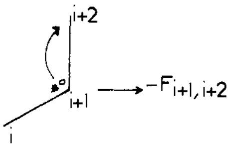
One must prove that, ϕ_1 and ϕ_2 being the two neutral determinants with full spin alternation

$$\langle \phi_1 | H^{\mathrm{eff}} | \phi_2 \rangle = \langle 1\bar{2}3...\bar{2}n | \bar{H}^{2n} | \bar{1}2\bar{3}...2n \rangle > 0 \ \forall n$$

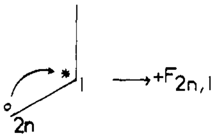
The 2nth-order perturbative process generating this effective interaction goes through (multi) ionic intermediate determinants which will be written according to the following rules: the AO's appear in their natural (cyclic) sequence; when two electrons are on the same center, the β-spin AO will be put in second position. The determinant 2^+6^- will be written $|1\bar{3}4\bar{5}6\bar{6}\bar{7}8]$. Let us examine the signs of the matrix elements associated with the 2n circular electron jumps, allowing for ϕ_2 to be reached from ϕ_1; as already noted each electron only jumps to the neighboring position. The negative signs will be associated to jumps of the β-spin electron from i to $i + 1$ such as

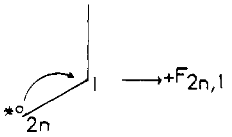


But it must necessarily be followed by another jump



also associated with a negative sign. The only exception concerns the events on the last $[2n - 1]$ bond for which





The 2nth-order spin-exchange process therefore corresponds to a negative numerator. Since the denominator $(-\Delta E)^{2n-1}$ is negative at the same order, the resulting contribution is necssarily positive.

Registry No. 1, 106-99-0; **2**, 1120-53-2; **3**, 4095-06-1; **4**, 115-11-7; **5**, 71-43-2; **6**, 5291-90-7; **7**, 13753-03-2; **8**, 497-20-1; **9**, 3227-90-5; **10**, 80673-42-3; **11**, 926-56-7; **12**, 63943-67-9; **13**, 513-81-5; **14**, 32796-95-5; **15**, 108-38-3; **16**, 502-86-3; **17**, 52385-09-8; **18**, 924-71-0.

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[16] R. Pauncz, "Alternant Molecular Orbital Method", W. B. Saunders, Philadelphia, 1967.

[17] L. Salem, *J. Chem. Educ.*, **55**, 344 (1978).

Electron-Transfer Catalysis. Radical Chain Mechanism for the Ligand Substitution of Metal Carbonyls

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Abstract: A novel chain process for the ligand substitution of metal complexes is revealed by bulk and transient electrochemical methods. The large turnover numbers that are obtained for the ligand substitution of the tris(acetonitrile) complexes of molybdenum and tungsten carbonyls with phosphines and isocyanides underscore the electrocatalytic phenomenon. The efficient chain process derives from the substitution lability of the cation radicals, which are formed by the one-electron oxidation of metal carbonyls and subsequently undergo rapid electron transfer, as in Scheme II. The driving force for ligand substitution is related to the relative stabilities of the cation radicals. Electron-transfer equilibria between these cation radicals can be evaluated from the standard reduction potentials $E°$ or the cyclic voltammetric peak potentials E_p. The initiation of the chain process is finely tuned to the value of $E°$ and E_p for the various metal carbonyls. The effectiveness of metal carbonyls as catalysts in the enhanced oxidation of nucleophiles such as triphenylphosphine is also described.

Ligand substitution of the octahedral complexes of the transition metals is usually considered to proceed via the even-numbered, 16- and 18-electron intermediates.[1,2] Thus the displacement of ligands from a series of group 6B metal carbonyls $LM(CO)_5$ by

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