The results are that $k_0 = 1.9 \times 10^9$ M^{-1} s^{-1} and $k_0' = 3.0 \times 10^7$ M^{-1} s^{-1}. It is noticeable that k_0' is much slower than the diffusion rate, while the same rate constant for other unhindered diradicals (triplet *o*-xylylenes and type II diradicals) is reported to be nearly diffusion controlled ($>10^9$ M^{-1} s^{-1}).[18a–d,45b] However, the fact that the magnitude of k_0 is comparable to the rate for tiplet quenching of various aromatic ketones[45b,48] indicates that all our data are internally consistent.

It is commonly assumed that the diradical species that react readily with oxygen (triplet) are in their triplet states.[7,18a–d,45b,49] Thus the rate constant k_0' may be regarded as that for the reaction between ^{3}A and O$_2$.

The data of experiment 6 in Table I (Φ(**4**) = 0.031) and of experiment 2 in Table III (0.1% yield of **4**) suggest that ^{3}A is also formed from either the direct photochemical or thermal cleavage of **2**.[50] It should be noted, however, that the product ratio **4**/**1** from the thermolysis (0.1/89 = 0.0011) is much smaller than that from the photolysis (0.031/0.20 = 0.16).

There are several factors to be considered in order to explain this discrepancy, e.g., (1) the difference in oxygen concentrations,[19] (2) effect of higher vibrational level reactions, and (3) the difference in Arrhenius activation parameters (E_a and log A). A possible explanation in terms of the last point is as follows. From consideration of energy levels and spin multiplicities described in Figure 6, the ISC process ^{1}B → ^{3}A may have smaller values for E_a and log A than the spin-allowed process ^{1}B → ^{1}A. As a result the path **2** → ^{1}B → ^{1}A → **1** can overwhelm the path **2** → ^{1}B → ^{3}A → **4** at the high temperatures required for thermolysis (134 °C). The same line of discussion was employed for competition between the triplet dimerization and the singlet ring closure of some trimethylenemethane diradicals.[7]

Experimental Section

Materials. 2,4,6-Triisopropylbenzophenone (**1**) and 4,6-diisopropyl-2,2-dimethyl-1-phenyl-1,2-dihydrobenzocyclobuten-1-ol (**2**) were prepared by a previous method.[20e] Hexane, methanol, acetonitrile, acetone, and benzene were of spectral grade and used as received. Valerophenone and *tert*-butylbenzene were distilled before use.

The isolation and structural assignment of the anthrone **3** and the peroxide **4** have already been reported.[20d,e]

The various instrumentations and the method for quantum yield measurements are the same as those described previously.[15] However, 254-nm irradiations were performed with a 10-W low-pressure mercury lamp (Vycor lifter) and their quantum yields are based on ferrioxalate actinometry. All compounds, **1**–**4** and acetophenone, were analyzed with high-pressure liquid chromatography (silica gel column, hexane–ethyl acetate eluent) with use of methyl 2-naphthyl ketone as an internal standard.

Thermolyses were carried out on a 5-mL scale in a 10-mL two-necked flask.

Acknowledgment. We are indebted to the Ministry of Education of Japan for financial aid under a special research project.

Registry No. 1, 33574-11-7; **2**, 33574-16-2; **3**, 86177-63-1; **4**, 86177-64-2; valerophenone, 1009-14-9; benzene, 71-43-2.

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[50] The product ratio Φ(**4**) vs. Φ(**2**) obtained from the photooxidation of **2** (experiment 6 in Table I) is Φ(**4**)/Φ(**2**) = 0.031/(1 − (0.20 + 0.031 + 0.01)) = 0.031/0.76 = 0.041. This value is slightly smaller than that obtained from the photooxidation of **1** (experiment 8 in Table I, Φ(**4**)/Φ(**2**) = 0.022/0.45 = 0.049), although the oxygen concentration for the former reaction conditions ([O$_2$] = 1.5 × 10^{-2} M in oxygen-saturated hexane[47]) is about eight times that for the latter reaction conditions ([O$_2$] = 1.9 × 10^{-3} M in air-saturated benzene[47]). This fact also supports the idea that the diradical species photogenerated from **1** and **2** are kinetically distinguishable (^{3}A and ^{1}B, respectively).

Looking at Chemistry as a Spin Ordering Problem

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Abstract: The effective valence-bond Hamiltonian of Heisenberg type previously derived for the lowest states of π systems of conjugated molecules allows the projection of the information on neutral situations that differ only by spin ordering. The analysis of the wave function in terms of through-space spin correlation shows the dominance of spin alternation in the ground state and the spin wave nature of the lowest triplet. The strength of a bond is translated by the probability of finding a local singlet arrangement on it. This index (local singlet probability) nicely correlates with the experimental bond lengths. For free radicals (and triplet states) the projected wave function allows a direct estimate of spin densities.

The quasi-degenerate perturbation theory (QDPT)[1–7] is a fascinating tool that allows the building of effective Hamiltonians in a deductive way, in which the information is reduced to a low-dimensional problem. The "exact" or initial problem $H\Psi_m = E_m\Psi_m$ is transformed by considering a limited subspace $\{S\}$ of dimension n; considering the projector P_S

$$P_S = \sum_{K\in S} |K\rangle\langle K|$$

one tries to find an effective Hamiltonian H^{eff} restricted to $\{S\}$ such that

$$\left.\begin{aligned} H^{\text{eff}}\psi_m &= E_m\psi_m \\ \psi_m &= P_S\Psi_m \end{aligned}\right\} \quad m = 1, n$$

the n eigenvalues of H^{eff} are eigenvalues of H, and the eigenvectors ψ_m are projections of the corresponding n eigenvectors of H. The QDPT algorithms allow the fulfillment of this challenge in a perturbative way. Other iterative variational procedures are also available for the same purpose,[8] derived from the Bloch equation.

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Previous papers[9] (here after called papers I and II) applied this approach[10] to the neutral states of π systems as treated through PPP[11] or Hubbard[12] Hamiltonians. For this model problem, it is worthwhile turning back to the basic lessons of valence bond theory; it is well-known that the lowest states of these homonuclear assemblies with one electron per site are essentially neutral, in the sense that the corresponding wave function has its largest components on valence bond determinants that bear only one electron on each site. These VB neutral determinants have the lowest energy and are degenerate in the VB matrix. One may then be tempted to consider the subspace S of neutral determinants as a quasi-degenerate subspace and to apply the QDPT to reach the eigenvalues of the "neutral" eigenstates of the total problem. This has been done in papers I and II. Of course the matrix elements of such an effective Hamiltonian can simply interchange spins on different sites, and the resulting H^{eff} belongs to the class of effective magnetic Hamiltonians or Heisenberg Hamiltonians.[13] Our previous approach may be viewed as an extension to higher orders of the famous Anderson treatment for the Mott insulators[14] in solid-state physics. We actually have shown that higher orders introduce, besides the second-order effective exchange between adjacent atoms, long range (1–3) exchanges between nonnearest neighbors and cyclic large contributions on four- and six-membered rings that represent circular motions of the electrons along the rings (i.e., ring currents). This fruitful preliminary exploration was concentrated on the energies, topological logic, transferability, and physical significance of the matrix elements of the effective Hamiltonian.

The present paper is devoted to the analysis of the projected wave function. The question relevant to that truncated wave function may be formulated as follows:

(i) The usual (complete) wave function is essentially analyzed through density matrices. The first-order density matrix has been widely used through its diagonal and off-diagonal elements (charge and bond-order index) to correlate them with molecular properties. The second-order density matrix (besides the one-electron model) allows to picture the charge correlation, i.e., the conditional probability for finding two electrons on two sites. Since the truncated wave functions deals only with neutral situations, the nontrivial information can concern only the spin repartition and its fluctuation. One should study whether information concerning the spin ordering should be used to interpret—for instance—the various strengths of the different bonds (as experimentally evident through their bond lengths) or the spin density distribution (as experimentally derivable from the ESR spectra), which are rather well reproduced by the first-order density matrix in the MO treatments. If the answer is positive and if it is possible to draw up a logical picture of the truncated wave function based on rules of spin distribution, then a new description of the electronic assembly of the molecule will emerge as governed by spin ordering and its fluctuation. The present paper gives the basic illustration of this new description of the molecular order, as results from the spin correlation analysis, from the appropriate bond-strength index and from the spin density analysis and discusses some epistemologic consequences of these deductive effective Hamiltonians.

(1) Spin Correlation Analysis

(A) Form of the Truncated Wave Function. The effective Hamiltonian proposed in papers I and II is built on the neutral determinants only (and can deliver only the energies of the eigenstates having large components on these neutral determinants).

The effective (or truncated) wave functions are linear combinations of neutral (neut) determinants:

$$\psi_m = \sum_{K \in \text{neut}} C_{mK} \phi_K \tag{1}$$

where the ϕ_K's all have one electron per site and only differ by their spin distribution. These neutral determinants have various numbers of spin-alternating bonds.

In the second-order effective Hamiltonian established previously, the energy of the (unique) determinant having all spins parallel (which is the eigenstate of highest multiplicity and $S_z = N/2$) is taken as conventional zero energy for the considered molecule. The second-order effective Hamiltonian reduces to

(i) diagonal operators

$$-g_{ij}(\mathrm{a}_{\bar{i}}^{+} a_j^{+} a_j a_{\bar{i}} + a_i^{+} a_{\bar{j}}^{+} a_{\bar{j}} a_i)$$

i and j being bonded where

$$g_{ij} = +2F_{ij}^{2}/\Delta E_{i\rightarrow j} \tag{2}$$

reflects the possible passage to ionic structures $\mathrm{I}^+\mathrm{J}^-$ on the chemical bonds, through the F_{ij} (β_{ij} in PPP notation) hopping integrals, $\Delta E_{i\rightarrow j}$ being the transition energy from the neutral situation to the ionic $\mathrm{I}^+\mathrm{J}^-$ zwitterion, in the ZDO approximation. For nonorthogonal valence bond approaches this coupling essentially involves an overlap (S') dependent factor $2FS'$ (a purely covalent contribution).

These diagonal operators may be written in a symbolic way as

$$H^{\mathrm{a}} = -\sum_{\text{bonds } ij} g_{ij}[|\bar{i}j\rangle(\bar{i}j| + |i\bar{j}\rangle(i\bar{j}|] \tag{3}$$

and they count the number of spin alternant bonds

$$(\phi_K|H^{\mathrm{a}}|\phi_{\mathrm{K}}\rangle = -g n_K^{\text{alt}} \tag{4}$$

if all bonds are identical, n_K^{alt} being the number of spin alternating chemical bonds in the determinant ϕ_K;

(ii) off-diagonal operators

$$g_{ij}(a_{\bar{i}}^{+} a_j a_{\bar{j}} a_i + a_i^{+} a_{\bar{j}}^{+} a_j a_{\bar{i}})$$

i and j being bonded, which may be written

$$g_{ij}[|i\bar{j}\rangle(\bar{i}j| + |\bar{i}j\rangle(i\bar{j}|]$$

and interchanges the spins on atoms I and J when the IJ bond exhibits a spin alternation.

This operator has only off-diagonal elements in the basis of the VB neutral determinants; it couples ϕ_K and ϕ_L if they are related by a single spin permutation across an IJ bond and only differ by this spin alternation:

$$H^{\mathrm{b}} = \sum_{\text{bonds } ij} g_{ij}[|i\bar{j}\rangle(\bar{i}j| + |\bar{i}j\rangle(i\bar{j}|] \tag{5}$$

$$H^{\text{eff}} = H^{\mathrm{a}} + H^{\mathrm{b}} + \text{higher orders} \tag{6}$$

From the nature of H^{a} and H^{b} it is easy to establish that

$$\sum_{L}(\phi_K|H^{\text{eff}}|\phi_L\rangle = 0 \tag{7}$$

From eq 4 and 6 it is evident that (i) the lowest energy determinants in the effective VB matrix are those that exhibit the largest number of spin alternations on chemical bonds; (ii) these lowest energy determinants are also the most coupled ones. As a result, it is clear that they will contribute largely to the lowest eigenvectors of the effective Hamiltonian, i.e., to the lowest truncated eigenvectors.

This remark had been formulated briefly in paper II, and a rough correlation has been established between the number of spin alternations of a determinant and its weight in the lowest eigenstate ψ_1: $|C_{1K}|$ decreases when n_K^{alt} decreases. From this point, one might try to analyze directly the lowest eigenstates in order to understand in greater detail and with a sufficient accuracy the content of ψ_1 and ψ_2, and the weights C_{1K} and C_{2K} on the various spin repartitions. This will be achieved in a forthcoming paper. In the present work we shall simply analyze the content of the wave function from statistical indices and show their efficiency.

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In practice all the numerical calculations of the truncated functions involve the small effective three-body fourth-order operators proposed in ref 9 (and six-body terms effective on six-membered rings).

(B) Spin Correlation Analysis. The first-order density matrix ρ of the projected wave functions would be trivially identical; when expressed in the basis of the local AO's, all diagonal terms are equal to 1, and the off-diagonal terms are zero since

$$\langle\phi_K|a_p^+a_p + a_{\bar{p}}^+a_{\bar{p}}|\phi_L\rangle = \delta_{KL} \qquad \rho_{pp} = 1$$
$$\langle\phi_K|a_p^+a_q|\phi_L\rangle = 0 \qquad \rho_{pq} = 0 \tag{8}$$

with ϕ_K and ϕ_L differing necessarily by two spin orbitals (i.e., by at least one spin interchange). As a consequence, one may notice that the Heisenberg Hamiltonians do not satisfy the conditions of the Hohenberg and Kohn theorem[15] since the energy is not determined from the first-order density matrix.

The first useful information is therefore contained in the second-order density matrix, the diagonal elements of which give the conditional probability $\mathcal{P}_{pq}$ of finding an electron with a given spin on atom p and an electron with the same (opposite for $\mathcal{P}_{p\bar{q}}$) spin on site q:

$$P_{pq} = a_p^+a_pa_q^+a_q = |pq\rangle\langle pq|$$
$$\mathcal{P}_{pq}^{\ m} = \langle\psi_m|P_{pq}|\psi_m\rangle \tag{9}$$

The practical calculation of such an index is exemplified in the Appendix for butadiene.

One may, for instance, study the probability of finding two electrons of opposite spins on atoms p and q (i.e., a spin alternation) through $P_{p\bar{q}} + P_{\bar{p}q} = |p\bar{q}\rangle\langle p\bar{q}| + |\bar{p}q\rangle\langle\bar{p}q|$ as a function of the distance between p and q:

$$\mathcal{P}_{pq}^{\ A,m} = \langle\psi_m|P_{p\bar{q}} + P_{\bar{p}q}|\psi_m\rangle \tag{10}$$

If the tendency to spin alternation is strong in the lower eigenstates, considering a linear polyene and assuming that atom 1 bears, for instance, an α spin, one should find a large probability of having simultaneously a β spin on atom 2, then a somewhat smaller but rather large probability of finding an α spin on atom 3, and so on. For large polyenes the conditional probability $\mathcal{P}_{1\bar{q}}$ should therefore oscillate above and below its asymptotic value 0.5 (equal probability of finding α or β spins in q when atom 1 bears an α spin), which represents a perfect lack of spin ordering; the amplitude of the oscillations should diminish when q increases, i.e., when the distance between the two considered atoms increases.

Figures 1 and 2 give the conditional probability for spin alternation in the two lowest states of $n = 8$ linear polyene. The result deserves some comments:

The spin ordering is stronger in the lowest triplet than in the singlet ground state. For the triplet state, the spin correlation remains very large between the first and the last atoms of octatetraene ($n = 8$), and one may see that state as a stationary spin wave covering the whole skeleton of the molecule. The difference between the two states in this respect will be discussed later on.

For the lowest singlet state, the spin alternation is important, but it appears at a short- or medium-range order.

One may consider as reference atom the second atom, third atom, or any internal atom as well, as pictured in Figure 1c,d, and two amazing features appear by comparing parts a–c of figures 1, for instance. First the probability of finding a spin alternation on a double bond ($\mathcal{P}_{1\bar{2}}, \mathcal{P}_{3\bar{4}} \cong 0.9$) is much larger than the corresponding probability for a single bond ($\mathcal{P}_{2\bar{3}}, \mathcal{P}_{4\bar{5}} \cong 0.67$); the bond alternation is reflected by the spin alternation probability. As a second remark one may notice that the spin alternation probability $\mathcal{P}_{ij}$ seems to depend essentially on the distance between i and j (and the number of intermediate double and single bonds) since, for instance, $\mathcal{P}_{1\bar{3}} \cong \mathcal{P}_{3\bar{5}}$.

The damped spin wave seems to have the same damping around the various points, and this long-range damping should be essentially independent of the basic effective exchange operator g (since the effective Hamiltonian is proportional to g, the effective functions do not depend on its amplitude).

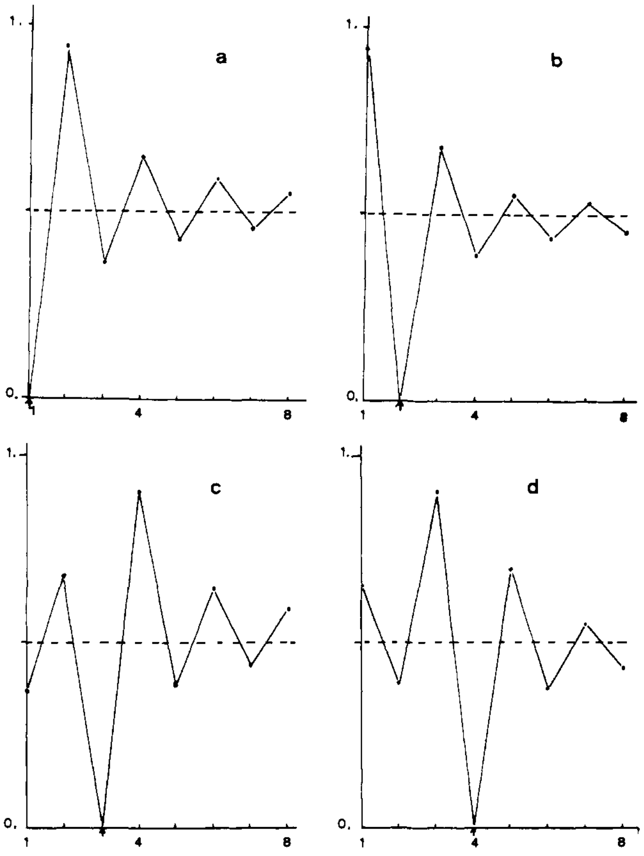


Figure 1. Probability for spin alternation $\mathcal{P}_{ij}^{\ A}$ (i.e., to find a β spin on j atom when i bears an α spin) in the ground-state singlet octatetraene: (a) $i = 1$; (b) $i = 2$; (c) $i = 3$; (d) $i = 4$.

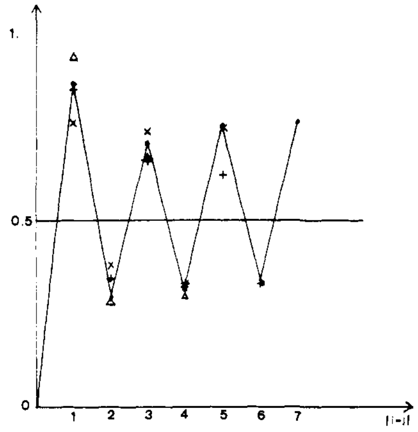
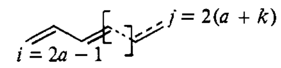
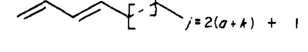


Figure 2. Probability for spin alternation $\mathcal{P}_{ij}^{\ A}$ between atoms i and j as a function of the i–j distance, in the lowest $S_z = 0$ triplet state of octatetraene, for different positions of atom i: (·) $i = 1$; (+) $i = 2$; (×) $i = 3$; (△) $i = 4$.

A more precise analysis shows that the $\mathcal{P}_{ij}^{\ A,o}$ probability depends on the number of single and double bonds connecting the atoms I and J. It is different for odd $|i - j| = 2k + 1$, according to the parity i, since for odd i



one finds $k + 1$ double and k single intermediate bonds while for even i



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(15) P. Hohenberg and W. Kohn, *Phys. Rev. B*, **136**, 864 (1964).

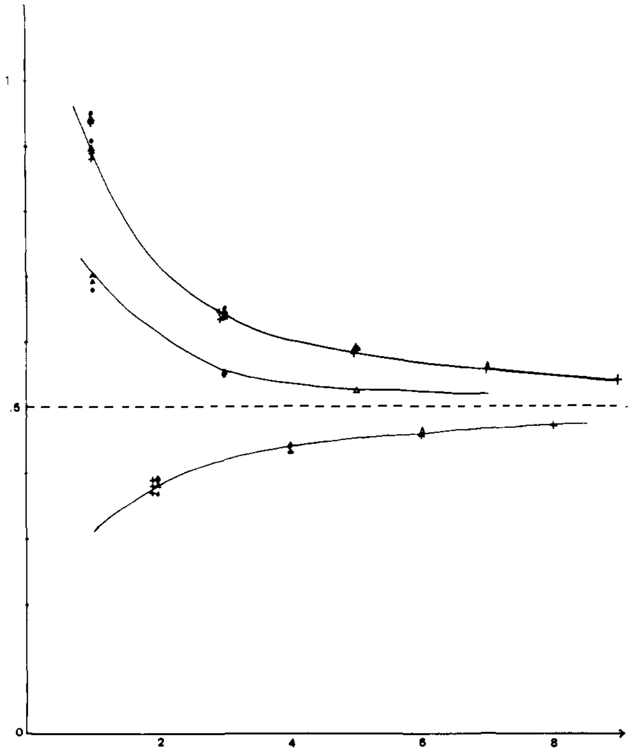
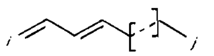


Figure 3. Probability for spin alternation $\mathcal{P}_{ij}^{A}$ as a function of the i–j distance in the series of linear polyenes (three to five double bonds). The upper curve in relative to $\mathcal{P}_{2k+1,2(k+l)}$, the middle one to $\mathcal{P}_{2k,2(k+l)+1}$, and the lower one to $\mathcal{P}_{k,k+2l}$ ($l > 0$).

one finds $k + 1$ single and k double intermediate bonds. For $2k + 1 = 1$, the spin correlation is of course larger on a double bond (~0.94) than on a single bond (≅0.67). For even $|i - j|$, the number of intermediate single and double bonds is equal, and $\mathcal{P}_{ij}(|i - j| = 2k)$ is independent of the parity of i



The conditional probabilities relative to the lowest singlet ψ_0 of a given polyene are distributed along three curves $\mathcal{P}_{ij}^{A\text{o}} = f(|i - j|)$ (cf. Figure 3), which exhibit an hyperbolic decrease. A satisfactory fitting may be obtained by the three following hyperbolas:

$$\mathcal{P}_{2k,2(k+l)+1}^{A,\text{o}} = 0.5 + 0.175/(2l + 1)$$

for odd $|i - j|$ when the spin wave starts on a weak bond;

$$\mathcal{P}_{2k-1,2(k+l)}^{A,\text{o}} = 0.5 + 0.44/(2l + 1)$$

for odd $|i - j|$ when the spin wave starts on a strong bond;

$$\mathcal{P}_{k,k+2l}^{A,\text{o}} = 0.5 - 0.125/l$$

for even $|i - j|$; one may notice that $(0.44)^{-1} + (0.175)^{-1} = (0.125)^{-1}$. The damping of the spin wave is not dependent on the size of the conjugated polyene; the values of $\mathcal{P}_{ij}$ are almost exactly transferable from one even polyene to a larger one, as apparent from Figure 3, where the values for $n = 6$, 8, and 10 have been reported, and are frequently indistinguishable.

The decrease of $\mathcal{P}_{ij}$ for odd polyenes follows a different hyperbolic trend, as is easily understood since the contrast between strong (double) and weak (single) bonds does not appear. As seen from Figure 4, the lowest doublet state also appears as a damped spin wave. The dispersion of spin alternations between bonded atoms $\mathcal{P}_{i,\overline{i+1}}$ is larger than in even polyenes.

The underlying logic for such a regular behavior of the conditional probability of spin alternation will be discussed elsewhere and will be exploited to build nonvariational almost exact a priori wave functions[16] to be used in large molecules where the research

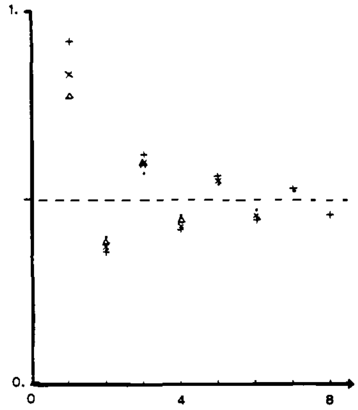


Figure 4. Probability for spin alternation $\mathcal{P}_{ij}^{A}$ as a function of the i–j distance in odd polyenes (C_9H_{11}) ground state, for different positions of atom i: (+) $i = 1$; (·) $i = 2$; (×) $i = 3$; (△) $i = 4$.

of the exact solution of the EVB Hamiltonian would become costly (≅20 atoms).

For nonlinear polyenes, i.e., branched molecules or ring-containing molecules, the same trends tend to appear, but the specificity of the molecular graph tends to make them less regular, and the connection with topology would deserve special attention.

If spin alternation appears as an important feature of the lowest eigenstates, one cannot say that it decreases regularly when going to higher eigenstates, and this fact will be understood quickly by analyzing some further indexes that are more directly related to energy.

(2) Probability of Finding a Singlet Arrangement between p and q and Its Energetic Relevance

The deviation of $\mathcal{P}_{ij}^{Am}$ from 1, or

$$1 - (\mathcal{P}_{\mathrm{ij}}^{m} + \mathcal{P}_{\bar{\mathrm{i}}\mathrm{j}}^{m})/2 = \mathcal{P}_{ij}^{m} + \mathcal{P}_{\bar{i}\bar{j}}^{m}$$

is the probability of finding the same spins on atoms i and j, i.e., an $S_z = 1$ ($\mathcal{P}_{ij}^{m}$) or $S_z = -1$ ($\mathcal{P}_{ij}^{m}$) triplet arrangement between these two centers. For an even number of atoms and for a total $S_z = 0$ problem, these two probabilities are equal:

$$\mathcal{P}_{ij}^{m} = \mathcal{P}_{\bar{i}\bar{j}}^{m}$$

One may be tempted to introduce the probability of finding an $S_z = 0$ triplet arrangement between atom i and j, which will appear as the mean value of the operator:

$$P_{ij}^{\text{To}} = \tfrac{1}{2}|i\bar{j} + \bar{i}j\rangle\langle i\bar{j} + \bar{i}j|$$

$$\mathcal{P}_{ij}^{\text{To},m} = \langle\psi_m|P_{ij}^{\text{To}}|\psi_m\rangle$$

and similarly the probability of finding a singlet arrangement between atoms i and j through

$$P_{ij}^{S} = \tfrac{1}{2}|i\bar{j} - \bar{i}j\rangle\langle i\bar{j} - \bar{i}j|$$

$$\mathcal{P}_{ij}^{S,m} = \langle\psi_m|\mathrm{P}_{ij}^{S}|\psi_m\rangle \tag{11}$$

It is evident that the probability of finding a spin alternation between atoms i and j is the sum of the probabilities of finding a singlet and finding an $S_z = 0$ triplet arrangement between these atoms:

$$\mathcal{P}_{ij}^{\text{To},m} + \mathcal{P}_{ij}^{S,m} = \mathcal{P}_{ij}^{A,m} \tag{12}$$

It is possible to demonstrate from the momentum algebra that for an even number of electrons the probabilities of finding $S_z = 1$, $S_z = -1$, and $S_z = 0$ triplet arrangements between any pair of atoms i and j are identical in the total singlet eigenfunctions

$$\mathcal{P}_{ij}^{m} = \mathcal{P}_{\bar{i}\bar{j}}^{m} = \mathcal{P}_{ij}^{\text{To},m} \tag{13}$$

if ψ_m is a singlet state. In view of eq 12 and 13 it becomes clear that

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[16] M. Said, D. Maynau, J. P. Malrieu, and M. A. Garcia Bach, *J. Am. Chem. Soc.*, in press.

$$\mathcal{P}_{ij}{}^{S,m} + 3\mathcal{P}_{ij}{}^{\mathrm{To},m} = 1$$

$$\mathcal{P}_{ij}{}^{S,m} = (3\mathcal{P}_{ij}{}^{\mathrm{A},m} - 1)/2 \qquad (14)$$

The probability of finding a spin alternation on bond ij and the robability of finding a singlet arrangement between these atoms re related through a linear relationship in singlet states.

Among these various spin correlation indexes, what is the elevant one for a convenient understanding of the energetic roperties?

If one turns back to the trivial two-electron two-center problem, he effective VB matrix is two-dimensional:

$$\begin{array}{cc} 1\bar{2} & \bar{1}2 \\ \left|\begin{array}{cc} -g & g \\ & g \end{array}\right| \end{array} \rightarrow \begin{array}{l} 1/\sqrt{2}(1\bar{2} - \bar{1}2) \text{ singlet}, E^{(1)} = -2g \\ 1/\sqrt{2}(1\bar{2} + \bar{1}2) \text{ triplet}, E^{(2)} = 0 \end{array}$$

Both states have the same spin alternation probability and different nergies. The singlet arrangement is the only one to be stabilized ince it is the only one to interact with the singlet $|a\bar{a}|$ and $|b\bar{b}|$ losed-shell ionic structures. This remark suggests that a relevant ndex for energetic purposes might be the probability of finding singlet spin arrangement between atoms p and q.

The energetic relevance of $\mathcal{P}_{ij}{}^{S,m}$ is immediately seen from eq –6:

$$E_m = \langle\psi_m|H^{\mathrm{eff}}|\psi_m\rangle$$
$$= \langle\psi_m|H^{\mathrm{a}} + H^{\mathrm{b}}|\psi_m\rangle + \text{higher order terms}$$

With neglection of terms of orders higher than 2 and *if all bonds re identical*:

$$g_{ij} = g \ \forall \ i \text{ and } j \text{ bonded}$$

$$E_m = -g\langle\psi_m|\sum_{\text{bonds } ij} [|i\bar{j}\rangle\langle i\bar{j}| + |\bar{i}j\rangle\langle\bar{i}j| - |i\bar{j}\rangle\langle\bar{i}j| - |\bar{i}j\rangle\langle i\bar{j}|]|\psi_m\rangle$$

$$= -g\langle\psi_m|\sum_{\text{bonds } ij} P_{ij}{}^{S}|\psi_m\rangle = -g\sum_{\text{bonds } ij} P_{ij}{}^{S,m}$$

For a molecule composed of identical (i.e., of equal lengths) bonds, he energy of a state m is proportional to the sum of the probabilities of finding singlet arrangements on its various bonds in the runcated wave function ψ_m. This statement is valid only if one estricts the effective Hamiltonian to its second-order contributions r to the effective exchange operators between adjacent atoms, ut these terms are by far the largest ones (except for evenngs-containing molecules). If the bonds are not equal, an nalogous expression of the energy might be obtained:

$$E_m = -2\sum_{\text{bonds } ij} g_{ij}\mathcal{P}_{ij}{}^{S,m} \qquad (15)$$

his result may be compared with the well-known result of Hückel models saying that the energy is proportional to the sum of the ond indexes:

$$E_m = \beta \sum_{\text{pq bonded}} \rho_{\mathrm{pq}} \qquad (16)$$

analogous statements may be found at the SCF level), but our esult is obtained with a correlated model, perfectly including the epulsion of the two electrons on the same site in ionic instantaeous situations.

Figure 4 reproduces some $P_{ij}{}^{S}$ singlet arrangement probabilities n the ground states of linear polyenes, and the strong difference etween strong (short) bonds ($2k - 1$, $2k$) and weak (long) bonds k, $2k + 1$) immediately appears, although the calculation was made from equal bond lengths. One may therefore conclude that hile the tendency to spin alternation is a general phenomenon, hich concerns both the strong and the weak bonds, the proper abilizing singlet interferences between the two possible spin ternation ($\alpha_i\beta_j - \beta_i\alpha_j$) essentially occurs on strong bonds (i.e., n the double bonds of the Kekulé graph).

As another consequence of eq 15 one may notice that if a bond is distorted (if its bond length is changed), resulting in a change g_{ij}, the first-order change in the energy of the state m

$$\Delta E_m = -2\mathcal{P}_{ij}{}^{S,m}\Delta g_{ij} \qquad (17)$$

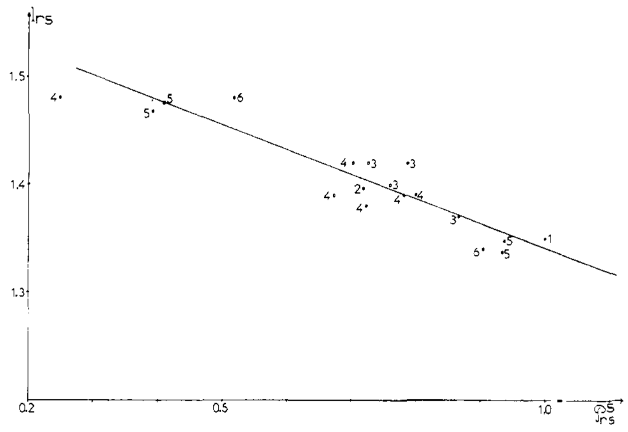


Figure 5. Correlation between bond lengths $\mathcal{P}_{rs}$ and the probability of finding a singlet arrangement $\mathcal{P}_{rs}{}^{S}$ between atoms r and s in the ground-state wave function ψ_0: (1) ethylene; (2) benzene; (3) naphthalene; (4) azulene; (5) fluorene; (6) butadiene.

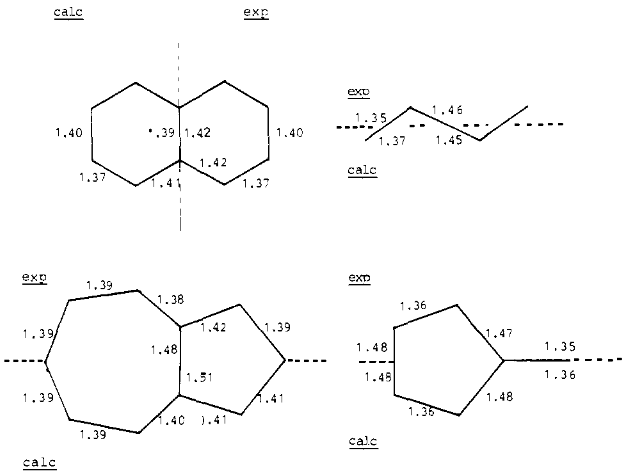


Figure 6. Theoretical (eq 18) vs. experimental bond lengths in naphthalene, butadiene, azulene, and fluorene.

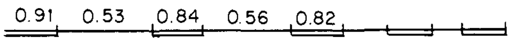
is proportional to the probability of finding a singlet arrangement between these atoms in the state m.

This relationship makes clearer the analogy between the bond index of the density matrix ρ_{ij} and our singlet probability $\mathcal{P}_{ij}{}^{S,m}$ and suggests using the latter index for predicting bond distances in conjugated molecules.

Figure 5 illustrates the correlation between the experimental bond lengths and the ground-state singlet probabilities for a series of conjugated polyenes including ethylene, butadiene, benzene, naphthalene, azulene, and fluorene.

The singlet probabilities are calculated by assuming equal bond lengths, and a better agreement might be achieved if a self-consistent procedure was started, with use of an empirical relation between the bond length and singlet probability, as is frequently done in the MO approach through the equivalent bond length/bond index correlation.

For instance, the values of singlet probabilities for linear polyenes exhibit a slight tendancy for bond equalization in the central part of the molecule (cf. decapentaene)



which might disappear after a proper bond length optimization. In the present problem an empirical linear relationship might take the form

$$l_{ij}\ (\text{Å}) = -0.225\mathcal{P}_{ij}{}^{S} + 1.57\ \text{Å} \qquad (18)$$

When applied to the $P_{ij}{}^{S}$ values calculated from equal bond lengths, one gets 1.41 Å for benzene and the values given in Figure 6 for naphthalene, azulene, fluorene, and butadiene.

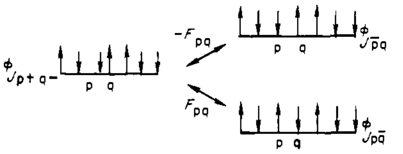
The nice agreement between experiment and the simplest level of our theory is encouraging. We should mention that it would allow the calculation of the conformations in the lowest triplet states and in the neutral singlet excited states such as the ^1A_g hidden state of linear polyenes. This remark will be exploited later on in an ab initio version of the magnetic model.[17]

(3) Probability for Ionic Situations

Although limited to the neutral situations, the projected wave functions ψ_m make it possible to reach immediately some information about the probabilities for having instantaneous ionic situations. Starting from ψ_m as a well-suited zeroth order wave function, one may be tempted, moving back to the original Hamiltonian, to couple this wave function with the ionic determinants $\Phi_{p^+q^-}$. It is clear that in the tight binding approximation at least, the first-order coupling occurs with the adjacent monoionic determinants in which the plus and minus charges take place on a chemical bond. If the coupling between neutral and ionic determinants is weak enough ($F/\Delta E$ small enough), then

$$\Psi_m = \psi_m + \sum_{\substack{\text{adjacent}\\ \text{monoionic}\\ \text{determinants}\\ \phi_{J_{p^+q^-}}}} \frac{(\phi_{J_{p^+q^-}}|H|\psi_m)}{\Delta E}\phi_{J_{p^+q^-}} \tag{19}$$

Now considering one of these typical determinants having a given spin distribution J_{pq} on atoms other than p and q, $\phi_{J_{p^+q^-}}$ interacts only with the two neutral determinants that present a spin alternation on the pq bond and that do not differ from $\phi_{J_{p^+q^-}}$ by the spin distribution J on the other atoms:



Each adjacent monoionic determinant $\phi_{J_{p^+q^-}}$ interacts with two neutral determinants ($\phi_{J_{\bar{p}q}}$ and $\phi_{J_{p\bar{q}}}$) only differing by their spin alternation on the pq bond. The matrix element

$$(\psi_m|H|\phi_{J_{p^+q^-}}) = C_{J_{+\bar{q}},m}(\phi_{J_{p\bar{q}}}|H|\phi_{J_{p^+q^-}}) + C_{J_{\bar{p}q},m}(\phi_{J_{\bar{p}q}}|H|\phi_{J_{p^+q^-}})$$
$$= F_{pq}(-C_{J_{\bar{p}q},m} + C_{J_{p\bar{q}},m}) \tag{20}$$

may be expressed as a sum between two contributions, which will tend to add if $C_{J_{\bar{p}q},m} = -C_{J_{p\bar{q}},m}$, i.e., if the $\bar{p}q$ and $p\bar{q}$ distribution appears with opposite signs in ψ_m, it will contribute to a singlet spin alternation on the pq bond. The probability of finding a p^+q^- zwitterion on bond pq and a given spin distribution J_{pq} on the other atoms is

$$\mathcal{P}_J{}^{p^+q^-} = (F/\Delta E)^2(C_{J_{\bar{p}q},m} - C_{J_{p\bar{q}},m})^2$$

and the probability of finding a p^+q^- distribution is obtained by summing over all spin distributions J:

$$\mathcal{P}^{p^+q^-} = \sum_J \mathcal{P}_J{}^{p^+q^-}$$

The same approach might have been followed when calculating the probability of finding a singlet distribution on the pq bond, introducing first the probability to find a singlet distribution on pq *and* a given spin distribution J on the other atoms

$$\mathcal{P}_{J_{pq}}{}^{S} = (C_{J_{\bar{p}q},m} - C_{J_{p\bar{q}},m})^2$$

and

$$\mathcal{P}_{pq}{}^{S} = \sum_J \mathcal{P}_{J_{pq}}{}^{S}$$

Therefore

$$\mathcal{P}_{p^+q^-} = (F/\Delta E)^2\mathcal{P}_{pq}{}^{S}$$

and since the same is true for the p^-q^+ distribution,

$$\mathcal{P}_{pq}{}^{ion} = \mathcal{P}^{p^+q^-} + \mathcal{P}^{p^-q^+} = 2(F/\Delta E)^2\mathcal{P}_{pq}{}^{S} \tag{21}$$

The probability of finding an instantaneous zwitterion on the pq bond is proportional to the probability of finding a singlet distribution on this bond in the truncated wave function ψ_m. The $2(F/\Delta E)^2$ factor is characteristic of the amplitude of the coupling between neutral and ionic states, i.e., of the charge-transfer probability.

This remark would allow one to predict a series of results:

(i) Since the long-distance charge-transfer situations p^+s^- (p and s nonbonded) and multiionic situations $p^+q^-r^+s^-$ appear only at higher orders of perturbation, through their interaction with the adjacent monoionic determinants previously studied, the weight of the ionic determinants in the exact wave function Ψ_m should be proportional to the sum of the probabilities of finding singlet spin alternations on chemical bonds (which is not a probability since the various situations are not orthogonal). Since the weight of the ionic determinants in Ψ_m may be written as

$$1 - |(\psi_m|\Psi_m)|^2/(\Psi_m|\Psi_m)$$

this quantity is proportional to

$$\sum_{\substack{pq\\ \text{bonded}}} \mathcal{P}_{pq}{}^{S}$$

and the truncated wave function gives directly some information on its complementary (lacking) part. This result illustrates the fact that the truncation of information is not as dramatic as one might have thought and that direct procedures are available to move back from the truncated wave function to the lacking information.

(ii) Since the sum of the singlet spin alternations on bonds is proportional to the energy of the neutral state (cf. eq 15), one may directly establish the following result. The weight of the ionic determinants in the exact wave function Ψ_m of the neutral states is proportional to the energy of the state (the zero of energy being taken at the energy of the neutral state of highest multiplicity):

$$1 - |(\psi_m|\Psi_m)|^2/(\Psi_m|\Psi_m) \propto E_m \tag{22}$$

This is an amazing result, since it tells us that the neutral/ionic mixture does not increase when one goes to the highest part of the spectrum of neutral states, in a region where the ionic states begin to appear, but on the contrary decreases regularly, to become zero as expected for the highest multiplicity state, which may be viewed as having all spins parallel, and cannot allow, therefore, any charge transfer. This remark is exactly opposite to intuition based on energetic grounds in terms of overlap between the neutral spectrum and the ionic spectrum, which would lead one to think that some convergence difficulty would appear for the states in this overlap region (near or above the lowest ionic singlet state, i.e., ^1B_u in linear polyenes), while the ground state actually exhibits the maximum mixing with ionic determinants and should therefore be the less convergent state in the quasi-degenerate perturbative approach (see Figure 7). This result is only apparently paradoxical; since all the energy stabilization of the neutral states comes from the coupling with the ionic determinants, the result of eq 22 might be reasonably expected on intuitive grounds.

(iii) Knowing the probability of finding a zwitterion on the various bonds (eq 21), it becomes easy to calculate the fluctuation of the electric field at any point. For alternant molecules, the π dipole is zero, but the electric field fluctuates around this zero value. This fluctuation may be viewed as essentially originating from the instantaneous charge transfers on bonds. The knowledge of the fluctuation of the electric fields is essential for two purposes: (i) If the considered system A is in interaction with a small closed-shell system B of polarizability α_B the van der Waals dispersion energy between systems A and B is proportionnal to the product:

$$-\tfrac{1}{2}\alpha_B\vec{E}_A{}^{2(B)}$$

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(17) M. Said, D. Maynau, and J. P. Malrieu, work in progress.

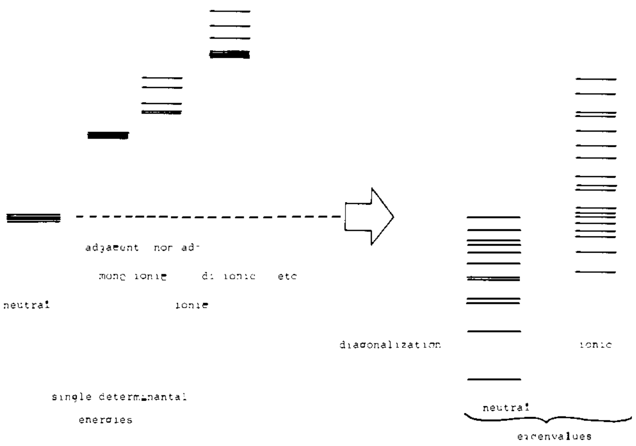


Figure 7. Schematic view of the change from the VB determinantal energies to the eigenvalues.

where $\vec{E}_A^{2(B)}$ is the fluctuation of the electric field created on system B by the system A. (ii) If the molecule has "core" electrons of significantly lower energy than the previously treated "valence" electrons, the core–valence interaction may be treated similarly by considering the fluctuation of the valence electric field on the various atomic core centers.[18,19]

(4) Spin Density Distribution

It is a well-known advantage of the VB approach that it may give directly negative spin densities in free radicals[20] (odd number of electrons), while the MO models require some refinements to reproduce these experimentally known spin densities (they need the use of (eventually projected) unrestricted Hartree–Fock wave functions[(21)] or spin polarizing excitations in the CI scheme). Our VB model gives directly positive and negative zeroth-order spin densities at atom p as the difference between the probability of finding α and β spins on this atom:

$$\rho_p = \langle\psi_m|P_p^\alpha|\psi_m\rangle - \langle\psi_m|P_p^\beta|\psi_m\rangle \qquad (23)$$

where

$$P_p^\alpha = a_p^+a_p = |p\rangle\langle p| \qquad P_p^\beta = a_{\bar{p}}^+a_{\bar{p}} = |\bar{p}\rangle\langle\bar{p}| \qquad (24)$$

are operators counting the numbers of α (or β) electrons on atom p. From a practical point of view the calculation is very rapid since it consists in adding the weight of all determinants where p is occupied by an α spin and substracting the sum of the weights of all determinants where p is occupied by a β spin:

$$\rho_p = \sum_{K \in S} C_{mK}^2 \, (-1)^{2\langle K|S_z(p)|K\rangle}$$

where $S_z(p)$ is the spin operator relative to the atom p. The calculated zeroth-order distribution is more contrasted than the experimental one as it appears, for instance, in allyl and benzyl (cf. Figure 8): the negative spin densities are too large, the positive ones also being excessive.

The fact that this zeroth-order picture of the spin density distribution appears too contrasted is easily understood from the fact that one also meets situations where the considered atom bears no electron (p^+) or two electrons (p^-) as occurs in the instantaneous ionic situations outside of ψ_m. These ionic situations should lower the local zeroth-order spin density by an amount that depends on the tendency of the considered atom to reach ionic situations.

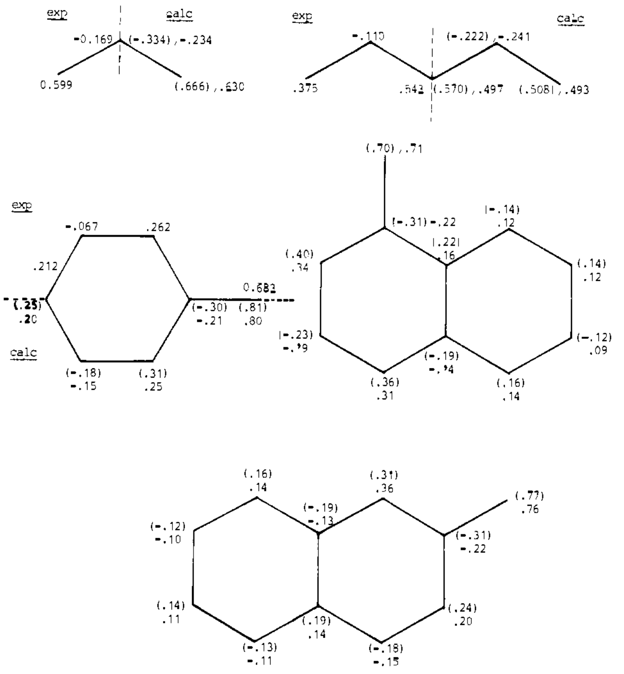


Figure 8. Zeroth- (between parentheses) and second-order corrected spin densities in some conjugated free radicals.

As previously discussed this probability should be proportional to

$$2(F/\Delta E)^2 \sum_{\text{q bonded to p}} \mathcal{P}_{pq}^{S}$$

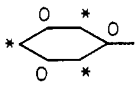
which suggests a corrected spin density formula (including some leading terms of the second-order correction to the spin density)

$$\rho_p^d = \langle\psi_m|a_p^+a_p - a_{\bar{p}}^+a_{\bar{p}}|\psi_m\rangle\left[1 - 2(F/\Delta E)^2 \sum_{\text{q bonded to p}} \mathcal{P}_{pq}^{S}\right] \qquad (25)$$

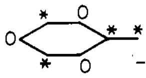
This correction does not require any further computational time. Figure 8 also reports these corrected spin densities for a few free radicals. It is seen that the agreement with experiment is good and comparable with that obtained from MO CI treatments, in a very straightforward way. The model provides a qualitative interpretation of the localization of large spin densities since the wave function is dominated by the most alternating spin distributions, namely,

$\underline{*\quad O\quad *}$ for allyl (energy $-2g$, coefficient = 0.816)

followed by $\underline{*\;*\;O}$ (energy $-g$, coefficient = 0.408)



for benzyl (energy $-7g$, coefficient = 0.575), which is followed by



(energy $-6g$, coefficient = 0.245), and by others at $-5g$ energy.

The leading rolė of spin alternation gives a straightforward explanation of the large spin densities in positions 1–3 in allyl, negative in 2, while it predicts a large dominant spin density on the external carbon of benzyl (bearing an α spin in the two lowest energy determinants), followed by the ortho and para positions (for which the second determinant partly cancels the effect of the first one).

This qualitative speculation is confirmed by the examination of the coefficients of the projected eigenvector (vide supra) and by the calculated zeroth-order spin densities reported in Figure 8. The reported spin densities are calculated by assuming equal bond lengths, while in benzyl, for instance, the external bond is much longer (in agreement with the singlet probability) and the agreement with experiment would be much better if correct bond

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lengths had been introduced together with a larger value of $\lambda = 2(F/\Delta E)^2$.

(5) Conclusion

For the basic model problem of π-conjugated systems, the effective valence bond approach leads to a rather unusual picture of the electronic assembly. The noncorrelated Hückel or Fock approaches lead to an energetic description in terms of monoelectronic energy levels and delocalized quasi-particles spread on the whole skeleton and governed by the electronic delocalization phenomenon through the nodal properties of the MO's. The introduction of the electronic correlation on this basic picture remains a rather obscure step and can only be intuitively followed when local bond electron pairs are exhibited in the Fermi sea. This localization step is essentially valid for molecules possessing a well defined Kekulēan formula; it is rather arbitrary for aromatic compounds and fails for open-shell systems such as radicals or diradicals. Nevertheless, the MO approach remains the dominant way of thinking and representation for both experimentalists and theoretical chemists.

The present approach proposes an alternative language and picture of the molecular electronic population. The MO approach introduces delocalized MO's that give a correct mean value of the population per atom (one electron) but that overestimate grossly the fluctuation of the population per atom (i.e., the situations where there are zero or two electrons on a given center), and the main task of correlation corrections is to reduce these fluctuations of the electronic density. The EVB description decides to disregard these fluctuations, which appear only implicitely through effective exchange operators coupling, interchanging the spins of the electrons on the various atoms, and reflecting the possibility of local charge transfers between atoms bearing electrons of opposite spins. The MO approach seems to deal with charge distribution, and its fluctuation, while the EVB approach keeps the mean distribution (one electron per center), disregards the charge fluctuation and transforms the problem into a spin distribution problem. The effective Hamiltonian that rules this spin distribution is a Heisenberg-like Hamiltonian. One should, however, keep in mind that the spin is not a dynamical variable, since our model only treats the spin-free electronic Hamiltonian and the spin serves only as an indicator.

It proposes some sort of stroboscopic view of the molecular electronic assembly where one sees only spin interchanges between neutral situations, the intermediate charge-transfer situations occurring during the blind phases between two glances. To use a different comparison, one may follow the sexual metaphore that is implicit in the chemical language as soon as electron pairs of different spins are proposed as the basic stone of the chemical bonding; Salem[22] recently made this basic picture explicit when he spoke of the "electron pair as faithful couple". This heterosexual couple of two opposite spins may be thought in terms of a doubly occupied delocalized energy level or in terms of a local bond or lone pair (occupying its own lodge in the R^3 space[23]). The present approach considers that the basic rule governing the electronic assembly is the tendency to put opposite spins along the chemical bonds (which are the channels of communication and exchange), i.e., to have spin alternations along the chemical bonds. But there is no longer two-by-two couplings between these electrons of opposite spins, the α spin on atom j may flirt (through implicit instantaneous ionic charge-transfer state) with either its left neighbor or its right neighbor, provided that they are of β spin. The preference for heterospinarity remains in the EVB model but without any privileged coupling, without formation of electron pairs. The resulting picture is something like a dance of the α and β spin electrons on the chemical graph, with dominant two by two exchanges on the chemical bonds but also some collective movements on the rings, as in old fashioned dances (simultaneous interchanges on the square and six-membered rings). The EVB model keeps the leading rule of heterosexuality but destroys the assumption of couples and proposes a more libertine representation of the spin pairing.

The present paper has shown that the lowest wave functions are dominated by the most spin alternating determinants; they result from a balance between the stability of the diagonal terms of these determinants and the stabilization obtained by the off-diagonal matrix elements coupling with less ordered determinants. The ground-state wave function appears as superposition of a slight disorder on basic spin ordered situations. For regular paired molecules there are two basic alternating situations, and the spin exchanges from them lead to different interferences in the lowest singlet and triplet states; the triplet state keeps stronger spin alternation.

This tendency is revealed by the through-space dynamic spin correlation analysis (i.e., the joint probability of finding opposite spins on two different atoms) that takes the place of the charge correlation analysis in the usual MO approaches. A one-to-one correspondence is possible between the MO and EVB treatments: (i) The first-order density matrix and the charge statistical analysis are replaced by a second-order density analysis in terms of spin correlation. The charge distribution problem becomes a spin ordering problem. (ii) The bond index, which qualitatively measures the "strength" of a chemical bond, is replaced by the probability of finding an instantaneous singlet spin alternation between atoms ij. The probability to find a charge transfer i^+j^- between these atoms is proportional to this index. (iii) The EVB approach provides of course a direct approach to spin densities where the negative spin densities are a natural consequence, and accurate estimates may be obtained easily.

It has been shown that the singlet probability index $\mathcal{P}_{ij}{}^S$ is an excellent tool to predict bond lengths in conjugated hydrocarbons. The basic analysis of the projected wave function as a superposition of damped spin waves has led us to propose nonvariational trial wave functions, the exceptional efficiency of which will be illustrated in another paper,[16] that opens to way to the treatment of larger conjugated molecules and eventually model clusters of atomic metals. The attempts to understand the chemical structure as a spin-ordering problem have a long story; one may quote for instance the AMO method[24] and the pioneering works of Ovchinnikov[25] and Bulaewskii[26] as well as those of Klein and collaborators.[27] As a renewal of interest, one should mention the very accurate analysis of the full CI wave functions recently performed by Hashimoto[28] and Fukutome.[29] Their analyses concern the full wave functions Ψ_m while the present paper deals only with their neutral components ψ_m, and these authors analyze simultaneously the charge and spin correlation functions, as well as the relation existing between them. For small ($n < 6$) molecules these spin correlation analyses are of course parallel to ours. The use of effective Hamiltonians allows one to go to larger systems where the research of the exact wave function would be difficult.

The preceding paper[9] discussed in detail the (anti) aromaticity problem, and one should recall that the $4n/4n + 2$ rule is identical with the Woodward–Hoffmann rule for electrocyclic reactions; the cyclic high order contributions stabilize the $4n + 2$ singlet state and destabilize the $4n + 2$ triplet state, i.e., facilitate the ground-state disrotatory cyclization, the conrotatory mode in the lowest triplet, while the reverse is true for the $4n$ cycles. There

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is therefore a complete one-to-one correspondence between the MO approach's essential results and the consequences of the effective valence bond model.[30]

The whole discussion has been derived by using a semiempirical effective valence bond Hamiltonian in that sense that it was derived from the Pariser-Parr-Pople N-electron Hamiltonian. A forthcoming paper[17] will show that the effective valence bond Hamiltonian may be derived from ab initio calculations as well (even in nonminimal basis sets), and this nonempirical EVB Hamiltonian will allow one to calculate directly the energy and conformations of conjugated molecules in the ground and excited neutral states without using any empirical relationship. The numerical predictive performances will be much better, but the whole analysis (given in the present paper) of the electronic assembly as being governed by spin ordering will be kept.

Appendix

The calculation of the statistical indices may be illustrated for the case of the lowest states of the butadiene molecule, for which, including small three body operators, the following holds:

	S^t	T^t
$1\overline{2}3\overline{4}$	0.556	0.651
$\overline{1}2\overline{3}4$	0.556	−0.651
$1\overline{2}\overline{3}4$	−0.412	0
$\overline{1}23\overline{4}$	−0.412	0
$\overline{1}\overline{2}34$	−0.144	0.276
$12\overline{3}\overline{4}$	−0.144	−0.276

The probability of finding a β spin on j when i bears on α spin $\mathcal{P}_{ij}{}^{\mathrm{A}}$ is given by

$$\mathcal{P}_{12}{}^{\mathrm{A},S^t} = [(0.556)^2 + (0.412)^2]/0.5 = 0.959$$

$$\mathcal{P}_{14}{}^{\mathrm{A},T^t} = [(0.651)^2 + (0.276)^2]/0.5 = 1.0$$

The probability of finding a singlet distribution between i and j may be calculated as follows:

$$\mathcal{P}_{23}{}^{S,S^t} = [{}^1\!/\!{}_2(0.556 + 0.144)^2] = 0.490$$

$$\mathcal{P}_{14}{}^{S,T^t} = [{}^1\!/\!{}_2(0.651 - 0.276)^2] = 0.140$$

One may see, for instance, that the strong spin alternation between atoms 1 and 4 in the lowest triplet state essentially corresponds to a triplet arrangement.

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(30) One frequently uses the terms of effective Hamiltonians for ad hoc operators which are required to mimic the behavior of the "exact" one in a certain range of energies and for some functional subspace.[31] One may, for instance, use least-square fittings to determine such classes of pseudo-Hamiltonians, as has been done by Durand et al. for the determination of core pseudopotentials[32] or monoelectronic pseudo-Hartree-Fock Hückel-type operators.[31] The analytic form of these pseudooperators remains quite arbitrary, and we think that *these pseudooperators should be distinguished from the effective operators* which are *deduced* from the "exact" ones by first principle operators such as the QDPT[1,6] (see, for instance, the work of Freed et al.[33]) or the wave operator formalism.[8] The deduced effective operators handle a projected information and are perfectly rigourous; they may be perfectly exact (if the perturbation expansion converges), giving exact energies and components of the exact wave functions in the model space. They may be thought of as exact projected Hamiltonians leading to exact (projected) alternative descriptions of the molecular electronic order; the above discussed spin ordering description is such an alternative exact effective (or projected) description, which is of course nonunique since it depends on the choice of the model space, which is unable to give valuable information on the states having small components on this model space, but which may represent a powerful instrument.

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The Ethylene Dication: A Theoretical Study of the $C_2H_4{}^{2+}$ Potential Energy Surface[1]

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Abstract: The $C_2H_4{}^{2+}$ potential energy surface was examined by ab initio molecular orbital theory corrected for electron correlation by means of Møller-Plesset perturbation theory to third order (MP3/6-31G**) using 6-31G* (and 3-21G) optimized geometries. The perpendicular (D_{2d}) ethylene dication, **1** (D_{2d}), is the global and only singlet $C_2H_4{}^{2+}$ minimum with an estimated heat of formation of 654 kcal/mol. The rotational transition structure, **2** (D_{2h}), is 28.1 kcal/mol higher in energy. This rotational barrier is remarkably large for such 14-electron species (compare H_2BBH_2 and $H_2B{-}CH_2{}^+$, 10.5 and 20.1 kcal/mol, respectively). The C_{3v} ethylidene dication, **4**, 21.3 kcal/mol higher in energy than **1**, is probably not a minimum, but may facilitate hydrogen scrambling. Although **1** is unstable thermodynamically toward proton loss (by 16 kcal/mol), the barriers for deprotonation (and homolytic cleavage (into two $CH_2{}^+$ cations)) are 68.8 and about 88.4 kcal/mol, respectively. The transition structure for cleavage of **4** into $CH_3{}^+$ and CH^+ lies 86.5 kcal/mol above **1** in energy. These large barriers are consistent with the experimental observation of $C_2H_4{}^{2+}$ in the gas phase.

Many important reactions of ethylene, the largest volume organic chemical produced today, involve oxidative processes.[3] The most basic oxidations of ethylene are the one-electron process leading to the radical cation, $C_2H_4{}^{+\cdot}$, and the two-electron loss leading to the dication, $C_2H_4{}^{2+}$. The ethylene radical cation is a commonly observed species in the gas phase and is produced,

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(1) Considered as Carbodications Part 6 by the group in Erlangen. For Part 5, see ref 16g.

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