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Table III. Evaluation of ϵ for CF_2 at 249 nm

$2[C_2F_4]_f$, mM	t_1, ms	$(OD)_{t_1}$	10^{-4} × slope,[a] s^{-1}	10^{-7} × $2k_2$, s^{-1} M^{-1}	ϵ(eq 21), M^{-1} cm^{-1}
0.0169	1.6	0.0221	1.5[c]	3.1	874
0.164	0.6	0.126	1.1[d]	3.3	921
0.0197	1.6	0.0236	1.8[c]	4.0	938
0.117[b]	0.1	0.280	1.1[d]	3.9	1021
0.272[b]	0.2	0.334	1.0[d]	3.4	1043
0.200[b]	0.2	0.311	1.0[d]	3.7	1156

[a] Slope of $(OD)^{-1}$ vs. t when $t \geqslant t_1$. Slope = $2k_2/\epsilon l$. [b] Experiments with $CDClF_2$. Other experiments involve $CHClF_2$. [c] l = 2.36 cm. [d] l = 3.26 cm.

at low E_{absd} should be rather typical.

Appendix

Molar Extinction Coefficient of CF_2 at 249 nm. While there was only marginal need to know the ϵ of CF_2 for the interpretation of time lags, a semiquantitative value was needed to show that after V–T relaxation, reaction indeed becomes thermal reaction. It is known that ϵ changes slowly with T.[45] However, for the present purposes it seemed adequate to treat ϵ as constant. On that basis ϵ could be derived from (a) a plot of optical density (OD) at 249 nm vs. time and (b) the amount of C_2F_4 produced. At 249 nm, CF_2 is the only component of the reacting system whose optical absorption is significant. The rate law for C_2F_4 formation is $d[C_2F_4]/dt = k_2[CF_2]^2$, where k_2 is nearly independent of T.[14,15,44,46]

After a sufficiently long time t_1 has elapsed, the gas temperature becomes low enough (<900 K) so that reversible decomposition of $CHClF_2$ (eq 2 and 3b) is practically quenched, according to available kinetic data.[14,15] Thus, when $t > t_1$, the sole reaction is (3a). The condition $t > t_1$ can be recognized experimentally because the decrease of OD with t then follows second-order kinetics; the slope of the straight-line plot of $(OD)^{-1}$ vs. t equals $2k_2/\epsilon l$ where l is the optical path length of the UV beam.

Let $[CF_2]_1$ denote $[CF_2]$ at $t = t_1$ and let $[C_2F_4]_f$ denote the final C_2F_4 concentration. The initial $[C_2F_4] = 0$, and when $t > t_1$ further reversible formation of CF_2 from $CHClF_2$ is negligible. We may therefore write (20). Change of variable to OD and

$$2[C_2F_4]_f = [CF_2]_1 + \int_0^{t_1} 2k_2[CF_2]^2 \, dt \qquad (20)$$

rearrangement yields (21). $(OD)_{t_1}$ and $2k_2/\epsilon l$ are known from

$$\epsilon = \left[(OD)_{t_1} + (2k_2/\epsilon l)\int_0^{t_1} (OD)^2 \, dt\right] \Big/ (2[C_2F_4]_f l) \qquad (21)$$

the plot of $(OD)^{-1}$ vs. t when $t \geq t_1$. $(OD)^2 \, dt$ is evaluated by numerical integration of optical density data for $0 \leq t \leq t_1$. Given l and $[C_2F_4]_f$, ϵ can therefore be determined.

Results for several experiments are listed in Table III. Precision of 10% is attained. The accuracy is lower, however, because the period of integration $0 \leq t \leq t_1$ includes the period of mixing of irradiated with nonirradiated gas when the UV path length l is not well defined. Final averages are ϵ (base 10) 1000 ± 200 cm^{-1} M^{-1} at 249 nm (monochromator FWHM ~ 2 nm) and $2k_2 = (3.6 \pm 0.7) \times 10^7$ s^{-1} M^{-1} at ~800 K.

Registry No. $CHClF_2$, 75-45-6; $CDClF_2$, 1495-14-3; C_2F_4, 116-14-3; CF_2, 2154-59-8.

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[49] Professor Colin Steel has obtained a particularly simple derivation of eq 1. Consider collisional V–V′ exchange according to (22). This is a

$$A^* + B \underset{k_r(T)}{\overset{k_f(T)}{\rightleftharpoons}} A + B^* \qquad (22)$$

state-to-state process only for vibrational states. Translational and rotational energies follow a statistical distribution dependent on the T/R temperature T. Hence k_f and k_r are rate constants dependent on the T/R temperature T of the ensemble, and $k_f(T)/k_r(T) = \exp(-[E_B - E_A]/kT)$. Let $T_{V,A}$ and $T_{V,B}$ denote "temperatures" defined by the relative populations A^*/A and B^*/B, respectively. At thermal equilibrium (eq) $T_{V,A} = T_{V,B} = T$. Thus $([A^*]/[A])_{eq} = \exp(-E_A/kT)$ and $([B^*]/[B])_{eq} = \exp(-E_B/kT)$. The V–V′ steady state (ss) is defined so that $k_f(T)([A^*][B])_{ss} = k_r(T)([A][B^*])_{ss}$. Furthermore, $([A^*]/[A])_{ss} = \exp(-E_A/kT_{V,A})$ and $([B^*]/[B])_{ss} = \exp(-E_B/kT_{V,B})$. Thus in the steady state, $\exp(-E_B/kT_{V,B})/\exp(-E_A/kT_{V,A}) = \exp(-[E_B - E_A]/kT)$, which reduces to (1).

A Valence Bond Effective Hamiltonian for Neutral States of π Systems. 1. Method

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Abstract: An N-electron topologically determined Hamiltonian is proposed. It results from the application of the quasi-degenerate many-body formalism to the VB-CI matrix where the neutral configurations are considered as the nearly degenerate perturbed subspace. At the second order, ionic configurations perturbatively introduce an effective (negative) exchange integral between bonded atoms, resulting in a single parameter Heisenberg Hamiltonian. A general recurrence formula is given for the higher orders corrections, which only introduce a second parameter. Due to the cancellation of unlinked contributions, the effective operators are only concerned with connected fragments of the molecular graph; they essentially result in a small effective exchange integral between nonadjacent atoms and important cyclic contributions for even rings (allowing two or three simultaneous spin exchanges along the cycle).

This paper presents an effort to find an effective N-electron Hamiltonian which might give some information about *several states* of the N-electron systems. Such information is especially desired when the lowest states become nearly degenerate and the efforts to improve a prefered single determinant (as done in the Hartree–Fock scheme) seem rather arbitrary. π-Electron systems have been chosen as a test case for a strategy consisting of building an effective VB-type Hamiltonian restricted to a class of VB configurations, and taking benefit of the powerful tool known as the "quasi-degenerate many-body perturbation theory".[1] The QDMBPT approach may be used first as a numerical tool for searching several quasi-degenerate roots in ab initio CI problems.[2] It may also be used to treat in a rational way the effect of a

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[1] B. H. Brandow, *Rev. Mod. Phys.*, **39**, 771 (1967) See also J. des Cloizeaux, Nucl. Phys. **20**, 321 (1960); I. Shavitt and L. T. Redmon, *J. Chem. Phys.*, **73**, 5711 (1980).

[2] D. Hegarty and M. A. Robb, *Mol. Phys.*, **37**, 1455 (1979).

0002-7863/82/1504-3021$01.25/0

sublying core on the valence electrons through the building of effective valence operators; most of the conceptual applications[3] of QDMBPT are concerned with the treatment of the σ-electron effect on the π systems of conjugated hydrocarbons or of the core inner shells on the valence electrons of atoms and diatoms. The present use of this perturbative approach is different since it does not tend to reduce the number of electrons but to reduce the size of the VB-CI problem.

For excited states and especially for nearly degenerate situations, extensive CI must follow the variational SCF single-determinant approaches. As soon as CI is considered as necessary, one may wonder whether the old VB-type approaches are not competitive. The main defects of the VB method are as follows: (i) the use of nonorthogonal basis sets which makes the computation difficult; (ii) the lack of evident partitioning in the CI matrix[4] (the double (or quadruple) substitutions processes allow such a partition in the classical HF + CI procedure).

The first difficulty disappears when one may introduce a transferable orthogonal basis set as assumed in the π-electron problems, due to the weak overlap between neighboring $2p_z$ atomic orbitals.[5] The second problem, the separation between neutral and ionic (and further on between mono, di, ... ionic) excited configurations, allows the introduction of some structure in the VB matrix. When analyzing the VB content of the MO wave functions, Hiberty noticed that the HF approximation greatly overestimates the weight of the ionic configurations (i.e., the fluctuation of the dipole moment) with respect to the "exact" (full CI) wave function which, for the lowest states, concentrates on the neutral VB components.[6] In view of these results, one might consider the set of neutral configurations as a nearly degenerate subspace spanning some sort of zeroth-order descriptions for the lowest states of the molecules. This paper applies the quasi-degenerate many-body perturbation theory[1] for treatment of the neutral states, building an effective Hamiltonian restricted to the neutral configurations perturbed by the action of the ionic states. The usual application of the perturbative many-body theory consists in perturbing a single H.F. configuration to any order,[7] while we start from a subspace and build an effective Hamiltonian for this subspace using perturbation theory to establish its structure.

The model is essentially governed by topology but in a more complex manner than the Hückel one, since it is an N-electron effective Hamiltonian. Instead of giving an approximation of the $(N-1)$-electron states (as do the monoelectronic HF or Hückel Hamiltonians through Koopman's theorem), it gives the lowest part of the N-electron spectrum. Limited to the second-order and the tight-binding approximation, the model gives a simple procedure to decide the multiplicity of the lowest state and a rationale for understanding the topological determination of the preferred multiplicity.

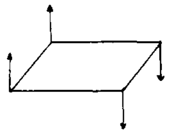
When applied to further orders, the model allows one to introduce nonadjacent interactions and cyclic specific contributions, using two parameters only. When compared to the exact solutions of the Pariser–Parr Hamiltonians for a series of 20 polyenes, our model gives, through diagonalization of small matrices, quantitative agreement with the *full* CI, as will be shown in the following paper.

I. Structure of the VB-Type CI Matrix

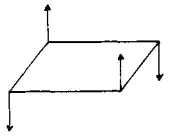
For an N-electron N-AO problem, one considers the N-electron determinants built in the minimal basis set; these determinants may be neutral (for instance, $|a\bar{b}cde\bar{f}|$ ($S_z = 1$)) with one electron per atom or ionic (for instance, $|abbc\bar{d}f|$ ($S_z = 0$, [B^-E^+] pair)) with positive and negative atoms. Due to the $[S_z, \mathbf{H}] = 0$ commutation, one may consider independently the various S_z values, which run from 0 (or $^1/_2$) to $N/2$ (or $(N+1)/2$). The following features are valid, whatever the S_z eigenvalue.

(i) The neutral determinants may be viewed as a block of lower energy than the ionic ones.

(ii) Their energies only differ through exchange integrals. These exchange integrals may be neglected in the ZDO approximation,[8] but the exchange integrals between bonded atoms (K) will be considered for deductive purposes. The $S_z = N$ or $(N+1)/2$ determinant (all spins parallel) is unique, and its energy will be taken as the reference energy E^0. It allows n exchange processes between adjacent atoms, if n is the number of bonds on the chemical graph, and therefore $-nK$ appears in the reference energy E^0. When α and β spins are simultaneously present in the determinant, exchange becomes impossible between adjacent atoms of different spins. Let us call $n_p{}^I$ the number of spin alternants along chemical bonds ($n_p{}^I \le n$) for determinant I; then the energy of this determinant is equal to $E^I = E^0 + n_p{}^I K$. For instance for cyclobutadiene ($S_z = 0$)

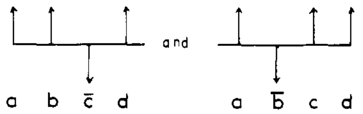


$E^I = E^0 + 2K$



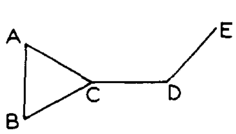
$E^I = E^0 + 4K$

(iii) The neutral determinants only interact through exchange integrals, since they differ through spin permutations. If one neglects nonadjacent exchange integrals, two determinants I and J interact if they only differ through a spin permutation process on two adjacent atoms. For instance between



For a given line (or column) of the matrix, one extradiagonal exchange integral appears (with a negative sign) for each spin alternation between bonded atoms of the determinant I. Therefore the line (or column) I of the matrix bears $n_p{}^I$ extradiagonal exchange integrals (with negative signs) as well as $n_p{}^I$ exchange integrals on the diagonal.

(iv) The neutral determinants interact with ionic determinants. In the well-known "tight-binding" approximation, they only interact with monoionic determinants where the [+−] pair appears on bonded atoms; such ionic states are obtained from a neutral determinant by a charge transfer of one electron from one atom to a bonded atom. For instance, let us consider the interaction between a neutral determinant, I ($|ab\bar{c}d\bar{e}|$), and a singly ionized [A^-C^+] determinant



$$\langle a\bar{a}bd\bar{e}|H||ab\bar{c}d\bar{e}|\rangle = -\langle a|F^{I}|c\rangle = -\langle a|h + \sum_{j=1}^{N} J_j - K_j \delta S(j,c)|c\rangle$$

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[3] For a review see B. H. Brandow, *Int. J. Quantum Chem.*, **15**, 207 (1979); S. Iwata and K. F. Freed, *J. Chem. Phys.*, **61**, 1500 (1974); *Chem. Phys. Lett.*, **28**, 176 (1974); *J. Chem. Phys.*, **65**, 1071 (1976); *Chem. Phys. Lett.*, **38**, 425 (1976); D. Mukherjee, R. K. Moitra, and A. Mukhopadyay, *Pramana*, **9**, 6 (1977); H. Sun and K. F. Freed, *Chem. Phys. Lett.*, **78**, 531 (1981).

[4] G. Rumer, Gotting Nach., 337 (1932); L. Pauling and G. W. Wheland, *J. Chem. Phys.* **1**, 62 (1933); O. Klement, O. Mader, and F. S. Huwigler, *Helv. Chim. Acta*, **43**, 2172 (1960); H. Nam-Tran and Ch. de Reyff, *J. Chim. Phys.*, **77**, 979 (1980).

[5] For a good review of the successes of π models see L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, 1966.

[6] P. Hiberty, Thesis, Orsay, France, 1977. In butadiene the weight of neutral components is 0.23 at the SCF level and 0.61 after CI; in benzene their weight is multipled by a factor 4 under CI.

[7] Such as in the Moller-Plesset Perturbation Theory (C. Moller and M. S. Plesset, *Phys. Rev.*, **46**, 618 (1934)) now widely used in ground- and excited-state calculations of molecules.

[8] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953); I. Fisher-Hjalmars, Adv. *Quantum Chem.*, **2**, 25 (1965).

and the integrals, for equal bond lengths, may be supposed to be transferable since they only differ through tricentric exchange integrals such as $\langle a|K_b|c\rangle$. In the same molecule the [A⁻B⁺] transfer gives

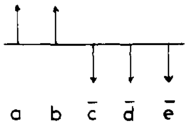
$$\langle a\bar{a}\bar{b}de|H||a\bar{b}\bar{c}de|\rangle = \langle a\bar{a}bd\bar{e}|H||ab\bar{c}d\bar{e}|\rangle + \langle a|K_b|c\rangle - \langle a|K_e|c\rangle$$

The spin repartition on the atoms which are not involved in the charge transfer is supposed to have no influence on the charge-transfer integral, which will be labeled F.

The neglect of charge-transfer integrals between nonadjacent atoms and the neglect of bielectronic double charge transfer are implied by the Pariser–Parr ZDO type Hamiltonian[8]

$$H^{\mathrm{PP}} = \sum_{pq} h_{pq}a_p{}^+a_{\mathrm{q}} + g_{pq}a_p{}^+a_q{}^+a_qa_p$$

Starting from a given neutral determinant, I, one may find $2n_{\mathrm{p}}{}^I$ ionic determinants interacting with it; for each spin alternation on a chemical bond in I, one may consider two ionic determinants of opposite dipoles. For instance the determinant for a linear molecule



interacts with

$$|ab\bar{b}\bar{d}\bar{e}|[\mathrm{B^-C^+}]$$

and with

$$|ac\bar{c}\bar{d}\bar{e}|[\mathrm{B^+C^-}]$$

There are therefore $2n_{\mathrm{p}}{}^I$ extradiagonal matrix elements on the line I in the block between neutral and ionic determinants.

(v) Among ionic determinants, the monoionic determinants between adjacent atoms have the lowest energy. If an ionic determinant [K⁺R⁻] is obtained by a (K → R) charge transfer from a neutral determinant, I, one may approximate

$$E(\mathrm{K^+R^-}) - E_I = I_{\mathrm{K}} - A_{\mathrm{R}} - J_{\mathrm{kr}}$$

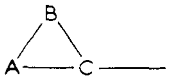
where I is the ionization potential, A the electroaffinity, and J_{kr} the Coulombic integral, which is larger when K and R are adjacent. The doubly ionic determinants [A⁻B⁺,D⁺E⁻] have higher energies since they require two ionizations.

(vi) A given monoionic determinant (such as $|a\bar{a}c\bar{d}e\bar{f}|$[A⁻B⁺]) interacts with *two* neutral determinants which are obtained by placing either the α-spin electron or the β-spin electron on the positive center (in our example with $|a\bar{b}c\bar{d}e\bar{f}|$ and $|\bar{a}bc\bar{d}e\bar{f}|$) without changing the spin distribution on the other atoms and with (nonadjacent) monoionic determinants, in which either the negative or positive center has been moved to an adjacent atom. For instance, [A⁻B⁺] interacts with [A⁻C⁺]

$$\langle a\bar{a}c\bar{d}e\bar{f}|H||a\bar{a}b\bar{d}e\bar{f}|\rangle = \langle c|F^{+,-}|b\rangle$$

where F^{+-} is now the Fock operator relative to an ionic determinant. In the Pariser–Parr approximations, this integral reduces to its monoelectronic part $\langle c|h|b\rangle = h_{cb}$ and is taken equal to the charge-transfer integral occurring between neutral and ionic determinants.

In general these determinants are nonadjacent monoionic determinants except for the triangular chemical graphs. For



[A⁻B⁺] may interact with [A⁻C⁺] and [A⁻C⁺] interacts with neutral determinants, but this is an exception.

A monoionic determinant also interacts with dionic determinants obtained by a second charge transfer between adjacent (previously neutral) atoms. For instance, [A⁻B⁺]$|a\bar{a}c\bar{d}e\bar{f}|$ interacts with [A⁻B⁺D⁺E⁻]$|a\bar{a}ce\bar{e}\bar{f}|$ through $-h_{de}$. These determinants have two independent adjacent charge transfers.

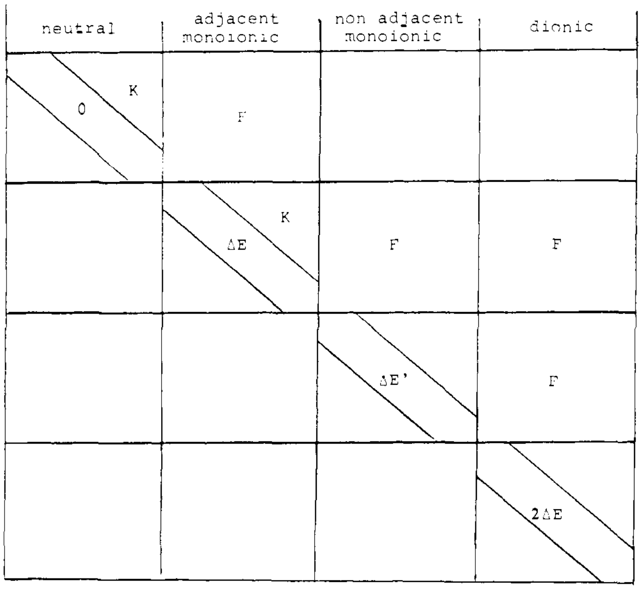


Figure 1. Schematic structure of the VB-CI matrix; F and K respectively indicate the existence of charge-transfer and exchange-only integrals in the off-diagonal block.

(vii) The dionic determinants interact among themselves and with trionic determinants etc, but these determinants have higher energies, and if a zeroth-order wave function is built from the neutral states, the adjacent monoionic determinants will be involved in the second order of energy, while the nonadjacent monoionic determinants and dionic determinants with two adjacent zwitterions are involved in the fourth order only, trionic determinants occurring only at the sixth order of perturbation etc (cf. Figure 1).

An analogy with the correlation many-body problem appears, a charge-transfer monoexcitation playing the same role as a double excitation process. The N consistence problem, which is so important in the many-body problem, must be kept in mind as well as the so-called linked cluster theorem.[9] The main difference now is that we no longer have a zeroth-order determinant (the Hartree–Fock solution) but a zeroth-order subspace (the neutral states).

II. Structure of the Effective Hamiltonian Restricted to Neutral Determinants

If the quasi-degenerate space is limited to the neutral determinants, which only differ by the spin part of the wave function, the effective Hamiltonian resulting from the application of QDMBPT to this zeroth-order subspace can only introduce effective spin operators, allowing for the exchange of the spins of two atoms, four atoms, etc. The proposed Hamiltonian therefore belongs to the general class of effective magnetic or Heisenberg Hamiltonians, which are quite popular in solid-state physics (see, for instance, ref 10).

The Second-Order Quasi-Degenerate Many-Body Perturbation Theory.[1] Let us suppose that the lowest states of our problem have large components on the neutral determinants (in other words that they are neutral states in the sense of VB theory). Then the space of neutral determinants (for a given value of S_z) may be considered as a nearly degenerate subspace. One might first diagonalize the VB matrix restricted to those determinants, which leads to a set of orthogonal multiconfigurational wave functions ψ_{m}

$$\psi_{\mathrm{m}} = \sum_K C_{mK}\phi_K \qquad P_{\mathrm{S}}HP_{\mathrm{S}}|\psi_{\mathrm{m}}\rangle = E_{\mathrm{m}}{}^0|\psi_{\mathrm{m}}\rangle$$

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(9) K. A. Bruckner, *Phys. Rev.*, **100**, 36 (1955); In the "Many Body Problem" (les Houches, 1958), Dunod, Paris, 1959. J. Goldstone, *Proc. R. Soc. London, Ser. A*, **239**, 267 (1959).

(10) C. Herring, "Magnetism", Vol. IIB, G. T. Rado and H. Suhl, Eds., Academic Press, New York, 1966.

where P_S is the projector on the neutral determinants, and perturb independently these wave functions as done in the CIPSI[11] or the MRDCI[12] formalisms. For the VB problems Cantu et al.[13] followed this procedure in their valence bond perturbation treatment. Kirtman and Cole[14] also derived a perturbation treatment of a single optimized VB configuration. An alternative approach consists of applying the quasi-degenerate many-body theory.[1,3,15,16] The method consists of building an effective Hamiltonian, restricted to the zeroth-order subspace;[17] the matrix elements of this Hamiltonian are obtained through a perturbation expansion of the interaction between the zeroth-order block and the remainder of the CI matrix; when performed to infinite order and provided, the perturbation expansion is convergent and the diagonalization of the effective Hamiltonian will give the *exact* energies and the correct *components* of the exact wave functions in the degenerate zeroth-order space. Let us suppose for instance that H^0 is such that all determinants have the same zeroth-order energy E_0^0. Then for the second order, I and $J \in S$,

$$\langle I|H^{\text{eff}(2)}|J\rangle = \langle I|H|J\rangle + \sum_{K \notin S} \frac{\langle I|H|K\rangle\langle K|H|J\rangle}{E_0^0 - E_K^0} \quad (1)$$

The diagonal terms H_{II}^{eff} of the matrix are perturbed in a classical manner by the determinants which do not belong to the degenerate subspace S. The I–J off-diagonal terms are modified under the influence of the determinants K which simultaneously interact with I and J. The perturbation development may be extended to higher orders, and diagrammatic representations of the series have been proposed.[1,15,16]

As a first step one may consider the content of the second-order effective Hamiltonian which immediately results from the points (i–v) of the preceding section. The diagonal terms are given by

$$H_{II} = E^0 + n_p^I K \rightarrow H_{II}^{\text{eff}} = E^0 + n_p^I(K - 2F^2/\Delta E) \quad (2)$$

since each neutral determinant I interacts with $2n_p^I$ monoionic determinants resulting from charge transfers on the n_p^I spin alternating chemical bonds of I.

Each monoionic determinant between bonded atoms [B^+C^-] interacts with two neutral determinants (cf. point vi) which are obtained by changing the $c\bar{c}$ pair into $b\bar{c}$ or $\bar{b}c$, and therefore off-diagonal contributions appear between two determinants which only differ by a spin exchange between two bonded atoms, i.e., at the positions of the H^0 matrix which already involved $a(-K)$ integral. One may notice that the [B^-C^+] monoionic determinant equally contributes to the same matrix element as does [B^+C^-] and that the $\langle I|H|K\rangle\langle K|H|I\rangle$ product is of negative sign

$$I = |a\bar{b}c\bar{d}\bar{e}f| \qquad J = |ab\bar{c}\bar{d}\bar{e}f| \qquad K = |ab\bar{b}\bar{d}\bar{e}f|$$

$$\langle I|H|K\rangle = -\langle c|F|b\rangle = -F \qquad \langle K|H|J\rangle = \langle b|F|c\rangle = F$$

Then in the effective matrix, each nonzero off-diagonal element is transformed according to the following rule $H_{IJ} = -K \rightarrow H_{IJ}^{\text{eff}} = -K + 2F^2/\Delta E$, where all adjacent monoionic determinants are assumed to lie at an energy ΔE above the neutral determinants. In other words the second-order influence of the ionic determinants changes the CI matrix restricted to the neutral determinants into an effective CI matrix where the exchange integrals are changed into effective exchange integrals reflecting the possible electron jumps between adjacent atoms occupied by different spins

$$K \rightarrow K^{\text{eff}} = K - 2F^2/\Delta E$$

The effective exchange integral has a *negative sign* as soon as $2F^2/\Delta E > K$. Its represents the local "superexchange" mechanism proposed by Anderson[18] to interpret the antiferromagnetic properties of solids and organometallic compounds.[10,19]

Examples. In order to make clearer the building of the effective matrices, one may consider the four-electron problem. In the following, the compact notation given in eq 3 will be used.

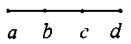
$$g_{kl} = K_{kl} - 2F_{kl}^2/\Delta E \quad (3)$$

The quintuplet ($S_z = \pm 2$)$|abcd|$ or $|\bar{a}\bar{b}\bar{c}\bar{d}|$ is unique, and its energy is taken as zero.

The $S_z = \pm 1$ matrices have four components. They necessarily involve, besides the $S_z = \pm 1$ components of the previously mentioned quintuplet, three triplets. The matrix

$$\begin{array}{cccc}
|\bar{a}bcd| & |a\bar{b}cd| & |ab\bar{c}d| & |abc\bar{d}| \\
g_{ab} + g_{ac} + g_{ad} & -g_{ab} & -g_{ac} & -g_{ad} \\
 & g_{ba} + g_{bc} + g_{bd} & -g_{bc} & -g_{bd} \\
 & & g_{ca} + g_{cb} + g_{cd} & -g_{cd} \\
 & & & g_{ad} + g_{bd} + g_{cd}
\end{array}$$

has the same structure as the Hückel matrix (and this is a general statement for $S_z = \pm(N/2 - 1)$), but the diagonal elements are not identical and they depend on the number of spin alternants in chemical bonds. The matrix may be specified for the linear problem



(butadiene)

$$\begin{matrix}
g & -g & 0 & 0 \\
 & 2g & -g & 0 \\
 & & 2g & -g \\
 & & & g
\end{matrix}$$

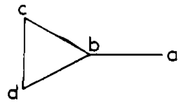
the solutions of which are 0 for the quintuplet, $+g(2 - \sqrt{2})$ for the antisymmetric triplet, 2g for the symmetric triplet, and $+g(2 + \sqrt{2})$ for the antisymmetric triplet

for the cyclic structure (cyclobutadiene)

$$\begin{matrix}
2g & g & 0 & g \\
 & 2g & g & 0 \\
 & & 2g & g \\
 & & & 2g
\end{matrix}$$

the solutions of which are 0 for the symmetric quintuplet, $2g$ for the doubly degenerate E triplet, and $4g$ for the B_{1g} triplet

for the nonalternant structure



$$\begin{matrix}
g & -g & 0 & 0 \\
 & 3g & -g & -g \\
 & & 2g & -g \\
 & & & 2g
\end{matrix}$$

the solutions of which are 0 for the quintuplet, g for the antisymmetric triplet, $3g$ for the symmetric triplet, and $4g$ for the antisymmetric triplet

for the alternant helix-type structure

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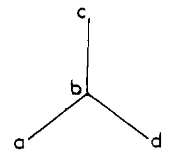


$$\begin{array}{cccc} g & -g & 0 & 0 \\ & 3g & -g & -g \\ & & g & 0 \\ & & & g \end{array}$$

the lowest triplet of which is symmetrical with a $4g$ energy

The $S_z = 0$ matrix has a $C_4^{\,2} = 6$ dimension and the form

$$\begin{array}{cccccc} |\overline{ab}cd| & |\bar{a}b\bar{c}d| & |\bar{a}bc\bar{d}| & |a\overline{bc}d| & |a\bar{b}c\bar{d}| & |ab\overline{cd}| \\ \sum\limits_{i,j} g_{ij} & -g_{bc} & -g_{bd} & -g_{ac} & -g_{ad} & 0 \\ & \Sigma g & -g_{cd} & -g_{ab} & 0 & -g_{ad} \\ & & \Sigma g & 0 & -g_{ab} & -g_{ac} \\ & & & \Sigma_g & -g_{cd} & -g_{bd} \\ & & & & \Sigma_g & -g_{bc} \\ & & & & & \Sigma_g \end{array}$$

When specified for each structure, it gives the lowest solutions

	linear	cyclic	nonalternant	helix
S	$(2+\sqrt{3})g$	$6g$	$5g$	$3g$
T	$(2+\sqrt{2})g$	$4g$	$4g$	$4g$

This second-order N electronic Hamiltonian is an Heisenberg–Dirac Hamiltonian since it only implies an effective exchange integral. As will be seen in the next section, higher order terms no longer enter into the Heisenberg scheme

$$H = \sum_{l}\sum_{l'} J_{ll'}\vec{S}_l\vec{S}_{l'} \tag{4}$$

The theoretical implications of this very simple model will be given in the following paper.

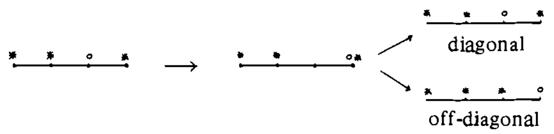
III. Higher Order Corrections

(1) Pedestrian Approach. The role of corrections besides order two was examined through a rapid analysis of the structure of the CI matrix (Figure 1).

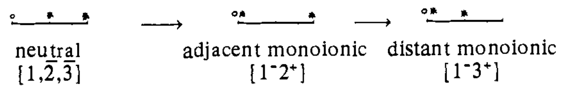
The monoionic determinants corresponding to the charge transfer between bonded atoms were responsible for the second-order contribution; as they only interact through negligible exchange integrals, there is no important third-order correction.

The fourth-order corrections will imply the two categories of determinants which interact with the adjacent charge-transfer determinants, namely, (i) the nonadjacent charge-transfer monoionic determinants (for instance, $[\mathrm{B^+C^-}]$ $|\bar{a}c\bar{c}de\bar{f}|$ interacts with $[\mathrm{B^+D^-}]|\bar{a}cd\bar{d}e\bar{f}|$ if C and D are bonded, through an F integral) and (ii) the dionic charge transfer determinants in which a second charge transfer takes place on another pair of bonded atoms (for instance, $[\mathrm{B^+C^-}]|\bar{a}c\bar{c}de\bar{f}|$ interacts with $[\mathrm{B^+C^-, E^+F^-}]|\bar{a}c\bar{c}df\bar{f}|$).

A simple picture of higher processes can be used, which follows the physical electron jump along the chain. Second-order contributions are simple back and forth processes.

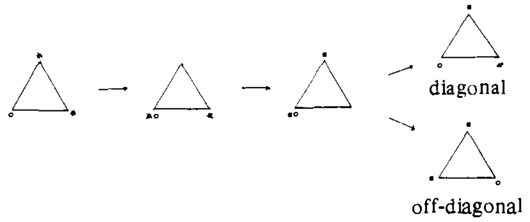


Third-order corrections are not efficient in noncyclic fragments

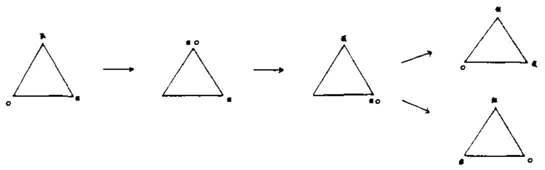


since the second step is either a neutral or a nonadjacent monoion and the back movement to a neutral state requires two more steps (fourth order).

A third-order process is possible if the second state also is an adjacent monoionic configuration which requires the fragment to be triangular

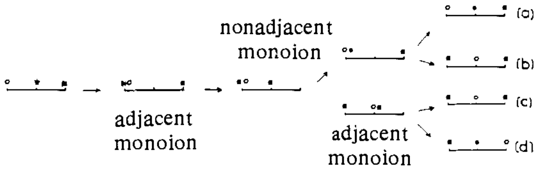


However other processes are possible which involve α spins instead of the β spins in the cyclic movement and therefore have opposite signs such as the following sequence which cancels the preceding contributions



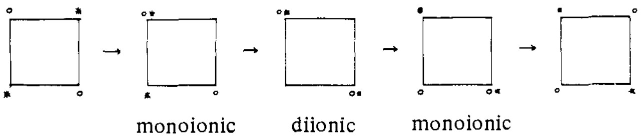
The triangular cycles do not introduce specific third-order corrections. (In the same way one may demonstrate that cyclic fifth order corrections cancel on pentagonal cycles, etc ...).

Fourth-order corrections will introduce some nonadjacent effective exchanges; turning back to the former three-atom noncyclic fragments, one may complete the process toward a neutral determinant as



These three-atom chains contribute respectively (a) to a diagonal term, (b and c) to an exchange between adjacent atoms, correcting its second-order value, and (d) to previously neglected exchange between [1–3] nonadjacent atoms.

Cyclic fragments may introduce fourth-order four-body corrections such as



This peculiar process through a dionic intermediate introduces a double-spin permutation.

(2) General Equations. From a more theoretical point of view, higher order corrections may be obtained by using the proper recurrence equations. Several studies were performed to establish equivalent forms of these equations.[1,15,16] The formalism used in this work is due to Levy.[20]

If P is the projector on the degenerate subspace ξ_0, T the evolution operator, and H the effective Hamiltonian and if

$$H\psi = E\psi$$

the following relations can be stated

$$TP\psi = \psi \qquad HP\psi = EP\psi \tag{5}$$

The total Hamiltonian H can be splitted into

$$H = H_0 + V \tag{6}$$

where H_0 is chosen in such a way that

$$[H_0,P] = 0 \tag{7}$$

The operators T and H can be written in the form of a power expansion of V

$$TP = \sum_{n=0}^{\infty} T_n P \tag{8a}$$

$$\bar{H} = \sum_{n=0}^{\infty} \bar{H}_n \tag{8b}$$

One gets at the nth order

$$T_n|I\rangle = Q(E_I - \mathrm{H}_0)^{-1}(VT_{n-1} - \sum_{p=1}^{n-1} T_p PVT_{n-p-1})|I\rangle \tag{9a}$$

$$\bar{H}_n = PVT_{n-1}P \tag{9b}$$

where $Q = 1 - P$ and $|I\rangle$ is a determinant belonging to the quasi-degenerate subspace ξ_0. One may notice that in this expansion the last term of the second member of eq 9a goes through intermediate states belonging to ξ_0, because of the presence of the P operator in this term. In our simple model, where $\langle I|V|J\rangle = 0$ when I and J are neutral determinants, the equations for the fourth- and sixth-order terms reduce to

fourth order

$$\langle I|\bar{H}_4|J\rangle = \sum_{\alpha,\beta,\gamma} \frac{\langle IV\alpha V\beta V\gamma \mathrm{V J}\rangle}{\Delta E\alpha\beta\gamma} - \sum_{\alpha\beta K} \frac{\langle IV\alpha VKV\beta VJ\rangle}{\Delta E\alpha\beta\Delta E\alpha} \tag{10a}$$

sixth order

$$\begin{aligned}\langle I|\bar{H}_6|J\rangle = {} & \sum_{\alpha,\beta,\gamma,\delta,\epsilon} \frac{\langle IV\alpha V\beta V\gamma V\delta V\epsilon VJ\rangle}{\Delta E\alpha\beta\gamma\delta\epsilon} - \\ & \sum_{\alpha\beta\gamma\delta K}\Bigg[\frac{\langle IV\alpha VKV\beta V\gamma V\delta VJ\rangle}{\Delta E\alpha\beta\gamma\delta}\,\frac{1}{\Delta E\alpha} + \\ & \frac{\langle IV\alpha V\beta VKV\gamma V\delta VJ\rangle}{\Delta E\alpha\beta\gamma\delta}\left(\frac{1}{\Delta E\alpha} + \frac{1}{\Delta E\beta}\right) + \\ & \frac{\langle IV\alpha V\beta V\gamma VKV\delta VJ\rangle}{\Delta E\alpha\beta\gamma\delta}\left(\frac{1}{\Delta E\alpha} + \frac{1}{\Delta E\beta} + \frac{1}{\Delta E\gamma}\right)\Bigg] + \\ & \sum \frac{\langle IV\alpha VKV\beta VLV\gamma VJ\rangle}{\Delta \mathrm{E}\alpha\beta\gamma}\left(\frac{1}{\Delta E\alpha^2} + \frac{1}{\Delta E_{\alpha\beta}}\right)\end{aligned} \tag{10b}$$

In these formulas, the product $\langle I|V|\alpha\rangle\langle\alpha|V|\beta...|\nu\rangle\langle\nu|V|J\rangle$ is written $\langle IV\alpha...\nu VJ\rangle$. The italic letters represent states that belong to ξ_0 (i.e., in this case neutral states) and the greek ones are not states of ξ_0 (i.e., ionic ones). The product $\Delta E\alpha\Delta E\beta...\Delta E\nu$ is written $\Delta E\alpha\beta...\nu$.

In both fourth- and sixth-order formulas, a first term, for which all intermediate states between $\langle I|$ and $|J\rangle$ are ionic, may be considered as the principal term of the development. In the fourth order, another term appears, with an opposite sign, that will be responsible for the cancellation of the contribution corresponding to disconnected graphs. The other terms appearing in the sixth-order equation are more numerous and are then more difficult to interpret but they play the same role. As in the case of fourth order, the three possibilities for the K neutral state to appear in the sequence are of opposite sign. The last term represents the only possibility to place two neutral states in the sequence. Its sign is opposite to the sign of the three preceding terms.

(3) Linked Cluster Rules. Our application of the QDMBPT differs from the original Brandow scheme[1] which implied that all the determinants with variable occupation numbers n_i of the so-called "valence" MO's were included in the degenerate subspace. Here we only have valence MO's and only consider a certain type of occupancy ($n_i = 1$, $\forall_i$) for the degenerate subspace. This is a peculiar case of the "general model space" formalism proposed by Hose and Kaldor.[16]

Most of the treatments assume a zeroth-order monoelectronic Hamiltonian (of the Moller–Plesset type[7])

$$H_0 = \sum_i \epsilon_i a_i^+ a_i \tag{11}$$

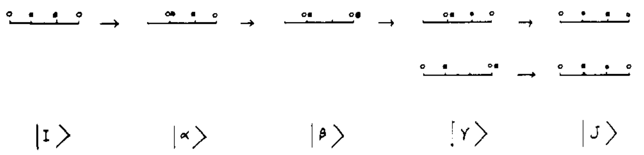
and this assumption plays an explicit role in the generalization of the linked cluster theorem[9] to the QDMBPT formalisms,[1,15,16] through the denominator additivity which allows the appropriate factorizations. One may notice that in the Moller–Plesset scheme our ionic determinants would be degenerate with the neutral ones and our model would break down. As noted by Brandow,[21] the use of a bielectronic H_0 operator is necessary to derive effective spin couplings.

The energy difference between the ionic and neutral states is due to the electronic repulsion between two electrons on the same center, and our zeroth-order Hamiltonian, of Epstein–Nesbet type[22]

$$H_0 = \sum_I |I\rangle\langle I|\langle I|H|I\rangle \tag{12}$$

is bielectronic in nature. This remark prevents the use of the usual QDMBPT diagrammatic expansion[1] and the direct use of the linked cluster theorem. Special diagrams might be defined for our problem, and it would be possible to show the existence of an appropriate linked cluster theorem, which results from the denominators additivity, the transition energy to a doubly ionic determinant being the sum of the transition energies to the monoionic ones, as results from eq 12.

We shall simply illustrate the unlinked cluster cancellations through fourth order by considering two independent charge-transfer proccsses $a \rightarrow b$ and $c \rightarrow d$. The processes through the ($b\bar{b}d\bar{d}$) dionic states, are supposed to lie at $2\Delta E$ above the neutral states



both contribute to the diagonal term of the $K = |\bar{a}bc\bar{d}|$ determinant through the factorization

$$-F_{ab}{}^2 F_{cd}{}^2/\Delta E^3$$

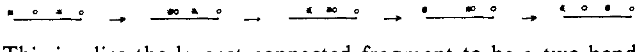
but the last term of eq 9a contains a term

$$-\langle I|V|\alpha\rangle\langle\alpha|V|I\rangle\langle I|V|\beta\rangle\langle\beta|V|J\rangle/\Delta E^3$$

of opposite sign to $F_{ab}{}^2F_{cd}{}^2/\Delta E^3$ which cancels the preceding contribution. The first term corresponded to an unlinked process since the back and forth movements of the two electrons were independent in separate fragments.

The formal demonstration of the linked cluster theorem for our model would be tedious; it results in a very simple *rule* when the tight-binding hypothesis is assumed; *the only contributions to the effective Hamiltonian are concerned with the connected fragments of the molecular graph.*

As a direct consequence, it is clear that nth-order contributions are at most concerned with n chemical bonds. It will be shown below that they imply n chemical bonds only if these n bonds form a circle. At order two, the only fragment is obviously one segment with a back and forth electron jump on it. In fourth order, the necessity of starting with a neutral determinant and of getting to another neutral one at the fourth step imposes *two forward and two backward jumps* (since each electron movement can be considered as a charge transfer that must be followed by another charge transfer toward the inverse direction) as in



This implies the largest connected fragment to be a two-bond fragment. On the contrary, in the case of cyclic fragments, the

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(20) B. Levy, Proceedings of the fourth seminar on computational methods in Quantum Chemistry, Orenäs, Sweden, 1978.

(21) B. H. Brandow, *Adv. Phys.*, **26**, 651 (1977).

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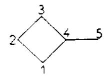
Table I. The Fourth-Order Hamiltonian of the Methylenecyclobutadiene, in Units $F^4/\Delta E^3$ [a,b]

12	13	14	15	23	24	25	34	35	45
14	−20	12	0	12	--20	2	0	0	0
	36	−20	2	−20	40	0	−20	2	0
		22	−8	0	−20	0	12	0	2
			14	0	0	0	0	−8	0
				14	−20	2	12	0	0
					48	−8	−20	0	0
						12	0	0	−8
							22	−8	2
								14	0
									4

[a] The basis determinant $|i\bar{j}k\bar{l}\bar{m}|$ is written *ik*. [b] Numbering as follows

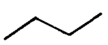
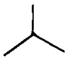


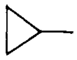
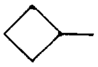
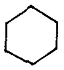
fourth-step neutral determinant can be reached by a cyclic movement using four segments, as it was shown in section III.1.

As a more general result a fragment will contribute to *n*th order if, containing n_1 segments belonging to cycles and n_2 that do not, one has the relation

$$n_1 + 2n_2 < n$$

In the sixth order, the possible fragments are those of fourth order and

The effective Hamiltonian $\bar{H}_n$ of a particular molecule is then obtained without any calculation as soon as one finds all the fragments belonging to it, by adding the different effective Hamiltonians $\bar{h}_{n_{i,s}}$ corresponding to the fragment *i*; the subscript *s* means that in the calculation of the matrix element $\langle I|\bar{H}|J\rangle$ the fragment *i* has a spin eigenvalue

$$S_{z_i} = s$$

The Hamiltonians $\bar{h}_{n_{i,s}}$ are calculated once for all and do not depend on the rest of the molecule.

(4) A Kit Hamiltonian. The effective *N*-electron Hamiltonian at order *n* will consist of two-body, three-body, ..., and *N*-body terms. We shall give all fourth-order terms and the main (cyclic) sixth-order terms. In order to simplify the results, one may benefit from the following theorem.

Theorem: at each order the sum of the terms of a column (or row) of the effective operator is zero.

Proof: the determinant where all spins are parallel ($S_z = N/2$) is an eigenfunction and its eigenvalue is zero at each order. The $S_z = 0$ matrix contains a component of this multiplet (as well as the other $S_z = 1, 2, \ldots$ matrices). It is well-known that for a *N*-open-shell configuration, the coefficients of the $S_z = 0$ highest multiplet on the various determinants are all equal to $N^{-1/2}$. Then by writing the eigenequation at the *n*th order

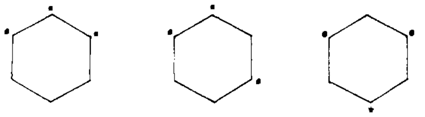
$$\left[\overline{H_n}^{\text{eff}}\right]\begin{bmatrix}1\\1\\1\\1\end{bmatrix} = 0\begin{bmatrix}1\\1\\1\\1\end{bmatrix}$$

implies that the sum of the terms of each line is zero in $\bar{H}_n^{\text{eff}}$. Since this is true for each order, it is true for the *n*th-order correction (QED).

A direct consequence is that it is sufficient to consider the off-diagonal contributions to each order, the diagonal contribution being equal to the sum of the off-diagonal contributions with a changed sign. The fourth (and main sixth) order off-diagonal terms will be given in a second quantization language as effective many-body operators.

For a further simplification, one may assume that all the monoionic determinants have the same energy ΔE, all the dionic determinants have the energy $2\Delta E$, etc. This assumption allows factorizations over various processes going through different nonadjacent monoionic or multiionic determinants, and the summation over the various perturbative paths at a given order is simply expressed then by an integer number. This new simplification is by no means necessary, and actual calculations might be performed by using various energies for the intermediate states according to the topology

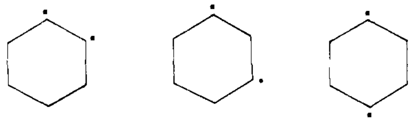
Table II. Sixth-Order Cyclic Operators



Three Types of ($S_z = 0$) Spin Configurations[a]

	123	124	125	126	134	135	136	145	146	156
123	−24	40	−30	12	−30	40	- 30	0	0	0
124		−24	40	−30	40	−140	112	40	−30	0
135						−24	40	40	−140	40

	234	235	236	245	246	256	345	346	356	456
123	12	−30	0	0	0	0	0	0	0	0
124	−30	112	−140	−30	40	0	0	0	0	0
135	0	40	−140	−140	504	−140	20	−140	40	0



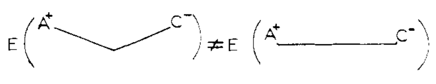
Three Types of ($S_z = 1$) Spin Configurations

	12	13	14	15	16	23	24	25	26	34	35	36	45	46	56
12	16	−30	40	−30	12	12	−30	40	−30	0	0	0	0	0	0
13		16	−30	40	−30	−30	112	−140	112	−30	40	−30	0	0	0
14			16	−30	40	0	−30	112	−140	40	−140	112	40	−30	0

One Line is Sufficient to Build the ($S_z = 2$) Complete Matrix

	1	2	3	4	5	6
1	−4	12	−30	40	−30	12

[a] Characteristic values in terms of $F_{12}F_{23}F_{34}F_{45}F_{56}F_{61}/\Delta E^5 = F^6/\Delta E^5$.



charge separation

$$E(A^+C^-) \neq E(A^+B^-)$$

and charge repartition

$$E(A^+B^-C^+D^-) \neq E(A^+B^-C^-D^+)$$

Our supplementary simplification may be viewed as the use of an Hubbard[23] Hamiltonian

$$H = \sum_{ij} h_{pq} a_p^{+} a_q + \sum_p g_{pp} a_p^{+} a_p^{+} a_p a_p \tag{13}$$

which takes only into account the repulsion of an electron pair on the same center, instead of the Pariser–Parr–Pople Hamiltonian.

The second-order off-diagonal terms are effective exchange operators

$$2\frac{F_{ij}^{\,2}}{\Delta E}(a_{\bar{i}}^{+} a_j^{+} a_i\, a_{\bar{j}} + a_i^{+} a_{\bar{j}}^{+} a_{\bar{i}} a_j)$$

(if i and j are bonded in the tight-binding hypothesis). As mentioned previously the odd order terms are zero; the fourth order off-diagonal terms already mentioned are concerned with either two-body fragments through a 1–2 exchange operator (going through neutral states)

$$(-8F_{ij}^{\,4}/\Delta E^3)(a_i^{+} a_{\bar{j}}^{+} a_{\bar{i}} a_j + a_{\bar{i}}^{+} a_j^{+} a_i a_{\bar{j}})$$

which should be added to the second-order term $2F_{ij}^{\,2}/\Delta E$ (the corresponding sixth-order term is $+64F_{ij}^{\,6}/\Delta E^2$, illustrating the sign alternation of the various orders), three-body linear fragments through a 1–3 exchange operator

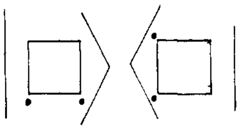
$$K_{jk} = (\sum_j 2F_{ij}^{\,2}F_{jk}^{\,2}/\Delta E^3)(a_i^{+} a_{\bar{k}}^{+} a_{\bar{i}} a_k + a_{\bar{i}}^{+} a_k^{+} a_i a_{\bar{k}})$$

where in the tight-binding hypothesis j must be bonded to both i and k

(one should notice that this effective integral is independent of the relative orientation of the two adjacent bonds), or cyclic four-body fragments (with $S_z = 0$ or ± 1 on the fragment), implying circulation of the electrons on the ring. For $S_z = 0$, one gets three cyclic operators

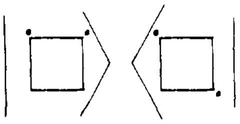
(i) $(8F_{ij}F_{jk}F_{kl}F_{li}/\Delta E^3)(a_i^{+} a_j^{+} a_{\bar{k}}^{+} a_{\bar{l}}^{+} a_i a_{\bar{j}} a_{\bar{k}} a_l + \text{inverse})$

which may be represented as

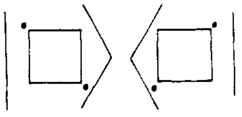


where the dots represent β spins,

(ii) $-(12\ F^4/\Delta E^3)$



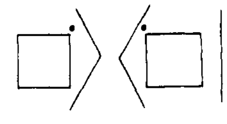
(iii) $(40\ F^4/\Delta E^3)$



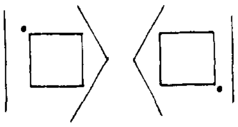
for a double-spin permutation, which is by far the largest fourth-order term

For $S_z = 1$, there exist only two operators

$(8F^4/\Delta E^3)$

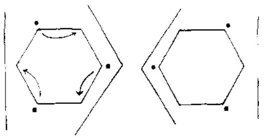


$(-12F^4/\Delta E^3)$



The cyclic operators must be added to the linear fragment operators. As an example Table I gives the total fourth-order Hamiltonian of the methylenecyclobutadiene molecule, in $F^4/\Delta E^3$ units. For a better understanding, one may expand the calculation of one of the matrix elements (corresponding to a 2–4 exchange) from the relevant fragments, namely, the $\langle 12\bar{3}\bar{4}\bar{5}|H|1\bar{2}\bar{3}4\bar{5}\rangle$ matrix element; there is no one-bond correction; there are two two-bond contributions (through $\overline{234}$ and $\overline{214}$), each of them equal to $2F^4/\Delta E^3$, and one cyclic four-bond contribution equal to $8F^4/\Delta E^3$, resulting in a total matrix element of $12F^4/\Delta E^3$.

The sixth-order cyclic contributions are numerous and reported in compact form in the Appendix and Table II. As in the case for the four-membered ring the largest off-diagonal matrix element is concerned with the simultaneous spin permutations

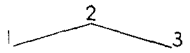


$504F^6/\Delta E^5$

The role of these cyclic terms will be discussed in the following paper. Using the fourth-order terms and the cyclic sixth-order terms allows the treatment of most conjugate compounds.

IV. Conclusion

The effective valence bond (EVB) Hamiltonian proposed in the present work allows a drastic shortcut in the size problem of VB techniques, since it is restricted to the neutral configurations, the effect of the ionic configurations being included by perturbation and resulting in a set of very simple topological rules. The fourth-order terms derived from the study of three-atom systems



and four membered rings are transferable in larger compounds; adding the aromatic sixth-order effects in benzenic rings allows for treatment most of the conjugated molecules through the diagonalization of reasonable matrices, the matrix elements of which are transferable. Several neutral states are then obtained to the same level of accuracy. The N consistency problem is avoided since the background for the theory is perturbative. One must notice that, in an early work, Bulaevskii[24] developed the same ideas of quasi-degenerate perturbation theory as Brandow and thought of a specific application to the "homopolar" (i.e., neutral) states of conjugated hydrocarbons but did not perform any application.

The problem of the role of the σ core on the π-electron states, which was the main purpose of previous applications,[3] of Brandow's formalism was not considered there. The instantaneous polarization of the core would lower the energy of the ionic configurations and might be included in the perturbation expansion. The ΔE value must be considered as lowered by this $\sigma\pi$ correlation effect, which the reduction of the monocentric bielectronic integral in the PPP models tries to reproduce. The inclusion of the core effects on our effective VB model will be discussed later on.

Of course the matrix elements of the EVB effective Hamiltonian in such a basis are essentially effective exchange terms, reflecting movements of electrons on the skeleton through ionic charge-

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[23] J. Hubbard, *Proc. R. Soc., London, Ser. A*, **276**, 283 (1963).

[24] L. N. Bulaevskii, *Zh. Eksp. Teor. Fiz.*, **51**, 230 (1966) (english edition, **24**, 154 (1967)).

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 $\tilde{H}_n$ at nth order. The unlinked cluster cancellations allow a very important shortcut in the calculation of the operator $\tilde{H}_n$, 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 $\tilde{h}_{n_{f_s}}$ 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).

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