Localized Bond Orbitals and the Correlation Problem

II. Application to π-Electron Systems

J. P. MALRIEU, P. CLAVERIE, and S. DINER

Institut de Biologie Physico-Chimique, Laboratoire de Biochimie Théorique
13, rue P. et M. Curie, Paris Vè.

The method presented in paper I of the series is tested in the case of highly delocalized π systems where convergence should be difficult. For π alternant hydrocarbons with regular geometries the summation of the terms to 4th order is possible using a few basic parameters and some caracteristics of the molecular topology. Several numerical applications are given: a good agreement with exact energy is obtained for butadiene and benzene.

Die in Teil I dieser Arbeit angegebene Methode wird für den Fall eines stark delokalisierten π-Elektronensystems, wo Konvergenz schlecht sein sollte, ausprobiert. Für geometrisch reguläre Kohlenwasserstoffe mit alternierenden π-Bindungen ist die Summation der Terme bis zur 4. Ordnung möglich, wenn man nur einige Basisparameter und charakteristische Eigenschaften der molekularen Struktur benutzt. Es werden verschiedene numerische Anwendungen angegeben: für Butadien und Benzol erhält man eine gute Übereinstimmung mit der exakten Energie.

La méthode proposée dans le 1er article de la série est mise à l'épreuve sur les systèmes π fortement délocalisés où elle devrait avoir de la peine à converger. Pour les hydrocarbures alternants avec géométries régulières il est possible d'effectuer les sommations de chaque type de contribution jusqu'au 4è ordre, en n'utilisant qu'un nombre réduit de paramètres de base et quelques caractéristiques de la topologie moléculaire. On donne plusieurs exemples numériques: les résultats obtenus pour le butadiène et le benzène sont très proches des résultats exacts.

1. Introduction

In a preceeding paper [1] we have presented the principle and the advantages of a method for the calculation of the ground state energy of molecules. This method consists of four steps:

One chooses a set of reasonable bond-orbitals, both bonding and antibonding.

One uses the bonding orbitals (or lone pairs) to build a fully localized determinant which represents the wave function according to the chemical formula. This determinant is the zeroth order wave function.

One uses the antibonding orbitals to build excited states (mono, di, ... n excited states). The CI matrix is constructed on this basis of determinants.

One develops the lowest eigenvalue and eigenstate by the Rayleigh-Schrödinger perturbation expansion.

We discussed the possible choice of the bond orbitals, the choice of the perturbation Hamiltonian and the use of diagramatic techniques. The purpose of the present paper is to give an initial series of applications to π problems.

Why do we choose the π systems to test this method? The convergence of the perturbation expansion from the SCF determinant for correlation problems has already been studied and the first terms of the series seem to give a reasonable evaluation of the correlation energy in the basis [2, 3, 4, 5], especially when one

uses localized bonding and antibonding orbitals [6]. But we start now from a determinant which does not include any delocalization, and with a higher energy. The stronger the delocalization in the system, the less correct is the fully localized determinant as zeroth order wave-function. The studies of the localizability according to various criteria [7, 9] confirm that the π systems are much more delocalized than the σ ones [6]. The localizability, which lies at about 8 % for benzene, reaches 98 or 99 % in typical σ systems [6]. Thus the delocalization is very important in aromatic molecules and the energy of a Kékulé-like determinant should be much higher than the SCF ones. The conclusion is that aromatic systems should be a crucial test of the method. If it converges on benzene, it should behave satisfactorily for the other molecules.

The second reason for a test study on π systems is that the Pariser-Parr approximations [10] are reliable. Moreover the alternant hydrocarbons present some special simplifications (no polarisation for instance). In their case one may elucidate simply the role of the topology and if one assumes an ideal geometry the algebraic derivations and the summations are very easy to perform. Under these favorable circumstances we have been able to make a fully explicit development up to fourth order. One will see also that in this case the relations between the Feynmann diagrams and the molecular graph appear clearly.

2. Simplifications Due to the Pariser-Parr Approximations

The PPP approximations [10] imply:

the zero differential overlap: $S_{pq} = 0$ for $p \neq q$;

the tri- and quadricentric bielectronic integrals and exchange integrals are zero: $(pq \mid rs) = (pq \mid pq) \, \delta_{pr} \delta_{qs}$;

the non diagonal core Hamiltonian matrix elements are zero, except for nearest neighbourgs atoms: $\beta_{pq} = 0$ if p and q are not linked;

the diagonal terms of the core Hamiltonian are written as

$$\alpha_p = W_{2p} - \sum_{q \neq p} (pq \mid pq)$$

where W_{2p} is the "ionization potential" of the $2p_z$ orbital of the atom p.

The fully localized orbitals (FLBO) which will be used are ethylenic orbitals. The "ground state" wave function will be the determinant build with "bonding" molecular orbitals only. The "antibonding" orbitals are used to built the "excited" configurations. (For π systems, the treatment is a special case of the method called "Molecules in Molecules" [11, 13] mainly used for excited states.)

Configuration interaction implies the calculation of all molecular orbital bielectronic integrals $(ik \mid jl) = \left\langle ik \left| \dfrac{1}{r_{12}} \right| jl \right\rangle$. But the localized molecular orbitals are defined on different atoms. Due to the reduction of the atomic bielectronic integrals to $(pq \mid pq) = g_{pq}$ the only non-zero molecular bielectronic integrals are of the type

$(i'j' \mid i''j'')$ when $\quad \begin{cases} i', i'' = i \quad \text{or} \quad i^* \\[2ex] j', j'' = j \quad \text{or} \quad j^* . \end{cases}$

2*

This is the main advantage of working in a basis of bond orbitals: instead of N^4 integrals of the same order of magnitude [4], one has only N^2 important elements in the configuration interaction matrix.

One gets further simplifications for the case of alternant hydrocarbons. The electronic charge on each atom must remain unity. There is no polarization and the intra-bond monoexcited states $\left(\dfrac{i^*}{i}\right)$ do not interact with the ground state.

One has $J_{ij} = (ij \mid ij) = J_{ij^*} = J_{i^*j} = J_{i^*j^*}$.

The transition energies keep a very simple form. One may verify easily that for the orbitals i and i^* one has for the monoelectronic energies

$$e_i = W_{2p} + \beta^i_{12} + J_{ii},$$

where β^i_{12} is the core integral between atoms 1 and 2 of bond i. And

$$e_{i^*} = W_{2p} - \beta^i_{12} + 2J_{ii^*} - K_{ii^*}.$$

Thus, if all double bonds have the same length, all the monoelectronic energies are equal to e or e^*. Then there are only two types of monoexcitation energies:

The polarisation transitions $\left(\dfrac{i^*}{i}\right)$ have the energies

$$
\begin{aligned}
\Delta E_{i \to i^*} = -E = e^* - e - (J_{ii^*} - K_{ii^*}) \\
= -2\bar{\beta},
\end{aligned}
$$

where $\bar{\beta}$ is the non diagonal core matrix element for the double bond.

The "charge-transfer" or "delocalization" transitions $\left(\dfrac{j^*}{i}\right)$ need a different transition energy which will depend on the relative geometrical position of the bonds i and j.

$$\Delta E_{i \to j^*} = -E_{ij} = e^* - e - J_{ij^*}$$

with

$$J_{ij^*} = \frac{1}{4}(g_{i1,j1} + g_{i1,j2} + g_{i2,j1} + g_{i2,j2}).$$

We shall be led to keep only the excitations towards the nearest neighbour bonds. In that case one has only two charge-transfer "excitation energies": the "cis" and "trans" transition energies for linear polyenes for instance.

We also need the "transition energies" towards diexcited configurations. In general this energy depends of the relative spins of the two excitations: For two different spins one has

$$\Delta E \left(\frac{j^* \bar{l}^*}{i \ \bar{k}}\right) = \varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k + J_{ik} + J_{j^*l^*} - J_{kl^*} - J_{ij^*} - J_{kj^*} - J_{il^*} + K_{ij^*} + K_{kl^*},$$

and if the two spins are the same,

$$\Delta E' \left(\frac{j^* l^*}{i k}\right) = \Delta E \left(\frac{j^* \bar{l}^*}{i \bar{k}}\right) - K_{ik} - K_{j^*l^*} + K_{il^*} + K_{kj^*}.$$

The exchange integrals are zero in our problem and these two excitations energies are identical. To the 3rd order we shall only consider the excitations of the following types (for equal double bond lengths)

$$\Delta E\left(\frac{i^* j^*}{ij}\right) = 2\varepsilon^* - 2\varepsilon - 2J_{ii^*} - 2K_{ii^*} = -2E$$

$$\Delta E\left(\frac{i^* i^*}{ii}\right) = -2E.$$

All the diexcitation transition energies useful to the third order are thus equal to $2E$.

3. Zeroth, First and Second Order Energies

One may verify that in the Pariser and Parr approximations the energy of the fully localized wave function is a sum of bond energies if the bond orbitals are homopolar: a cancellation occurs between the sum of coulombic integrals in $\sum_i 2\langle i|h|i\rangle$ and the sum of coulombic integrals in $\sum_i \sum_j 2J_{ij} - K_{ij}$. (Note that this is no longer true for polar molecules, and this forbids the calculation of resonance energies as the differences between the SCF energy and the energy of the fully localized determinant.)

$$E^0 = \sum_i E_i.$$

If all the double bonds have the same length, $E_i = \varepsilon = 2W_{2p} + 2\bar{\beta} + \frac{1}{2}(g_{11} - 3g_{12})$, and the zeroth order energy is obtained from the number n_i of double bonds:

$$E^0 = n_i \varepsilon.$$

The first order energy correction is zero by definition of the perturbation matrix.

The second order correction involves the mono- and diexcited configurations. As the polarization states $\left(\frac{i^*}{i}\right)$ are not involved, we must consider the delocalization or charge transfer states $\left(\frac{j^*}{i}\right)$. With the PP approximations for bielectronic integrals $(ik|j^* k) = 0 \; \forall \, k$, and

$$\left\langle 0|H|\left(\frac{j^*}{i}\right)\right\rangle = \langle i|h|j^*\rangle = \beta_{ij^*}.$$

This integral will be non zero if the two double bonds are adjacent. Then

$$\beta_{ij^*} = \pm \frac{\beta}{2},$$

if β is the monoelectronic integral between two atoms singly bonded in the Kékulé formula. The sign depends on the sign of the coefficient of the molecular orbital j^* on the atom adjacent to the bond i. Let us call n_{ij} the number of neighbour bonds. One may consider the monoexcitations $\left(\frac{j^*}{i}\right)$, $\left(\frac{\bar{j}^*}{\bar{i}}\right)$, $\left(\frac{i^*}{j}\right)$ and $\left(\frac{\bar{i}^*}{\bar{j}}\right)$, and the

second order correction due to monoexcited states is

$$\sum_{i<j} 4\,\frac{\beta_{ij}^2}{E_{ij}}\,.$$

If all the single bonds have the same length and if all neighbour bonds are in the same geometrical relation (all trans in linear polyenes, all cis in benzene and naphtalene), one may write

$$\left.\begin{aligned}|\beta_{ij}| &= -\frac{\beta}{2}\\[4pt] E_{ij} &= E'\end{aligned}\right\}\ \forall,\ i \text{ and } j \text{ adjacent}$$

and the contribution becomes $\dfrac{\beta^2}{E'}\,n_{ij}$.

The diexcited configurations which play a role in the 2nd order correction belong to two types:

The interbond diexcitations $\left(\dfrac{i^*j^*}{ij}\right)$ give most of the inter-pair correlation [6, 14] contribution. The matrix element with the ground state is

$$(ij \mid i^*j^*) = \pm\,\frac{1}{4}\,[g_{i1\,j1} + g_{i2\,j2} - g_{i1\,j2} - g_{i2\,j1}]$$

	i^*			j^*	
	$+$	$-$		$+$	$-$
	$+$	$+$		$+$	$+$
	1	2		1	2
	i			j	

At long distances the bielectronic integrals decrease as $1/r$. It is easy to see that the integral $(ij \mid i^*j^*)$ decreases as $1/r^3$, and one recognizes here a term analogous to the dispersion contribution in the expression of intermolecular forces. This integral decreases very rapidly with the distance. It is thus possible:
either to take the sum of all these diexcitations, and one gets

$$\sum_{i<j}\sum 4\,\frac{(ij \mid i^*j^*)^2}{\Delta E\left(\dfrac{i^*j^*}{ij}\right)}\quad \text{(corresponding to the diagrams of Fig. 2 a, Part I)}$$

or to neglect the long distance terms and to keep the interactions between adjacent bonds only. If all these bonds are in the cis-position (as in benzene or naphtalene) or in the trans-position (as in linear polyenes), we may write $(ij \mid i^*j^*) = b$. The quantity b is negative and we get the contribution

$$\frac{4b^2}{2E}\,n_{ij} = \frac{2b^2}{E}\,n_{ij}\,.$$

The other possible diexcitation concerns only one bond $\left(\dfrac{i^* \bar{i}^*}{i \bar{i}}\right)$ and leads to the pair correlation contribution[1]:

$$\sum_i \frac{(ii \mid i^* i^*)}{E\left(\dfrac{i^* \bar{i}^*}{i \bar{i}}\right)} \; ;$$

the integral $a = (ii \mid i^* i^*) = \frac{1}{2}(g_{11} - g_{12})$ is important and is reduced by the parametric PP reduction of the short distance bielectronic integrals. Thus one understands very clearly why the correlation energy in π systems in mainly dependent on the values of g_{11} and g_{22}.

The second order correction appears as a sum of bond energies and bond interactions energies.

$$\varepsilon^2 = \frac{a^2}{2E}\, n_i + \left(\frac{\beta^2}{E'} + \frac{2b^2}{E}\right) n_{ij}\,.$$

4. Third Order Corrections

In our problem, due to the nullity of ε^1 and $\langle \Phi_I|V| \Phi_I\rangle$, the 3rd order correction is given by

$$\varepsilon^3 = 2 \sum_{\substack{I<J \\ \underbrace{\quad}_{\neq 0}}} \frac{\langle 0 |V| \Phi_I\rangle \langle \Phi_I |V| \Phi_J\rangle \langle \Phi_J |V| 0\rangle}{(E_0 - E_I)(E_0 - E_J)}\,.$$

The configurations Φ_I and Φ_J belong to Ψ^1, and it is sufficient to analyse the three following possibilities:

1. Interaction of Monoexcited States

In general the monoexcited states $\left(\dfrac{j^*}{i}\right)$ and $\left(\dfrac{l^*}{k}\right)$ do not interact. They may only interact if $k = i$ or $l^* = j^*$. If $\Phi_I = \left(\dfrac{j^*}{i}\right)$ and $\Phi_J = \left(\dfrac{k^*}{i}\right)$ we get the diagram of Fig. 4a.

$$\frac{\beta_{ij^*}\,\beta_{j^* k^*}\,\beta_{ik^*}}{E'^2}\,.$$

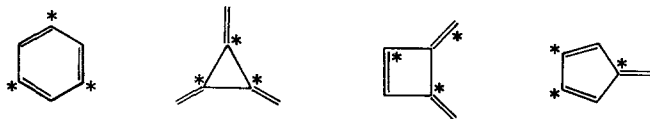The bonds i, j and k must be adjacent, which requires one of the following topologies.

Fig. 3

---

[1] We used this terminology in order to compare with Kutzelnigg's results but it would be better to use Sinanoğlu's notation of "intra-bond and inter-bond correlation energies".

We only consider the first topology, the only one to be found frequently in alternant hydrocarbons.

The sign of the contribution does not depend on the choice of the signs of the coefficients on the excited orbitals, since these orbitals always appear an even number of time and one may verify that in our case we get $\dfrac{\beta^3}{8E'^2}$. Taking into account the two spin possibilities we get

$$\frac{\beta^3}{2E'^2}\, v_{ijk}$$

where v_{ijk} is defined by $v_{ijk} = \sum\limits_{i}\sum\limits_{\substack{j<k\\ \neq i}}\sum 1$, i, j, and k being adjacent two by two.

It is clear that in the topological graph ⬡ this number is 3. We shall introduce $n_{ijk}^{\triangle}$, the number of Kékulé-like diagrams in the chemical formula.

One may verify that the interaction of states $i\,|\,j^*$ and $k\,|\,j^*$ leads to the same contribution, and the interaction of the monoexcited states gives finally $\dfrac{3\beta^3}{E'^2}\, n_{ijk}^{\triangle}$. This contribution is negative and important.

2. Interaction of Mono- and Di-Excited Configurations

The states $\left(\dfrac{j^*}{i}\right)$ cannot interact with the states $\left(\dfrac{i^*\,\bar{i}^*}{i\,\bar{i}}\right)$, $\left(\dfrac{k^*\,l^*}{k\,l}\right)$ and $\left(\dfrac{k^*\,i^*}{k\,i}\right)$. Then there only remains the interaction with $\left(\dfrac{i^*\,j^*}{i\,j}\right)$.

$$\langle i\bar{j}^* \ldots j\bar{j}\,|H|\, i\,\bar{i}^* \ldots j\bar{j}^*\rangle = -\langle i\bar{j}^* \ldots j\bar{j}\,|H|\, i\,j^* \ldots j\bar{i}^*\rangle$$
$$= -\beta_{ji^*}.$$

We get the contribution $-\dfrac{\beta_{ij^*}\,\beta_{ji^*}(ij\,|\,i^*j^*)}{E'\,E} = \dfrac{\beta^2 b}{8E'\,E}$.

Taking into account the two spin possibilities and the analogous interaction of $\left(\dfrac{i^*}{j}\right)$ with $\left(\dfrac{i^*\,j^*}{i\,j}\right)$ we get $\dfrac{\beta^2 b}{E'\,E}\, n_{ij}$, which is negative, as b, and corresponds to diagrams of Fig. 4 b.
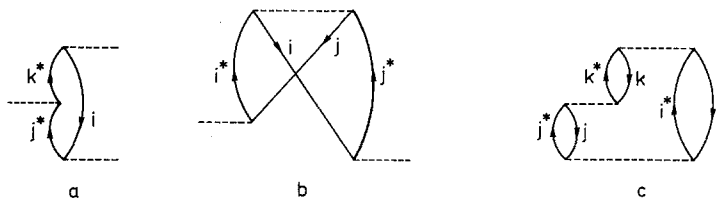

Fig. 4. Third order diagrams (see the text)

3. Interaction of Diexcited States

The states $\left(\dfrac{i^*\, \bar{i}^*}{i\,\bar{i}}\right)$ and $\left(\dfrac{j^*\, \bar{j}^*}{j\,\bar{j}}\right)$ cannot interact. But $\left(\dfrac{i^*\, \bar{i}^*}{i\,\bar{i}}\right)$ can interact with $\left(\dfrac{i^*\, j^*}{i\,j}\right)$ with the matrix element $(i^*j \mid ij^*) = b$. Taking into account the four spin possibilities, and the interchange of the role of bonds i and j we get $\dfrac{4ab^2}{E^2}\, n_{ij}$, which is positive. This corresponds to a special case of diagram 4c. The interacting diexcited configurations may be of the type $\left(\dfrac{i^*\, j^*}{i\,j}\right)$ and $\left(\dfrac{i^*\, k^*}{i\,k}\right)$. This leads to the matrix element $(j^*k \mid jk^*) = b$. If we neglect the long range interactions the three bonds i, j, k must be adjacent as in § 4, 1°). One has thus 8 spin-possibilities and one gets $\dfrac{12b^3}{E^2}\, n_{ijk}^{\triangle}$, a negative quantity.

It is important to remember that we work in a basis of single determinants and that we distinguish between $\left(\dfrac{i^*\, j^*}{i\,j}\right)$ and $\left(\dfrac{i^*\, \bar{j}^*}{i\,\bar{j}}\right)$. These two configurations interact with the matrix element $(j^*j \mid jj^*) = K_{jj^*} = a$. This gives the term $\dfrac{ab^2}{4E^2}$. Taking into account the two possible spins for i and the possible permutation of i and j we get the positive contribution

$$\frac{2ab^2}{E^2}\, n_{ij}\,.$$

The third order correction is given by

$$\varepsilon^3 = \left(\frac{\beta^2 b}{E'E} + \frac{6ab^2}{E^2}\right) n_{ij} + \left(\frac{3\beta^3}{E'^2} + \frac{12b^3}{E^2}\right) n_{ijk}^{\triangle}\,.$$

One may remark that if b is small compared to β and a (which is always the case in π systems) *the main term is* $\dfrac{3\beta^3}{E'^2}\, n_{ijk}^{\triangle}$ *which is negative: in benzene-like systems we shall have an important negative third order correction while in polyene-like systems the third order correction will be small, and positive or negative according to the ratio* a/β.

It seems at this step that the nth order correction involves for the first time "n-body" terms and many "$(n-p)$-body" corrections. In our problem the energy corrections are immetiatly obtained by counting the pairs of adjacent double bonds and the number of Kékulé-like formulas in the chemical localized graph.

We would stress on the fact that for a given type of Goldstone's diagram one gets different order of magnitudes for the corresponding elements according to the labelling of the lines: this is due to the fact that the intra pair correlation matrix elements a are much larger than the interpair contributions b.

All these remarks will be confirmed by the analysis of the fourth order correction.

5. Fourth Order Correction

The general 4th order contribution has the form given in Eq. (2), but we must calculate first the contribution of the so called EPV diagrams, corresponding to the RS diagrams with a single non-zero Goldstone component.

A. 4th Order EPV Diagrams Contributions

Let us divide the 2nd order correction to the energy ε^2 and the first order correction to the wave function Ψ^1 into their contribution from the monoexcited states ($\varepsilon^{2,1}$ and $\Psi^{1,1}$) and their contribution from the diexcited states ($\varepsilon^{2,2}$ and $\Psi^{1,2}$). We must analyse the non cancelling terms coming from $\varepsilon^{2,1}\langle \Psi^{1,1} \mid \Psi^{1,1}\rangle$, $\varepsilon^{2,2}\langle \Psi^{1,2} \mid \Psi^{1,2}\rangle$, $\varepsilon^{2,2}\langle \Psi^{1,1} \mid \Psi^{1,1}\rangle$ and $\varepsilon^{2,1}\langle \Psi^{1,2} \mid \Psi^{1,2}\rangle$.

a) $\varepsilon^{2,1}\langle \Psi^{1,1} \mid \Psi^{1,1}\rangle$. The contribution coming from $\left(\dfrac{j^*}{i}\right)$ in ε^2 and $\left(\dfrac{k^*}{i}\right)$ in Ψ^1 are not cancelled. They give $-\dfrac{\beta_{j^*}^2}{E'}\times\dfrac{\beta_{ik^*}^2}{E'^2}$. This implies that i is linked to j and k, but k and j are not necessarily adjacent (see Fig. 5). If we call $n_{ijk}^\wedge$ the number of such
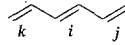

Fig. 5

topological subsystems in the molecular graph[2], we get $-\dfrac{\beta^4}{4E'^3} n_{ijk}^\wedge$. We could change the role of occupied and virtual orbitals and get an equal contribution. As a special case we must consider the contributions of $\left(\dfrac{j^*}{i}\right)$ both in ε^2 and Ψ^1; taking into account the two spin possibilities and the interchange of i and j, we get

$$-\frac{\beta_{ij^*}^2\beta_{kj^*}^2}{E'^3} \rightarrow -\frac{\beta^4}{4E'^3} n_{ij}.$$

b) $\varepsilon^{2,2}\langle \Psi^{1,2} \mid \Psi^{1,2}\rangle$. There is no cancellation with the general summation for the contribution of $\varepsilon^{2,2}$ coming from $\left(\dfrac{i^*\,j^*}{ij}\right)$ and of Ψ^1 coming from $\left(\dfrac{i^*\,k^*}{ik}\right)$. There are 8 spin possibilities and j and k may be inverted: thus we obtain

$$-\frac{b_{ij}^2 b_{ik}^2}{E^3} \quad \text{hence} \quad -\frac{2b^4}{E^3} n_{ijk}^\wedge.$$

There are some special cases:

$$\left(\frac{i^*\,j^*}{ij}\right) \text{ in } \varepsilon^2, \quad \left(\frac{i^*\,\bar{j}^*}{i\bar{j}}\right) \text{ in } \Psi^1 \rightarrow -\frac{b_{ij}^4}{8E^3} \rightarrow -\frac{b^4}{E^3} n_{ij},$$

$$\left(\frac{i^*\,j^*}{ij}\right) \text{ in } \varepsilon^2 \text{ and } \Psi^1 \rightarrow -\frac{b_{ij}^4}{8E^3} \rightarrow \frac{b^4}{2E^3} n_{ij},$$

___

[2] If each bond is adjacent to the two others (graphs of Fig. 3) the corresponding graph contributes 3 times to $n_{ijk}^\wedge$; if we note by $m_{ijk}^\wedge$ the number of graphs corresponding strictly to Fig. 5 (i.e. only one bond adjacent to the two others), we therefore have $n_{ijk}^\wedge = m_{ijk}^\wedge + 3 n_{ijk}^\triangle$.

$$\left(\frac{i^* \bar{i}^*}{i\bar{i}}\right) \text{ in } \varepsilon^2 \text{ (or } \Psi^1) \text{ and } \left(\frac{i^* j^*}{ij}\right) \text{ in } \Psi^1 \text{ (or } \varepsilon^2) \to -\frac{a_i^2 b_{ij}^2}{8E^3} \to -\frac{2b^2 a^2}{E^3} n_{ij},$$

$$\left(\frac{i^* \bar{i}^*}{i\bar{i}}\right) \text{ in both } \varepsilon^2 \text{ and } \Psi^1 \to -\frac{a_i^4}{8E^3} \to -\frac{a^4}{8E^3} n_i.$$

This last term will be the only 4$^{\text{th}}$ order contribution if bonds do not interact. It is the sum of the 4$^{\text{th}}$ order corrections for each bond, and will be the only 4$^{\text{th}}$ correction proportional to n_i.

c) $\varepsilon^{2,1}\langle \Psi^{1,2} | \Psi^{1,2}\rangle$ and $\varepsilon^{2,2}\langle \Psi^{1,1} | \Psi^{1,1}\rangle$. In $\varepsilon^{2,1}\langle \Psi^{1,2} | \Psi^{1,2}\rangle$ the products of terms coming from $\left(\frac{j^*}{i}\right)$ in $\varepsilon^{2,1}$ by terms coming from $\left(\frac{j^* k^*}{jk}\right)$ in $\Psi^{1,2}$. We get thus

$$-\frac{\beta_{ij^*}^2 b_{jk}^2}{4E' E^2} \to -\frac{\beta^2 b^2}{2E' E^2} n_{ijk}^{\wedge}.$$

In a similar manner

$$\left(\frac{j^*}{i}\right) \text{ in } \varepsilon^2 \text{ and } \left(\frac{i^* k^*}{ik}\right) \text{ in } \Psi^1 \text{ give } -\frac{\beta^2 b^2}{2E' E^2} n_{ijk}^{\wedge},$$

$$\left(\frac{j^*}{i}\right) \text{ in } \varepsilon^2, \left(\frac{i^* j^*}{ij}\right) \text{ in } \Psi^1 \text{ give } -\frac{\beta^2 b^2}{4E' E^2} 3n_{ij},$$

$$\left(\frac{j^*}{i}\right) \text{ in } \varepsilon^2, \left(\frac{i^* \bar{i}^*}{i\bar{i}}\right)\left(\text{or } \left(\frac{j^* \bar{j}^*}{j\bar{j}}\right)\right) \text{ in } \Psi^1 -\frac{\beta^2 a^2}{2E' E^2} n_{ij}.$$

If one reverses the role of ε^2 and Ψ^1 one gets exactly the same contributions except for the fact that the denominators are then $E'^2 E$ instead of $2E' E^2$.

The sum of the contributions from the EPV diagrams are then

$$-\left[\frac{\beta^4}{4E'^3}[2n_{ijk}^{\wedge} + n_{ij}] + \frac{2b^4}{E^2}\left(n_{ijk}^{\wedge} + \frac{3}{4} n_{ij}\right) + \frac{2b^2 a^2}{E^3} n_{ij} + \frac{a^4}{8E^3} n_i\right]$$

$$-\frac{\beta^2}{2E' E}\left[\frac{1}{2E} + \frac{1}{E'}\right][(4n_{ijk}^{\wedge} + 3n_{ij})b^2 + 2n_{ij}a^2],$$

$$A = -n_{ijk}^{\wedge}\left[\frac{\beta^4}{2E'^3} + \frac{2b^4}{E^3} + \frac{2\beta^2 b^2}{E'^2 E} + \frac{\beta^2 b^2}{E' E^2}\right]$$

$$-n_{ij}\left[\frac{\beta^4}{4E'^3} + \frac{3b^4}{2E^3} + \frac{2b^2 a^2}{E^3} + \frac{3\beta^2 b^2}{2E'^2 E} + \frac{3\beta^2 b}{4E' E^2} + \frac{\beta^2 a^2}{E'^2 E} + \frac{\beta^2 a^2}{2E' E^2}\right]$$

$$-n_i \frac{a^4}{8E^3}.$$

This is a sum of positive elements, some of them being important (particularly the terms in β^4, a^4 and $\alpha^2 \beta^2$).
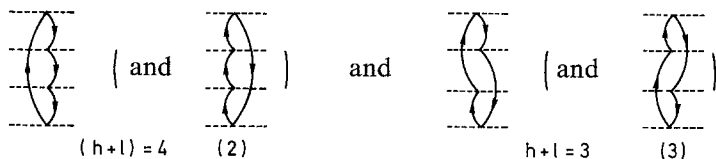
Now one must calculate the general summation

$$\sum_I \sum_J \sum_K \frac{\langle 0 |V| \Phi_I\rangle \langle \Phi_I |V| \Phi_J\rangle \langle \Phi_J |V| \Phi_K\rangle \langle \Phi_K |V| 0\rangle}{(E_0 - E_I)(E_0 - E_J)(E_0 - E_K)}.$$

We shall arrange the discussion by considering that Φ_I and Φ_K must belong to Ψ^1 and be mono- or di-excited configurations.

$$\vdots$$
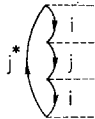
B. Φ_I and Φ_K Monoexcited

a) Φ_J-Monoexcited. Φ_J may only differ by one orbital from Φ_I and Φ_K. The possible unlabelled diagrams are then
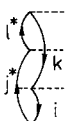
The first diagrams correspond in general to $\Phi_I = \left(\dfrac{j^*}{i}\right)$, $\Phi_J = \left(\dfrac{j^*}{k}\right)$ and $\Phi_K = \left(\dfrac{j^*}{l}\right)$. This leads to the product $\beta_{ij^*}(-\beta_{ik})(-\beta_{kl})\beta_{lj^*}/E'^3$. The sign of this quantity depends on the corresponding topological graph. In the dimethylene-cyclohexa-diene like graphs IV-2 the sign of the quantity changes when i, j, k and l change their position and the sum is zero (see Appendix). The same cancellation does not occur for the octatetraene like graph IV-4 and one thus gets $-\dfrac{\beta^4}{E'^3}\,n_{ijkl}^{\square}$, where $n_{ijkl}^{\square}$ is the number of octatetraene like diagrams in the chemical formula. The chain $\Phi_I = \left(\dfrac{j^*}{i}\right)$, $\Phi_J = \left(\dfrac{k^*}{i}\right)$, $\Phi_K = \left(\dfrac{l^*}{i}\right)$ (second diagram) gives an equal contribution. In these diagrams, several orbitals may be in common. Starting from
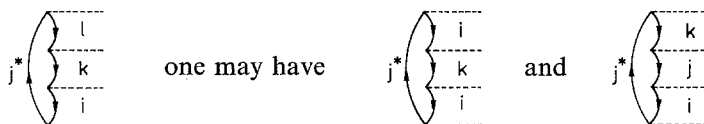
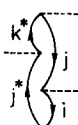
the first diagram gives $\dfrac{\beta_{ij^*}^2\,\beta_{ik}^2}{E'^3}$, and $+\dfrac{\beta^4}{4E'^3}\,n_{ijk}^{\wedge}$ and the second one the reverse quantity. They cancel. A more peculiar case is given by the diagram
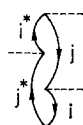
which gives $-\dfrac{\beta_{ij^*}^2\,\beta_{ij}^2}{E'^3}$ and $+\dfrac{\beta^4}{4E'^3}\,n_{ij}$. In the same way, starting from one gets only $+\dfrac{\beta^4}{4E'^3}\,n_{ij}$.

The diagram corresponds to $\Phi_I = \left(\dfrac{j*}{i}\right)$, $\Phi_J = \left(\dfrac{j*}{k}\right)$ and $\Phi_K = \left(\dfrac{l*}{k}\right)$

and give $-\dfrac{\beta_{ij*}\beta_{ik}\beta_{j*l*}\beta_{kl*}}{E'^3} = -\dfrac{\beta^4}{E'^3}\,n_{ijkl}^{\square}$. As special cases one meets,

    which gives $\dfrac{\beta^4}{4E'^3}\,n_{ijk}^{\wedge}\left(-\dfrac{\beta_{ij*}\beta_{ij}\beta_{j*k*}\beta_{jk*}}{E'^3}\right),$

    which gives $\dfrac{\beta^4}{4E'^3}\,n_{ijk}^{\wedge}\left(-\dfrac{\beta_{ij*}\beta_{ik}\beta_{i*j*}\beta_{ki*}}{E'^3}\right),$

    which gives $-\dfrac{\beta^4}{4E'^3}\,n_{ij}\left(-\dfrac{\beta_{ij*}\beta_{ij}\beta_{i*j*}\beta_{ji*}}{E'^3}\right).$

These diagrams lead to the contribution $\dfrac{\beta^4}{4E'^3}\left[-4n_{ijkl}^{\square}+2n_{ijk}^{\wedge}-n_{ij}\right]$ the

symmetrical diagrams give the same contribution. Summing the contribu-

tions of the chains of monoexcited states one gets

$$a)\Rightarrow \dfrac{\beta^4}{E'^3}\left[-4n_{ijkl}^{\square}+n_{ijk}^{\wedge}\right].$$

b) Φ_J-Diexcited. Here we must avoid the unlinked Goldstone diagrams[3]. Starting from $\left(\dfrac{j*}{i}\right)$ for Φ_I and going to $\left(\dfrac{j*\,l*}{i\,k}\right)$ as Φ_J, we have a linked RS diagram by going back to Φ_0 through $\left(\dfrac{l*}{i}\right)$ and $\left(\dfrac{j*}{k}\right)$. This corresponds to the following diagrams,

, and

---
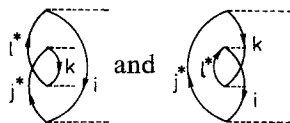
[3] In order to get the cancellations allowed by the linked cluster theorem it is necessary to use $2E'$ instead of $2E$ for the transition energies to diexcited configurations of the type $\left(\dfrac{j*\,l*}{i\,k}\right)$.

and to the products $-\beta_{ij*}\beta_{kl*}\beta_{kj*}\beta_{il*}$. One may verify that the study of signs and numeration of the possibilities gives (see Appendix)

$$\frac{\beta^4}{E'^3}\, n_{ijkl}^{\varhexagon}\quad \text{for the chemical graph}$$

$$-\frac{\beta^4}{E'^3}\, n_{ijkl}^{\square}\quad \text{for the graphs}\quad\text{and}$$

(IV-0)

$$0\quad \text{for}\qquad\text{and}$$

(IV-1)   (IV-3)
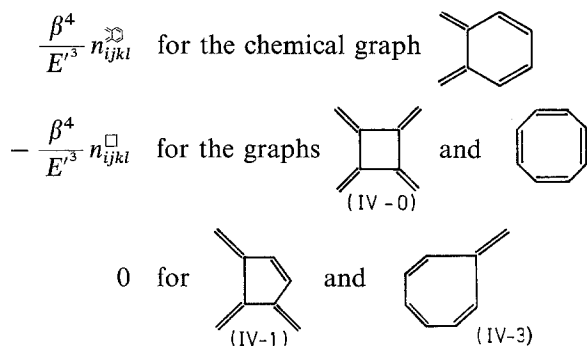
The two successive excitations must be of the same spin, and this avoids the special cases in which the second excitation would include one of the spin orbitals concerned in the first one. But the second excitation may be of the polarization type $\left(\dfrac{k*}{k}\right)$ instead of $\left(\dfrac{l*}{k}\right)$. In the chain $\Phi_I=\left(\dfrac{j*}{i}\right)$, $\Phi_J=\left(\dfrac{j*k*}{ik}\right)$, $\Phi_K=\left(\dfrac{k*}{i}\right)$ or $\left(\dfrac{j*}{k}\right)$, we must calculate the matrix element $\langle j*\bar{i}k\bar{k}\,|H|\,j*\bar{i}k*\bar{k}\rangle$, which may be compared to $\langle i\bar{i}k\bar{k}\,|H|i\bar{i}k\bar{k}*\rangle$ known to be zero:

$$\langle j*\bar{i}k\bar{k}\,|H|\,j*\bar{i}k*\bar{k}\rangle=(j*k\,|\,j*k*)-(ik\,|\,ik*).$$

In the molecular Kékulé-like graph this is equal to $\alpha=\frac{1}{2}(g_{13}-g_{14})$. This new parameter α appearing in the theory will be smaller but of the same order of magnitude as a and much larger than b. Each chain gives $-\dfrac{\beta^3\alpha}{16E'^3}$ and taking all possibilities, one gets $-3\dfrac{\beta^3\alpha}{2E'^3}\,n_{ijk}^{\triangle}$.

Moreover the unlinked RS diagram
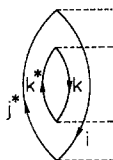
corresponding to the chain of states $\left(\dfrac{j*}{i}\right),\left(\dfrac{j*k*}{ik}\right),\left(\dfrac{j*}{i}\right)$ involves linked bielectronic parts.

One may verify by the same procedure that they give a contribution equal to $\dfrac{\beta^2\alpha^2}{E'^2E}\,(3n_{ijk}^{\triangle}+\frac{1}{4}m_{ijk}^{\wedge})$[4].

A special case concerns $k=\bar{i}$ or $\bar{j}$ and gives $\dfrac{\beta^2\alpha^2}{4E'^2E}\,n_{ij}$.

---

[4] This case is treated in detail at the end of the paragraph 3, 2) of paper I.

Then b) $\Rightarrow \dfrac{\beta^4}{E\,E'^2}\,(n_{ijkl}^{\bowtie} - n_{ijkl}^{\square}) - 3\,\dfrac{\beta^3\,\alpha}{2E'^3}\,n_{ijk}^{\triangle} + 3\,\dfrac{\beta^2\,\alpha^2}{E'^2\,E}\,(3n_{ijk}^{\triangle} + \tfrac{1}{4}m_{ijk}^{\wedge}) + \dfrac{\beta^2\,\alpha^2}{4E'\,2E}\,n_{ij}$

if one does not take into account the graphs IV–0.

c) Φ_J-*Triexcited.* Starting from $\left(\dfrac{j^*}{i}\right)$ the only triexcited states to which we may go are of the type $\left(\dfrac{j^*\,k^*\,l^*}{i\,k\,l}\right)$, but we cannot come back to a monoexcited state without a zero matrix element $\langle \Phi_J\,|V|\,\Phi_K\rangle$ or an unlinked diagram.

The whole paragraph B gives then:

$$B = \dfrac{\beta^4}{E'^3}\,[-5n_{ijkl}^{\square} + n_{ijkl}^{\bowtie} + n_{ijk}^{\wedge}] + \left(3\,\dfrac{\beta^2\,\alpha^2}{E'^2\,E} - \dfrac{3}{2}\,\dfrac{\beta^3\,\alpha}{E'^3}\right)n_{ijk}^{\triangle} + \dfrac{\beta^2\,\alpha^2}{4E'^2\,E}\,n_{ijk}^{\wedge} + \dfrac{\beta^2\,\alpha^2}{4E'^2\,E}\,n_{ij}\,.$$

C. Φ_I Monoexcited, Φ_K Diexcited (or the Reverse)

In all this paragraph one may invert the role of Φ_I and Φ_K and one must introduce the factor 2 coming from the interchange of the place of the mono and the diexcited states.

a) Φ_J-*Monoexcited.* If $\Phi_I = \left(\dfrac{j^*}{i}\right)$ and $\Phi_K = \left(\dfrac{k^*\,l^*}{k\,l}\right)$, one cannot find any monoexcited state which interacts with both Φ_I and Φ_K. Thus one may try $l = i$ or j. The following cases must be considered:

$$\Phi_I = \left(\dfrac{j^*}{i}\right), \qquad \Phi_J = \left(\dfrac{i^*}{i}\right), \qquad \Phi_K = \left(\dfrac{i^*\,k^*}{i\,k}\right).$$
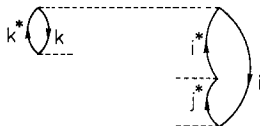
The matrix element $\left\langle\left(\dfrac{i^*}{i}\right)|H|\left(\dfrac{i^*\,k^*}{i\,k}\right)\right\rangle$ is equal to $(i^*\,k\,|\,i^*\,k^*) - (i\,k\,|\,i\,k^*) = 0$

for homopolar bonds. $\Phi_I = \left(\dfrac{j^*}{i}\right)$, $\Phi_J = \left(\dfrac{k^*}{i}\right)$, $\Phi_K = \left(\dfrac{i^*\,k^*}{i\,k}\right)$ gives, $-\dfrac{\beta_{ij^*}\beta_{j^*k^*}\beta_{ki^*}\beta_{ik}}{4E^2\,E'}$

and $+\dfrac{3\beta^3\,b}{2E'^2\,E}\,n_{ijk}^{\triangle}$.

$(h+l) = 3$
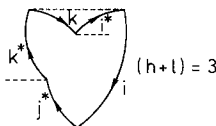
$$\Phi_I = \left(\dfrac{j^*}{i}\right), \qquad \Phi_J = \left(\dfrac{j^*}{k}\right), \qquad \Phi_K = \left(\dfrac{j^*\,k^*}{j\,k}\right)$$

gives the same contribution and the symmetrical diagram.

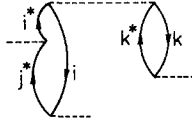The more peculiar cases $\Phi_K = \left(\dfrac{i^* \bar{i}^*}{i\bar{i}}\right)$ and $\Phi_K\left(\dfrac{i^* j^*}{ij}\right)$ do not give any contribution.

b) Φ_J-*Diexcited*. There is no diexcited configuration which interacts with both $\left(\dfrac{j^*}{i}\right)$ and $\left(\dfrac{k^* l^*}{kl}\right)$.

α) $\Phi_I = \left(\dfrac{j^*}{i}\right)$, $\Phi_J = \left(\dfrac{j^* k^*}{lk}\right)$, $\Phi_K = \left(\dfrac{i^* k^*}{ik}\right)$ leads to the matrix element $(j^* k \mid j^* k^*) - (ik \mid ik^*) = \alpha$. One gets $\dfrac{\beta_{ij^*} \alpha \beta_{i^* j^*} b_{ik}}{4E^2 E'}$.

This contribution corresponds to the diagram:

The symmetrical diagram gives an equal contribution.

The total contribution of these two types of diagrams is $2\left(-\dfrac{\alpha \beta^2 b}{E' E^2}\right) 3 n_{ijk}^{\triangle}$.

β) Another possible chain is $\Phi_I = \left(\dfrac{j^*}{i}\right)$, $\Phi_J = \left(\dfrac{j^* i^*}{ik}\right)$, $\Phi_K = \left(\dfrac{i^* k^*}{ik}\right)$ which

corresponds to the diagram and gives the product $\dfrac{\beta_{ij^*} \beta_{ki^*}(-\beta_{j^* k^*}) b_{ik}}{4E^2 E'}$.

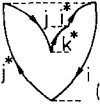Their final contribution is $\dfrac{\beta^2 b}{E^2 E'} \dfrac{3}{4} n_{ijk}^{\triangle}$. An equal contribution is obtained from

the symmetrical diagram

γ) The chain $\Phi_I = \left(\dfrac{j^*}{i}\right)$, $\Phi_J = \left(\dfrac{i^* j^*}{ij}\right)$, $\Phi_K = \left(\dfrac{i^* k^*}{ik}\right)$ corresponds to the

diagram and gives $-\dfrac{\beta_{ij^*} \beta_{ji^*} b_{jk} n_{ik}}{4E^2 E'}$ and $3 \dfrac{\beta^2 b^2}{E' E^2} n_{ijk}^{\triangle}$.

An equal contribution arises from the diagram in which the roles of occupied and virtual orbitals have been permuted.

δ) The chain $\Phi_I = \left(\dfrac{j^*}{i} \right)$, $\Phi_J = \left(\dfrac{j^* k^*}{ij} \right)$, $\Phi_K = \left(\dfrac{i^* j^*}{ij} \right)$ corresponds to the

diagram and gives $- \dfrac{\beta_{ij^*} \beta_{jk^*} \beta_{i^*k^*} b_{ij}}{4 E^2 E'}$ and $+ \dfrac{\beta^3 b}{E^2 E'} \dfrac{3}{4} n_{ijk}^{\triangle}$.

One may change the role of occupied and virtual orbitals with $\Phi_J = \left(\dfrac{j^* i^*}{ik} \right)$ and get an equal contribution.

One must consider now the special cases where $k = i$ deriving from:

α) The chains of states $\left(\dfrac{j^*}{i} \right)$, $\left(\dfrac{j^* \bar{i}^*}{i \bar{i}} \right)$, $\left(\dfrac{j^* \bar{i}^*}{j \bar{i}} \right)$ and $\left(\dfrac{j^*}{i} \right)$, $\left(\dfrac{j^* \bar{j}^*}{i \bar{j}} \right)$, $\left(\dfrac{i^* \bar{j}^*}{i \bar{j}} \right)$.
The second chain leads to the matrix element $+ \beta_{ij^*} [(j^* j \,|\, j^* j^*) - (ij \,|\, ij^*)] \, \beta_{i^* j^*} b_{ij}$.
As $(j^* j \,|\, j^* j^*) = 0$ and $(ij \,|\, ij^*) = -\dfrac{\alpha}{2}$, we get $\dfrac{b \beta^2 \alpha}{4 E' E^2} n_{ij}$. Since the first chain

turns out to give the same contribution, we finally get $\dfrac{b \beta^2 \alpha}{2 E' E^2} n_{ij}$. The chains

$\left(\dfrac{j^*}{i} \right)$, $\left(\dfrac{j^* \bar{i}^*}{i \bar{i}} \right)$, $\left(\dfrac{i^* \bar{i}^*}{i \bar{i}} \right)$ and $\left(\dfrac{j^*}{i} \right)$, $\left(\dfrac{j^* \bar{j}^*}{i \bar{j}} \right)$, $\left(\dfrac{j^* \bar{j}^*}{j \bar{j}} \right)$ give raise to $+ \dfrac{\beta^2 a \alpha}{2 E' E^2} n_{ij}$.

β) and δ) give no special case, since all excitations must be of the same spin. As special cases from γ) one may consider the chains

$$\left(\dfrac{j^*}{i} \right), \quad \left(\dfrac{i^* j^*}{ij} \right), \quad \left(\dfrac{i^* \bar{i}^*}{i \bar{i}} \right) \left(\text{or} \left(\dfrac{j^* \bar{j}^*}{j \bar{j}} \right) \right) \quad \text{which gives} \quad \dfrac{\beta^2 b a}{E' E^2} n_{ij},$$

$$\left(\dfrac{j^*}{i} \right), \quad \left(\dfrac{i^* j^*}{ij} \right), \quad \left(\dfrac{i^* \bar{j}^*}{i \bar{j}} \right) \left(\text{or} \left(\dfrac{\bar{i}^* j^*}{\bar{i} j} \right) \right) \quad \text{which gives also} \quad \dfrac{\beta^2 b a}{E' E^2} n_{ij}.$$
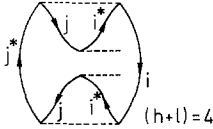
c) Φ_J-*Triexcited*. Starting from $\left(\dfrac{j^*}{i} \right)$ we may only go to triexcited states of the type $\left(\dfrac{j^* k^* l^*}{ikl} \right)$. It is not possible to go back from this type of configurations to a $\left(\dfrac{k^* l^*}{kl} \right)$ diexcited state with a linked diagram.

The contribution of § C may be summarized as equal to

$$C = \dfrac{\beta^2}{E' E} \left[3 n_{ijk}^{\triangle} \left(\dfrac{\beta b}{E'} + \dfrac{\beta b}{E} + \dfrac{2 \alpha b}{E} + \dfrac{b^2}{E} \right) + \dfrac{n_{ij}}{E} \left(\dfrac{b \alpha}{2} + \dfrac{a \alpha}{2} + 2 b a \right) \right].$$

D. Φ_I and Φ_K Diexcited

a) Φ_J Monoexcited. $\Phi_I = \left(\dfrac{i^*j^*}{ij}\right)$ may only interact with $\left(\dfrac{j^*}{i}\right)$; with $\left(\dfrac{i^*}{i}\right)$

it gives $(i^*j^* \mid i^*j) - (ij^* \mid ij) = 0$. The only possible chain is then $\left(\dfrac{i^*j^*}{ij}\right), \left(\dfrac{j^*}{i}\right)$

$\left(\text{or } \dfrac{i^*}{i}\right)\left(\dfrac{i^*j^*}{ij}\right)$, and is represented by which gives

$\dfrac{b_{ij}^2 \beta_{i^*j}^2}{4E^2 E'}$ and $\dfrac{\beta^2 b^2}{4E^2 E'} n_{ij}$.

b) Φ_J-Diexcited. Let us distinguish three types of diexcited states

Type 1 are the dispersion diexcitations $\left(\dfrac{i^*j^*}{ij}\right)$.

Type 2 are the intrabond diexcitations $\left(\dfrac{i^*i^*}{ii}\right)$. Both belong to Ψ^1.

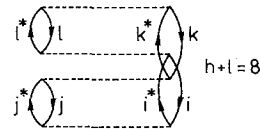Type 3 will be the other diexcited states which do not belong to Ψ^1.
Φ_I and Φ_K may be of types 1 and 2, Φ_J may be of types 1, 2 or 3.

α) 3 excitations of Type 1. The chain $\left(\dfrac{i^*j^*}{ij}\right), \left(\dfrac{i^*k^*}{ik}\right), \left(\dfrac{l^*k^*}{lk}\right)$ gives a "ring
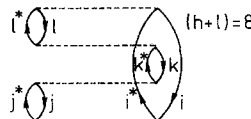
diagram", the contribution $\dfrac{b_{ij} b_{ik} b_{il} b_{kl}}{8E^3}$ and

$$\dfrac{16b^4}{E^3}(n_{ijkl}^{\square} + n_{ijkl}^{\infty}).$$

One must consider the following special cases:

$l = j$ $\qquad \left(\dfrac{i^*j^*}{ij}\right), \left(\dfrac{i^*k^*}{ik}\right), \left(\dfrac{j^*k^*}{jk}\right) \rightarrow \dfrac{12b^4}{E^3} n_{ijk}^{\triangle},$

$k = \bar{j}, \; l = k$ $\qquad \left(\dfrac{i^*j^*}{ij}\right), \left(\dfrac{j^*\bar{j}^*}{i\bar{j}}\right), \left(\dfrac{k^*\bar{j}^*}{k\bar{j}}\right) \rightarrow \dfrac{6b^3 a}{E^3} n_{ijk}^{\triangle},$

$k = \bar{j}, \; l = \bar{i}$ $\qquad \left(\dfrac{i^*j^*}{ij}\right), \left(\dfrac{i^*\bar{j}^*}{i\bar{j}}\right), \left(\dfrac{\bar{i}^*\bar{j}^*}{\bar{i}\bar{j}}\right) \rightarrow \dfrac{b^2 a^2}{E^3} n_{ij}.$

Another ring diagram corresponds to the chain

$\left(\dfrac{i^*j^*}{ij}\right), \left(\dfrac{i^*k^*}{ik}\right), \left(\dfrac{i^*l^*}{il}\right)$ and the product $\dfrac{b_{ij} b_{jk} b_{kl} b_{il}}{8E}$ which gives $\dfrac{16b^4}{E^3}(n_{ijkl}^{\square} + n_{ijkl}^{\infty})$

with the following special cases:

$$l=j \text{ (or } \bar{j}) \quad \left(\frac{i^*j^*}{ij}\right), \left(\frac{i^*k^*}{ik}\right), \left(\frac{i^*j^*}{ij}\right), \left(\text{or} \left(\frac{i^*\bar{j}^*}{ij}\right)\right) \rightarrow \frac{12b^4}{E^3} n_{ijk}^{\triangle},$$

$$k=\bar{j}, \; l=k \quad \left(\frac{i^*j^*}{ij}\right), \left(\frac{i^*\bar{j}^*}{i\bar{j}}\right), \left(\frac{i^*k^*}{ik}\right) \qquad \rightarrow \frac{6b^3a}{E^3} n_{ijk}^{\triangle},$$

$$k=\bar{j}, \; l=j \quad \left(\frac{i^*j^*}{ij}\right), \left(\frac{i^*\bar{j}^*}{i\bar{j}}\right), \left(\frac{i^*j^*}{ij}\right) \qquad \rightarrow \frac{b^2a^2}{E^3} n_{ij}.$$

$\beta)$ Φ_I of Type 2, Φ_J and Φ_K of Type 1.

$$\left(\frac{i^*\bar{i}^*}{i\bar{i}}\right), \left(\frac{i^*j^*}{ij}\right), \left(\frac{k^*j^*}{kj}\right) \quad \text{gives} \quad 12\frac{b^3a}{E^3} n_{ijk}^{\triangle}$$

with the special case $k=i$

$$\left(\frac{i^*\bar{i}^*}{i\bar{i}}\right), \left(\frac{i^*j^*}{ij}\right), \left(\frac{\bar{i}^*j^*}{\bar{i}j}\right) \rightarrow 2\frac{b^2a^2}{E^3} n_{ij}.$$

The chain $\left(\frac{i^*\bar{i}^*}{i\bar{i}}\right), \left(\frac{i^*j^*}{ij}\right), \left(\frac{i^*k^*}{ik}\right)$ gives also $12\frac{b^3a}{E^3} n_{ijk}^{\triangle}$ and the special case $k=\bar{j}$, which leads to $2\frac{b^2a^2}{E^3} n_{ij}.$

$\gamma)$ Φ_I and Φ_K of Type 1, Φ_J of Type 2. The chain $\left(\frac{i^*j^*}{ij}\right), \left(\frac{i^*\bar{i}^*}{i\bar{i}}\right), \left(\frac{i^*k^*}{ik}\right)$ or $\left(\frac{k^*\bar{i}^*}{k\bar{i}}\right)$ gives $4\frac{b^4}{E^3} n_{ijk}^{\triangle}$ and we have a special case if $k=j$, with a corresponding contribution of $\frac{4b^4}{E^3} n_{ij}.$
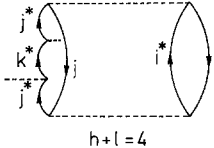
$\delta)$ If Φ_I and Φ_K are of Type 2, Φ_J cannot be of Type 2. The chains $\left(\frac{i^*\bar{i}^*}{i\bar{i}}\right),$ $\left(\frac{i^*j^*}{ij}\right), \left(\frac{i^*\bar{i}^*}{i\bar{i}}\right)$ or $\left(\frac{j^*\bar{j}^*}{j\bar{j}}\right)$ give $2\frac{b^2a^2}{E^3} n_{ij}.$

$\varepsilon)$ Φ_J of Type 3. The chains $\left(\frac{i^*j^*}{ij}\right), \left(\frac{i^*k^*}{ik}\right), \left(\frac{i^*k^*}{ik}\right)$ and $\left(\frac{i^*j^*}{ij}\right), \left(\frac{i^*j^*}{ij}\right),$ $\left(\frac{i^*k^*}{ik}\right)$ give $-\frac{b_{ij}\beta_{j^*k^*}\beta_{jk}b_{ik}}{8E^3}$ and give $\frac{b^2\beta^2}{E^3}\frac{3}{2} n_{ijk}^{\triangle}$. This corresponds to the diagrams:

$$h+l=5 \qquad \qquad h+l=5$$
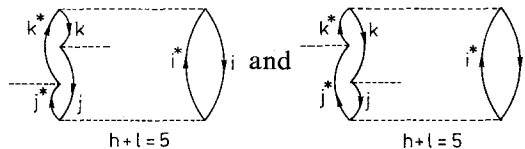
and introduce some special cases. If $k = \bar{i}$ we get the chains $\left(\dfrac{i^*\bar{j}^*}{i\bar{j}}\right)$, $\left(\dfrac{i^*\bar{i}^*}{i\bar{j}}\right)$,

$\left(\dfrac{i^*\bar{i}^*}{i\bar{i}}\right)$ and $\left(\dfrac{i^*\bar{j}^*}{i\bar{j}}\right)$, $\left(\dfrac{i^*\bar{j}^*}{i\bar{i}}\right)$, $\left(\dfrac{i^*\bar{i}^*}{i\bar{i}}\right)$ which give the contribution $\dfrac{b\,a\,\beta^2}{2E^3}\,n_{ij}$.

If $j = i$ one gets the symmetrical chains (already taken into account) of the preceeding ones. The chains $\left(\dfrac{i^*\bar{i}^*}{i\bar{i}}\right)$, $\left(\dfrac{i^*\bar{j}^*}{i\bar{i}}\right)$, $\left(\dfrac{i^*\bar{i}^*}{i\bar{i}}\right)$ or $\left(\dfrac{i^*\bar{i}^*}{i\bar{i}}\right)$, $\left(\dfrac{i^*\bar{i}^*}{i\bar{j}}\right)$, $\left(\dfrac{i^*\bar{i}^*}{i\bar{i}}\right)$ give $\dfrac{\beta^2 a^2}{4E^3}\,n_{ij}$.

Another type of diagram is and the symmetrical one

h+l=4

which correspond to the chains $\left(\dfrac{i^*j^*}{ij}\right)$, $\left(\dfrac{i^*k^*}{ij}\right)$, $\left(\dfrac{i^*j^*}{ij}\right)$ or $\left(\dfrac{i^*j^*}{ij}\right)$, $\left(\dfrac{i^*j^*}{ik}\right)$, $\left(\dfrac{i^*j^*}{ij}\right)$. Their contribution $\dfrac{b_{ij}^2\beta_{j^*k^*}^2}{8E^3}$ or $\dfrac{b_{ij}^2\beta_{jk}^2}{8E^3}$ is equal to $\dfrac{b^2\beta^2}{2E^3}n_{ijk}^{\wedge}$. The special labelling in which $k = \bar{i}$ give the contribution $\dfrac{b^2\beta^2}{4E^3}\,n_{ij}$.

c) Φ_J-Triexcited. A diexcited configuration $\left(\dfrac{i^*j^*}{ij}\right)$ may only interact with triexcited configurations of types $\left(\dfrac{i^*k^*l^*}{ijl}\right)$ or $\left(\dfrac{i^*j^*l^*}{ijk}\right)$. In the first case the matrix element is $(j^*l \mid k^*l^*) = 0$. In the second one we get $\beta_{k^*l^*}$, but to come back from $\left(\dfrac{i^*j^*l^*}{ijk}\right)$ to a diexcited state belonging to Ψ^1 one must build an unlinked diagram.

If we go to $\left(\dfrac{i^*j^*k^*}{ijk}\right)$ we meet the following matrix element

$$(i^*k \mid i^*k^*) - (ik \mid ik^*) + (j^*k \mid j^*k^*) - (jk \mid jk^*) = 0.$$

There is no exception and the triexcited states do not give any contribution.

d) Φ_J-Quadriexcited. The general chain is $\Phi_I = \left(\dfrac{i^*j^*}{ij}\right)$, $\Phi_J = \left(\dfrac{i^*j^*k^*l^*}{ijkl}\right)$, $\Phi_K = \left(\dfrac{i^*l^*}{il}\right)$, $\left(\dfrac{i^*k^*}{ik}\right)$, $\left(\dfrac{j^*l^*}{jl}\right)$, or $\left(\dfrac{j^*k^*}{ik}\right)$. This corresponds to a diagram like

h+l=8
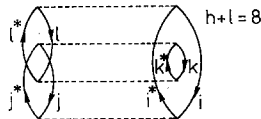
and gives $\dfrac{b_{ij}b_{kl}b_{kj}b_{li}}{16E^3}$ or finally: $\dfrac{16b^4}{E^3}(n_{ijkl}^{\square} + n_{ijkl}^{\bowtie})$.

Special labellings give particular contributions.

$$l = k \qquad\qquad \rightarrow 6\,\frac{b^3\,a}{E^3}\,n_{ijk}^\triangle,$$

$$l = \bar{i} \qquad\qquad \rightarrow 2\,\frac{b^4}{E^3}\,n_{ijk}^\wedge + 6\,\frac{b^3\,a}{E^3}\,n_{ijk}^\triangle,$$

$$k = \bar{i} \quad \text{and} \quad l = \bar{j} \rightarrow \left(\frac{b^4}{2} + b^2\,a^2\right)\frac{n_{ij}}{E^3}.$$

The sum of the contribution of § D is:

$$D = \frac{1}{E^3}\left\{ (n_{ijkl}^\square + n_{ijkl}^\bowtie)\,48b^4 + n_{ijk}^\triangle\left(24b^4 + 48b^3\,a + 3\,\frac{b^2\,\beta^2}{2}\right)\right.$$
$$+ n_{ijk}^\wedge\left(6b^4 + \frac{b^2\,\beta^2}{2}\right) + n_{ij}\left(9\,\frac{b^4}{2} + 9b^2\,a^2 + \frac{b\,a\,\beta^2}{2} + \frac{b^2\,\beta^2}{4}\left(1 + \frac{E}{E'}\right) + \frac{a^2\,\beta^2}{4}\right\}.$$

Final expression of the 4$^{\text{th}}$ order energy correction:

$$\varepsilon^4 = n_{ijkl}^\square\left(-5\,\frac{\beta^4}{E'^3} + 48\,\frac{b^4}{E^3}\right) + n_{ijkl}^\bowtie\left(\frac{\beta^4}{E^3} + 48\,\frac{b^4}{E^3}\right) + m_{ijk}\,\frac{\beta^2\,\alpha^2}{4E'^2\,E}$$

$$+ 3n_{ijk}^\triangle\left(-\frac{\beta^3\,\alpha}{E'^3} + \frac{\beta^3\,b}{E'\,E}\left(\frac{1}{E} + \frac{1}{E'}\right) - 2\,\frac{\beta^2\,\alpha\,b}{E'\,E^2} + \frac{\beta^2\,b^2}{E^2}\left(\frac{2}{E'} + \frac{1}{2E}\right)\right.$$

$$\left.+ 8\,\frac{b^4}{E^3} + 16\,\frac{b^3\,a}{E^3} + \frac{\beta^2\,\alpha^2}{E'^2\,E}\right)$$

$$+ n_{ijk}^\wedge\left(+\frac{\beta^4}{2E'^3} + 4\,\frac{b^4}{E^3} + \frac{\beta^2\,b^2}{E}\left(\frac{1}{2E^2} - \frac{1}{E'^2} - \frac{2}{EE'}\right)\right.$$

$$+ n_{ij}\left(-\frac{\beta^4}{4E'^3} - \frac{\beta^2\,a^2}{E}\left(\frac{1}{E'^2} + \frac{1}{2E'\,E} - \frac{1}{4E^2}\right) + \frac{\beta^2\,a\,\alpha}{2E'\,E^2}\right.$$

$$+ \frac{\beta^2\,b^2}{4E}\left[\frac{3}{E'^2} + \frac{1}{E^2} - \frac{5}{E'\,E}\right]$$

$$\left.+ \frac{\beta^2\,b\,\alpha}{2E'\,E^2} + \frac{\beta^2\,b\,a}{2E^2}\left(\frac{4}{E'} + \frac{1}{E}\right) + 3\,\frac{b^4}{E^3} + 7\,\frac{b^2\,a^2}{E^3} + \frac{\beta^2\,\alpha^2}{4E'^2\,E}\right)$$

$$+ n_i\left(-\frac{a^4}{8E^3}\right).$$

The expression of higher order energy corrections exhibit the same form, but become more and more complex. In the 4$^{\text{th}}$ order correction "four body" terms appear for the first time, but we are compelled to distinguish the geometrical shape of the four molecular graphs. The three and two body corrections are numerous and very important. New types of three body terms appear, corresponding to new geometrical graphs ($n_{ijk}^\wedge$), and new parameters begin to be involved as α. The various contributions have opposite signs and different orders of magnitudes according to the power of b, which is much smaller than the other parameters, as it will be seen in the numerical applications.

Another very important conclusion from this treatment is that the triexcited states never contribute (except for the EPV diagrams). This is a very satisfactory result since many works had postulated or shown that they play a minor role. On the contrary the monoexcited polarisation states $\left(\dfrac{i*}{i}\right)$ lead to non negligible contributions.

6. Numerical Applications

We have applied the method to linear polyenes and aromatic compounds.

A. Butadiene and Other Polyenes

We have performed three calculations on the trans-butadiene π system with the Pariser-Parr [10], Mataga [15] and "theoretical" parameters [16] proposed by Koutecky et al. [17]; these authors performed the full configuration interaction which gives the exact solution of the problem. Staemmler and Kutzelnigg made a 2nd order calculation on the basis of SCF delocalized orbitals and the pair APSG localized calculation [5]. Diner, Claverie and Malrieu have obtained somewhat better results with a 2nd order perturbation treatment using localized SCF orbitals [6].

Butadiene having only two adjacent double bonds, the neglect of long range interactions in our treatment is no longer an approximation (the same is true for benzene). We give in Table 1, the values of the basic parameters E, E', β, a, α, b

Table 1. *Basic parameters of the perturbation expansion for the π system of butadiene (Pariser-Parr (PP), Mataga (M) and "Theoretical" (T) values of integrals [17])*

	PP	M	T
E	− 5.840	− 5.100	− 6.400
E'	− 7.847	− 6.580	− 9.568
β	− 1.680	− 2.130	− 2.370
a	1.577	2.732	4.137
b	− 0.055	− 0.115	− 0.365
α	1.705	1.155	2.465

for the three sets of integrals and one may verify that β, α and a are of the same order of magnitude and much larger than b. The Pariser-Parr parametrization reduces both a and b, i.e. the pure correlation effects. Mataga's parametrization gives small transition energies and a large intra pair correlation effect. The theoretical parameters give a still larger value of a but somewhat larger transition energies. The PP set gives the best convergence.

One may see from Table 2 that the 2nd order correction throws the energy into the region of the exact solution, and below it. In that peculiar case the third order correction is small. This is due to the fact that with only two double bonds there is no $\dfrac{\beta^3}{E^2}\, n_{ijk}^{\triangle}$ term, and that the other third order terms are proportional

Table 2. Energy corrections and percentage of the correlation energy for the π system of butadiene (in eV)

	PP parameters			M parameters			Theoretical parameters		
	Energy correction	Energy	% of the correl. energy obtained	Energy correction	Energy	% of the correl. energy obtained	Energy correction	Energy	% of the correl. energy obtained
Fully localized D^t		-89.730			-75.942			-90.828	
2nd order FLBO	-0.787	-90.518	102.6	-2.157	-78.100	113.3	-3.302	-94.131	114.1
3rd order FLBO	-0.003	-90.521	103.4	-0.007	-78.107	113.8	+0.041	-94.090	112.4
4th order FLBO	+0.015	-90.506	99.5	+0.265	-77.840	92.5	+0.373	-93.717	94.3
SCF		-90.091	0		-76.629	0		-91.432	0
2nd order delocal. [4] a	-0.365	-90.456	85.7	-1.206	-77.835	92.9	-2.099	-93.531	88.7
2nd order local. [6]	-0.402	-90.493	96.6	-1.262	-77.891	97.2	-2.451	-93.883	103.6
APSG local. [5]			93.1			90.0			93.0
Exact [17]	-0.416	-90.507	100	-1.298	-77.927	100	-2.365	-93.797	100

a The slight differences from Ref. [5] is due to the fact that we worked in a basis of single determinants, while Staemmler and Kutzelnigg used spin eigenfunctions

to b, which is small. Only two terms of opposite signs remain and the sign of the total contribution depends on the relative magnitudes of a and $|\beta|$: the 3rd order correction is negative for PP and M parameters, and positive for T ones. The smallness of the 3rd order correction is thus due to the specificity of the problem, and the fact that the 4th order correction is larger does not demonstrate that the perturbation does not converge.

The fourth order correction is about one tenth of the 2nd order one and positive. This is mainly due to EPV diagrams. This correction is too large and throws the energy on the other side of the exact solution, but improves the result. The correction is essentially due to the terms which do not involve b and which are in β^4, $\beta^2 a^2$, $\beta^2 a\alpha$, and a^4. In fact, it seems that it could be possible to treat the whole problem as a multi-perturbation in β, a and b. These perturbations are not of the same order of magnitude and it could be worthwhile for practical problems and even in σ systems to go to the fourth order in β and a, and to the third only in b. This would simplify the expressions of the perturbation correction and insure a sufficient accuracy.

At any rate the results obtained are among the best ones obtained and give less than 10% error on the correlation energy. They are obtained without the use of any computer, in a few minutes.

For other polyenes the number of bonds (n_i) and of adjacent bonds (n_{ij}) increases proportionaly to the number of carbon atoms while $n_{ijk}^{\triangle}$ remains zero: this explains why the total energy increases as n and explains very simply the previous results obtained in the basis of delocalized and localized orbitals [4, 6].

B. Benzene and Other Aromatic Compounds

In the case of linear polyenes the delocalization was not as important as the intrabond correlation and of course the 2nd order was already near the true energy. It is no longer the case for benzene in which the localizability is rather poor. And in fact, for usual values of parameters ($\beta = -2.80$ eV, short distances reduced bielectronic integrals) the 2nd order corrected energy is not so good as the SCF energy (see Table 3). But in that case, there exists a strong negative third order correction $\left(\text{due to } \dfrac{\beta^3}{E'^2} n_{ijk}^{\triangle} \right)$ which brings the energy halfway between the SCF and the 2nd order corrected energy. The fourth order correction is still negative: the perturbation expansion does not present the oscillations that we found in the

Table 3. *Energies of the benzene π systems (eV)*

Basic parameters	Energies	Correction	Corrected energy
$E = -5.610$	Fully localized deter.		-170.564
$E' = -7.131$	2nd order FLBO	-4.118	-174.682
$\beta = -2.805$	3rd order FLBO	-1.410	-176.092
$a = 1.615$	4th order FLBO	-0.280	-176.372
$b = 0.32$	SCF energy		-175.774
$\alpha = 1.20$	2nd order correl. energy	-0.530	-176.304
	Exact energy (Full CI) [20]	-0.52	-176.294

case of linear polyenes. This is due to the terms in $n_{ijk}^{\triangle}$, which give several negative large contributions. The successive corrections are in a ratio $\cong \frac{1}{4}$ and the series seem to converge.

Benzene is a highly peculiar case: in naphtalene for instance the fully localized determinant has an energy of -331.801 eV and the 2nd order correction gives -337.989 eV. The SCF energy is -337.083 eV and the 2nd order correlation energy is 1.451 eV. In that case the 2nd order corrected FLBO is already halfway between the SCF and the 2nd order correlation-corrected energies. The same is true for anthracene. The third order correction lowers the energy more. It is amazing to show that a simple census of the number of double bonds, adjacent double bonds and kekulean diagrams in the localized chemical formula gives at a glance the evolution of the so called "resonance energies" in the series of polyacenes. It parallels the results of Hückel or PP calculations, but the concept of resonance energy has received too many and too serious cristicisms and we do not give details on that question.

C. Heterocyclic Compounds

We also have included some detailed third order results for heterocyclic molecules (Table 4). The derivation of the general formulas for polar systems will be given in the next paper. One uses reasonable bond polarities and the polarization energy becomes very weak.

Conclusions

Our treatment seems to call for the following remarks:

1. It is very handy and makes clear the important terms of the first orders; it enables us to select the most important contributions of 3rd and 4th orders, and can be useful even for σ systems: for bonds at long distances the Pariser-Parr approximations may be considered as sufficient for the 3rd and 4th order contributions.

2. It shows that it is difficult to keep only certain types of diagrams. The ring diagrams for instance do not play the main role at 4th order. Different diagrams give various contributions of similar orders of magnitudes and opposite signs. A given type of diagram leads to terms of different orders of magnitude according to the number of times they involve the intra-pair correlation. In fact it would be interesting to consider the inter-pair correlation as a smaller perturbation than the intra-pair correlation and delocalization and to leave it at the fourth order. This would garantee most of the 4th order correction.

3. It shows in a much clearer and much more correct way than the diagonalization of the Hückel Hamiltonian the role of the molecular topology. The formulae derived herein give the energy as a sum of bond, bond-pairs, bond-triplets, etc ... energies. The connection with graph-theory is simpler here and many amazing problems found during the preceeding treatment (sign of the four body corrections for instance) could be treated with the help of the graph-theory. But we think that quantum chemistry must leave the formal field of "π-ology" and leave these questions as training problems.

Table 4. *Energy terms of the perturbation development[a] (non reduced Slater exponents)*

Energy term	Hexatriene	Benzene	Naphtalene	Anthracene	Uracile	Cytosine	Adenine	Guanine
Zeroth order[b]	+0.592	+4.018	+4.628	+ 8.307	+2.974	+3.493	+8.255	+6.635
m_1[c]	0.000	-0.000	0.000	0.000	-0.003	-0.015	-0.296	-0.304
m_2[d]	-0.570	-2.233	-3.029	- 5.458	-3.148	-3.415	-5.896	-5.810
Zeroth order + monoexcited[b]	+0.022	+1.786	+1.599	+2.849	-0.177	+0.063	+2.063	+0.521
d_1[e]	-3.970	-5.406	-8.511	-12.321	-7.047	-6.150	-8.814	-9.097
d_2[f]	-0.069	-0.576	-1.048	- 1.472	-0.058	-0.192	-0.804	-0.462
After second order[b]	-4.017	-4.197	-7.960	-10.944	-7.282	-6.279	-7.555	-9.038
$m_1 - d_1$[g]	0.000	0.000	0.000	0.000	-0.048	-0.026	-1.174	-1.219
$m_1 - m_1$[g]	0.000	0.000	0.000	0.000	0.000	0.002	0.037	0.027
$m_1 - m_2$[g]	0.000	0.000	0.000	0.000	0.007	-0.014	-0.064	0.211
$m_1 - d_2$[g]	0.000	0.000	0.000	0.000	0.000	-0.005	-0.130	-0.077
$m_2 - d_2$[g]	-0.030	-0.319	-0.398	- 0.710	-0.035	-0.124	-0.456	-0.252
$d_1 - d_2$[g]	+0.092	+1.009	+1.768	+ 2.638	0.113	0.320	+1.572	0.819
$m_2 - m_2$[g]	0.000	-0.707	-0.778	- 1.343	0.138	-0.089	-1.452	-0.491
$d_2 - d_2$[g]	0.044	0.339	0.716	1.108	0.052	0.160	0.620	0.404
Third order correction	0.105	0.322	1.308	1.692	0.227	0.222	-1.047	-0.579
After third order[b]	-3.912	-3.865	-6.652	-9.252	-7.055	-6.057	-8.602	-9.617
Correlation energy (SCF) (2nd order)	-2.671	-3.040	-4.655	- 5.943	-4.195	-3.576	-4.060	-4.542
Correlation energy (localized SCF)[h] (2nd order)	-3.759	-3.532	-6.020	- 7.730	-5.664	-4.606	-4.593	-6.015

[a] All energy terms in eV.

[b] Underlined quantities are expressed with respect to the SCF energy.

[c] Polarization term in monoexcitations $\left(\dfrac{i^*}{i}\right)$.

[d] Charge transfer term in monoexcitations $\left(\dfrac{j^*}{i}\right)$.

[e] Diexcitations intra-bond correlation $\left(\dfrac{i^*\bar{i}^*}{i\bar{i}}\right)$.

[f] Diexcitations, inter-bond correlation $\left(\dfrac{i^*j^*}{ij}\right)$.

[g] Interaction of the terms mentioned under c, d, e, and f.

[h] Ruedenberg localization.

4. It shows very clearly the role of the parameters, and peculiarly the role of coulombic integrals through four basic parameters a, b, α, β. One sees easily the effect of reduction of the coulombic integrals at short distances and we demonstrate once more (in a different way than Koutecky's recent paper [18] since not linked to the SCF formalism) that only differences between parameters are important.

5. One may examine recent cristicisms against the concept of aromaticity [19]: it is true that the Kékulé formula is a good enough starting point for the interpretation of certain quantities. However it appears clearly that there is a qualitative difference between the convergence rate of polyenes and benzene: this is linked to the ratio of the matrix elements over the transition energies; i.e. to the ratio of the β values for single and double bonds.

6. By its good behaviour in the "*a priori*" hopeless case of benzene, the method gives signs of persistent convergence, and one may hope for an analogous behaviour for σ systems.

The next paper will give a generalisation of the method taking into account polarization effects and some applications to saturated systems.
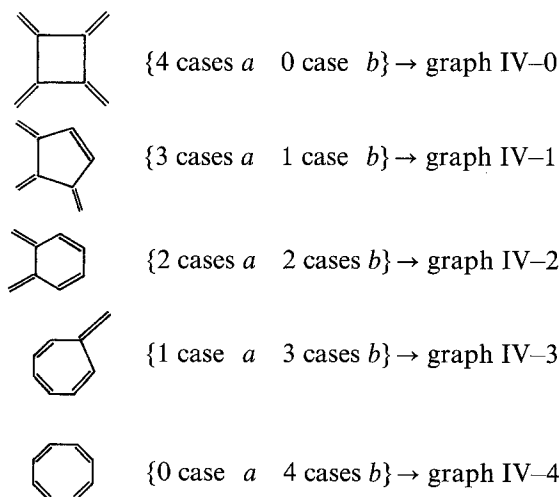

Appendix

Molecular graphs involving 4 double bonds which play a role in the 4th order energy correction.

In these graphs, each double bond must be adjacent to two others. A given double bond i may be linked to its two neighbours by the same atom:

 (Case a)   or by both its atoms: (Case b)
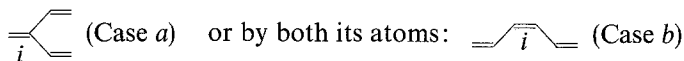
As a result there are 5 types of graphs involving four double bonds as mentioned above according to the number of b-like configurations:

 {4 cases a 0 case b} → graph IV–0

 {3 cases a 1 case b} → graph IV–1

 {2 cases a 2 cases b} → graph IV–2

 {1 case a 3 cases b} → graph IV–3

 {0 case a 4 cases b} → graph IV–4

In the Section B, a) of Paragraph 5, the contribution of the graphs IV–0, IV–1, IV–3 have not been considered; anyway, such graphs do not occur frequently in usual alternant hydrocarbons.

It is easy to see how the contributions of the various graphs can be calculated. For example, in the section quoted above, we have to sum $2\dfrac{\beta_{ij^*}\beta_{ik}\beta_{kl}\beta_{lj^*}}{E'^3}$ (the factor 2 corresponds to the two spin possibilities) for all possible labelings of the orbitals in a given graph. To have a non-zero numerator, i and l on one hand, j^* and k on the other hand must be non-adjacent; we therefore have 8 possible labelings (we first put j^* on one of the 4 bonds (4 possibilities), then k must be on the opposite bond; we may put i on one of the 2 remaining bonds (and l on the last one), hence the 8 possibilities). β_{ik} and β_{kl} are equal to $\dfrac{\beta}{2}$, and $\beta_{ij^*}\beta_{lj^*} = +\dfrac{\beta^2}{4}$ if j^* is of type (a) and $-\dfrac{\beta^2}{4}$ if j^* is of type (b). In a graph IV–p (where $p = 0, 1, 2, 3, 4$), among the 4 possible positions for j^*, p of them are of type (b), and since there are still two possible labelings once j^* is fixed, among the 8 possible labelings, $2p$ correspond to j^* of type (b), and $2(4 - p)$ to j^* of type (a); hence the total contribution of a graph IV–p:

$$\frac{\beta^2}{2E'^3}\left[2p\left(-\frac{\beta^2}{4}\right) + 2(4-p)\left(\frac{\beta^2}{4}\right)\right] = \frac{\beta^2}{2E'^3}\left[4(2-p)\frac{\beta^2}{4}\right] = (2-p)\frac{\beta^4}{2E'^3}.$$

Hence:

$$\text{for IV–0}\quad\text{the contribution}\quad \frac{\beta^4}{E'^3},$$

$$\text{for IV–1}\quad\text{the contribution}\quad \frac{\beta^4}{2E'^3},$$

$$\text{for IV–2}\quad\text{the contribution}\quad 0,$$

$$\text{for IV–3}\quad\text{the contribution}\quad -\frac{\beta^4}{2E'^3},$$

$$\text{for IV–4}\quad\text{the contribution}\quad -\frac{\beta^4}{E'^3}.$$

These molecular graphs also occur in the Section β, b), where the product to be treated is $\beta_{ij^*}\beta_{kl^*}\beta_{kj^*}\beta_{il^*}$; i and k on one hand, j^* and l^* on the other hand must be opposite (i.e. non adjacent). A treatment analogous to the preceding one leads to the results given in the main text $\left(0\text{ for IV–1 and IV–3, }+\dfrac{\beta^4}{E'^3}\text{ for IV–2 and }-\dfrac{\beta^4}{E'^3}\text{ for IV–0 and IV–4}\right)$.

References

1. Diner, S., J. P. Malrieu, P. Claverie: Part I of the series. See also a preliminary note: Diner, S.,J. P. Malrieu, P. Claverie, and F. Jordan: Chem. physic. Letters **2**, 319 (1968).
2. Grimaldi, F.: J. chem. Physics **43**, 559 (1965).
3. Claverie, P., S. Diner, and J. P. Malrieu: Int. J. quant. Chem. I, 751 (1967).
4. Diner, S., J. P. Malrieu, and P. Claverie: Theoret. chim. Acta (Berl.) **8**, 390 (1967).
5. Staemmler, V., and W. Kutzelnigg: Theoret. chim. Acta (Berl.) **9**, 67 (1967).
6. Diner, S., J. P. Malrieu, F. Jordan, and M. Gilbert: Theoret. chim. Acta (Berl.) [to be published (Part III of this series)].
7. Boys, S. F.: In: Quantum theory of atoms, molecules and the solid state. P. O. Löwdin (Ed.). New York: Academic Press 1966.
8. Edmiston, C., and K. Ruedenberg: Rev. mod. Physics, **34**, 457 (1963).
9. Magnasco, V., and A. Perico: J. chem. Physics **47**, 971 (1967).
10. Pariser, R., and R. G. Parr: J. chem. Physics **21**, 466, 767 (1953).
11. Simpson, W. T.: J. Amer. chem. Soc. **73**, 5363 (1951); **77**, 6164 (1955).
12. Murrell, J. N.: J. chem. Soc. (London) **37**, 1162 (1962).
13. Pople, J. A., and S. M. Walmsley: Trans. Farad. Soc. **58**, 441 (1962).
14. Sinanoğlu, O.: J. chem. Physics **37**, 191 (1962).
15. Mataga, M., and K. Nishimoto: Z. physik. Chemie (Frankfurt) **13**, 140 (1967).
16. Parr, R. G., and R. S. Mulliken: J. chem. Physics **18**, 1338 (1950).
17. Koutecky, J., J. Cizek, J. Dubsky, and K. Hlavaty: Theoret. chim. Acta (Berl.) **2**, 462 (1964).
18. — J. chem. Physics **47**, 1501 (1967).
19. Musher, J. I.: In: Adv. in Magn. Resonance, vol. II, p. 177. J. S. Waugh (Ed.). New York: Academic Press 1966.
20. Koutecky, J., K. Hlavaty, and P. Hochmann: Theoret. chim. Acta (Berl.) **3**, 341 (1965).

Dr. S. Diner
Institut Biologie Physico-Chimique
13, rue Pierre et Marie Curie
Paris V^e (France)