Direct Evaluation of Cyclic Contributions to the π Energy of Conjugated Hydrocarbons from Strongly Localized Zero-Order Pictures[†]

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Received: April 02, 2008; Revised Manuscript Received: May 19, 2008

This paper presents a new procedure for identifying that part of the π electronic energy of conjugated hydrocarbons which results from cyclic circulation of electrons around a ring. It first shows that one may calculate perturbatively the ground state energy of the Hückel Hamiltonian from a strongly localized Kekulé-type zero-order wave function. The contributions due to cyclic circulation of the electrons appear explicitly, in terms of the interatomic hopping integral t, at the second order in cyclobutadiene (where it is equal to $-t$ (antiaromatic)) and at third order in benzene, where its value is $0.5t$ (aromatic). Conjugated isomers of benzene are also considered. The cyclic circulation contributions for an N-membered ring are shown to depend strongly on the molecular graph in which it is embedded. A general expression is found for the cyclic contribution to the π energy of a ring, the Kekulé graph of which contains N double bonds alternating with N single bonds. It is the energy of the ring, plus the sum of the energies of the N subsystems that result from one double-bond removal, minus the sum of the energies of the N open systems that result from one single-bond cut. This new aromaticity index, $\mathrm{ACE}_{\mathrm{MC}}$, may be seen as the enthalpy of a hyperhomodesmotic chemical equation. In contrast to the index $\mathrm{ACE}_{\mathrm{DC}}$ previously defined from a *double* cut of the ring, the multiple-cut $\mathrm{ACE}_{\mathrm{MC}}$ exhibits the expected asymptotic disappearance of the cyclic energy as the ring size tends to infinity. In the multiple-cut approach, aromaticity persists in bond-alternating rings, but, in contrast to the total π energy, the purely cyclic contribution tends to resist distortion. Extension of the approach to charged, branched and heterosubstituted rings are discussed, as well as its *ab initio* transcription.

I. Introduction

The concept of (anti)aromaticity[1] plays an important role in rationalization of the chemical properties of conjugated systems containing rings. This concept has several definitions, quantified through various effects. Aromaticity is sometimes related to *energetic aspects*, namely, a specific energy stabilization of $(4n + 2)$-membered rings;[2] *structural aspects*, illustrated by the bond-length equalization in benzene or weak bond-length alternation in benzenoids; existence of *ring currents* as evidenced by NMR properties;[3] specific patterns in the *electron density*.[4] Conversely, antiaromaticity is often related to energy destabilization, or strong bond length alternation in $4n$-membered rings.

The present paper is devoted to the energetic aspect of the problem. We propose to quantify aromaticity through the part of the π-electron energy resulting from the cyclic circulation of the electrons around the ring. In contrast to the usual ways of estimating resonance and aromatic stabilization energies,[2] this approach is not biased by mismatch of numbers of bonds between the aromatic structure and the acyclic reference. All conjugated systems, cyclic or acyclic, have significant π delocalization energy. The proper definition of the delocalization energy requires reference to a strongly localized picture, which in turn must be defined. Whatever that choice, the cyclic contribution is only one part of the total π delocalization energy. Identification of the properly cyclic contribution to π delocalization is not completely straightforward[5] and several variants have been proposed. Evaluation through a double cut of the ring $\mathbf{A}\bigcirc\mathbf{B}$ into two closed-shell fragments A and B was recently reported.[6] Starting from the product of the wave functions of the fragments, a second order perturbative expansion allowed isolation of the properly cyclic energy correction as

$$\varepsilon_{cyc}(\mathrm{AB}) = \mathrm{E(AB)} + \mathrm{E}^0(\mathrm{A}) + \mathrm{E}^0(\mathrm{B}) - \mathrm{E}(\mathbf{A}\frown\mathbf{B}) - \mathrm{E}(\mathbf{A}\smile\mathbf{B})$$

In the double-cut approach, the cyclic interfragment delocalization energy $\varepsilon_{\mathrm{cyc}}(\mathrm{AB})$ is therefore the energy of the ring *plus* the energies of the two fragments A and B resulting from the double cut, *minus* the energies of the two moieties $\mathbf{A}\frown\mathbf{B}$ and $\mathbf{A}\smile\mathbf{B}$ resulting from single cuts. This aromatic cyclic energy (ACE, which we will denote here by $\mathrm{ACE}_{\mathrm{DC}}$ to specify its double-cut origin) translates into a homodesmotic chemical scheme and gives consistent estimates of (anti)aromaticity.[6] $\mathrm{ACE}_{\mathrm{DC}}$ performs better than the Breslow resonance energy[7] in this respect, but because of the truncation of the perturbative expansion at second order, it may still incorporate small noncyclic delocalization contributions[6] that are removed by the improvement suggested in the present work.

[†] Part of the "Sason S. Shaik Festschrift".

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10.1021/jp802839n CCC: \$40.75

The present paper starts from an even more strongly localized zero-order wave function, product of bond molecular orbitals (MO) which correspond to the double bonds of a Kekulé structure. To distinguish, bonds supporting these MOs are called Bonds, while the single bonds of the Kekulé graph are called bonds. This strategy has been used in a recent study of cyclic effects in periodic lattices. [8]

This approach will be followed explicitly to fourth order of perturbation in section II with the Hückel Hamiltonian, exhibiting the origin of the antiaromatic contributions in cyclobutadiene and cyclooctatetraene, and the aromatic contribution in benzene in terms of the intersite hopping integral t, usually labeled β in quantum chemistry textbooks. Branched-ring isomers are also considered.

Although based on the perturbative expansion introduced in section II, section III may be read in stand-alone fashion. The expansion supports an additive expression of the energy in terms of Bond energies, two-Bond energies reflecting the energy gain due to the delocalization between two adjacent Bonds, and many-Bond increments. Consideration of acyclic hydrocarbons containing a set of N Bonds with given spatial connectivity enables a definition, by difference, of the specific N-Bond noncyclic increment. Then, if a ring is built from an acyclic arrangement of N Bonds by addition of a connection, it is possible to define the properly cyclic contribution to the energy. The desired cyclic energy is shown to be equal to the energy of the ring *plus* the sum of the energies of the subsystems resulting from one Bond removal, *minus* the sum of the energies of the acyclic moieties resulting from a single cut. This evaluation, which gives useful estimates of the cyclic energy, is based on a *multiple cut* of the ring starting from a Kekulé structure and is referred to as $\mathrm{ACE_{MC}}$. It may be translated into a hyperhomodesmotic chemical scheme, the enthalpy of which would give the cyclic energy contribution. The evaluation of $\mathrm{ACE_{MC}}$ is generalized to rings substituted by conjugated chains, ionic hydrocarbons and heterocycles.

Section IV compares the performance of $\mathrm{ACE_{DC}}$[6] and $\mathrm{ACE_{MC}}$ aromatic cyclic energies. Whereas the former includes a small noncyclic three-Bond delocalization, the latter exhibits the correct asymptotic behavior, as it tends to zero for rings of infinite size. Distortivity of the π-delocalization energy is then discussed briefly. It is shown that, although the noncyclic part of the π-energy is responsible for universal distortivity, the cyclic correction in even-membered rings has a maximum for equal bond lengths, i.e., fights against distortion. However, it is insufficient to prevail over the first factor and it turns out that the additive so-called σ-core potential is responsible for the equality of bond lengths. Although reduced, the cyclic energy effect remains nonzero in distorted geometries.

II. Perturbative Identification of the Cyclic Contribution to the Energy in the Weak Electron-Repulsion Limit

The strategy used in this section may be summarized as follows: we first define a strongly localized reference wave function which incorporates the delocalization energies between pairs of adjacent atoms constituting the double bonds of a Kekulé structure. This function is taken as the starting point of a perturbative expansion. Order by order: (a) The second-order correction introduces the delocalization between adjacent double bonds and is noncyclic (except for cyclobutadiene). (b) The third order is present only in rings involving three and only three double bonds, and appears as the cyclic energy. (c) The fourth order introduces delocalization energy between next-nearest neighbor double bonds, and this is noncyclic (except in rings built from four double bonds). Analytical expressions for each of these contributions are derived below.

II.A. The Purely Additive Reference. Many approaches to this problem rest on $\sigma-\pi$ separability, and we shall not consider here the possible contributions of the σ electrons to aromaticity. Even in approximations that do not allow fluctuations in the numbers of σ and π electrons, separation of the energy into a sum of σ and π electronic energy is not uniquely defined.[9] We prefer to partition the energy with respect to a reference state in which π electrons are present, but which is free of all π-electron delocalization. This is the π-open shell multiplet of highest multiplicity, i.e., where all electrons have parallel spins. E_{Mmax} is the energy of this state. It incorporates $\sigma-\pi$ interaction energy, with one electron per π atomic orbital, as well as the repulsion of the π electrons in this frozen distribution. This one-electron population is also the mean population in the singlet ground state, where the π electrons *are* delocalized. The exact energy of the ground state is

$$E_{\mathrm{GS}}=E_{\mathrm{Mmax}}+E_{\pi\mathrm{deloc}} \tag{1}$$

This definition of the delocalization energy refers to a strongly localized function, free from any intersite delocalization. The term $E_{\pi\mathrm{deloc}}$ incorporates the delocalization energy between adjacent atoms, as well as other, more collective contributions. The energy of the highest-spin multiplet can be considered as additive if some approximations are accepted. The first is the additivity of σ-bond energies. The others involve the energy

$$E_{\pi\mathrm{elec,Mmax}}=\sum\nolimits_{\mathrm{p}}\varepsilon_{\mathrm{p}}+\sum\nolimits_{\mathrm{pq}}(J_{\mathrm{pq}}-K_{\mathrm{pq}}) \tag{2}$$

(where ε_{p} is the one-electron energy of the localized p atom-centered orbital and J_{pq} and K_{pq} the two-electron coulomb and exchange integrals between π atomic orbitals p and q). $E_{\pi\mathrm{elec,Mmax}}$ is additive in terms of atom−atom interactions, and is dominated by nearest neighbor repulsions. Additivity of E_{Mmax} follows.

II.B. Strategies for Estimating the π Delocalization Energy from Strongly Localized Zero-Order Pictures in the Correlation-Free Limit. In this limit, one may take the Hückel tight-binding Hamiltonian to be valid. It is written in terms of intersite hopping integrals and creation/annihilation operators as

$$H=\sum\nolimits_{\mathrm{pq\ bonded}}t_{\mathrm{pq}}(a^{+}{}_{\mathrm{p}}a_{\mathrm{q}}+a^{+}{}_{\mathrm{q}}a_{\mathrm{p}}) \tag{3}$$

taking the sum of the atomic one-electron energies ($\varepsilon_{\mathrm{p}}=\varepsilon$, $\forall$p) as the zero of energy. Then the π-electron energy is attributable entirely to delocalization, the energy of the highest spin multiplet (E_{Mmax}) being zero. The exact energy of a finite system is easily calculated as the sum of the lowest eigenenergies of H,

$$\mathrm{H}\varphi_i=\varepsilon_i\varphi_i \tag{4}$$

For a $2n$-electron closed-shell system

$$E=\sum_{i=1}^{n}2\varepsilon_i \tag{5}$$

This approach does not discriminate between noncyclic and cyclic contributions to the energy. To perform such a partition one needs to construct the energy as a sum of contributions explicitly corresponding to well-defined movements of electrons around the molecular skeleton. This construction of the molecular energy will start from strongly localized zero-order wave functions and will follow a perturbation-based approach.

II.B.1. Choice of a Localized Reference Function. The most strongly localized zero-order picture puts the electrons in atomic orbitals, according to a valence bond (VB) picture.[10] It is possible, even then, to identify cyclic contributions to the energy, as shown elsewhere for periodic lattices,[8] although this requires use of a sophisticated modified coupled cluster formalism. For systems defined on $2n$ sites with $2n$ electrons we start from a nondegenerate strongly localized wave function based on a partition of the atomic orbitals into bonded pairs, which we shall call Bonds, with definition of a bonding and an antibonding orbital for each of these pairs. For the homopolar Bond I, defined on AOs i_1 and i_2, the bonding MO is:

$$\varphi_i = (i_1 + i_2)/\sqrt{2} \tag{6}$$

with energy

$$\varepsilon_i = \langle \varphi_i | h | \varphi_i \rangle = \langle i_1 | h | i_2 \rangle = t_i \tag{7}$$

where h is the monoelectronic Hamiltonian. The antibonding MO is

$$\varphi_i{}^* = (i_1 - i_2)/\sqrt{2} \tag{8}$$

with energy

$$\varepsilon_{i^*} = \langle \varphi_{i^*} | h | \varphi_{i^*} \rangle = -\langle i_1 | h | i_2 \rangle = t_{i^*} = -t_t \tag{9}$$

The zero-order wave function is $\phi_0 = |\prod_i \varphi_{i\alpha}\varphi_{i\beta}|$. It is associated with a Kekulé structure. Thus for the benzene molecule, we construct the wave function from one of the two Kekulé pictures. The energy of this wave function is $E_0 = \sum_i 2\varepsilon_i = \sum_i 2t_i$. If N is the number of Bonds and if they have equal hopping integrals $t_i = t\ \forall i$, then $E_0 = 2Nt$.

This energy involves intrabond delocalization energy only. The Bond MOs φ_i and $\varphi_i{}^*$, and the determinant ϕ_0, are eigenfunctions of the zero-order Hamiltonian $H_0 = \sum_i t_{i_1 i_2}(a_{i_1}{}^+ a_{i_2} + a_{i_2}{}^+ a_{i_1})$ where $a_{i_1}{}^+$ creates an electron in the AO i_1 and a_{i_2} annihilates an electron in the AO i_2.

II.B.2. Inter-Bond Second-Order Delocalization and the Antiaromaticity of 4-Membered Rings. The perturbation operator V

$$V = H - H_0 \tag{10}$$

involves the hopping integrals that couple atoms of different Bonds, through the single bonds of the Kekulé structure,

$$V = \sum_{ij} t_{i_1 j_1}(a_{i_1}{}^+ a_{j_1} + a_{j_1}{}^+ a_{i_1}) + t_{i_1 j_2}(a_{i_1}{}^+ a_{j_2} + a_{j_2}{}^+ a_{i_1}) + \ldots \tag{11}$$

This operator may be expressed as well in the basis of the Bond MOs as

$$V = \sum_{ij} t_{ij^*}(a_i{}^+ a_{j^*} + a_{j^*}{}^+ a_i) + t_{i^*j}(a_{i^*}{}^+ a_j + a_j{}^+ a_{i^*}) + t_{ij}(a_i{}^+ a_j + a_j{}^+ a_i) + t_{i^*j^*}(a_{i^*}{}^+ a_{j^*} + a_{j^*}{}^+ a_{i^*}) \tag{12}$$

where a_i empties the spin−orbital φ_i and $a_{j^*}{}^+$ puts an electron in φ_{j^*}.

The perturbation operator is responsible for electron delocalization between the Bonds, proceeding via the bonds. To second order this delocalization goes through charge transfer (CT), i.e., electron jumps, from a bonding φ_i to an antibonding orbital φ_{j^*}, i.e., from the interaction between ϕ_0 and a CT determinant $\phi_{ij^*} = a_{j^*}{}^+ a_i \phi_0$,

$$\langle \phi_0 | H | \phi_{ij^*} \rangle = \langle \varphi_i | H | \varphi_{j^*} \rangle = t_{ij^*} \tag{13}$$

The zero-order energy of the determinant ϕ_{ij^*} is

$$\langle \phi_{ij^*} | H_0 | \phi_{ij^*} \rangle = E_0 + \varepsilon_{j^*} - \varepsilon_i = E_0 + (t_{j^*} - t_i) = E_0 - \Delta E_{ij^*} \tag{14}$$

where $t_{j^*} = -t_j$, and the second-order energy correction is

$$E^{(2)} = \sum_{ij} \frac{t_{ij^*}{}^2}{t_i - t_{j^*}} \tag{15}$$

Except in 3- and 4-membered rings, nearest-neighbor (NN) Bonds I and J are connected by a unique bond, i.e., a pair of atoms, for instance i_2 and j_1, and then, according to Figure 1, $t_{ij^*} = t_{i_2 j1/2}$.

If all Bonds are equivalent $t_i = t$ and $t_{\mathrm{i}^*} = -t$, $\forall_i$. If all bonds are equivalent, $t_{ij^*} = -t_{ji^*} = t'/2$, $\forall\ \langle i, j\rangle_{NN}$. The second-order correction introduces the delocalization between adjacent Bonds, i.e., over four atoms, and this delocalization energy is additive. Taking into account the four CTs across a bond (α and β electrons, from I to J or from J to I), one may write

$$E^{(2)} = 4\sum\nolimits_{\text{bonds}} (t'/2)^2/2t = (t'^2/2t)n_{\mathrm{b}} \tag{16}$$

where n_{b} is the number of bonds. If Bonds and bonds have equal lengths, $t' = t$, and

$$E^{(2)} = 0.5tn_{\mathrm{b}}. \tag{17}$$

According to this crude approximation, inserting an internal double bond in a conjugated chain gives an energy gain of $2.5t$ ($2t$ for the double bond energy, plus $0.5t$ for the delocalization through the single bond), which is an estimate of the energy per carbon pair in an infinite polyene. One may compare this value to the exact Hückel energy differences between linear C_6H_8 and C_4H_6 ($2.59t$), between C_8H_{10} and C_6H_8 ($2.53t$) and to the exact π energy of polyacetylene per Bond ($8/\pi t = 2.546t$). This comparison shows that short-range delocalization dominates the π delocalization energy.

A more accurate evaluation of the CT amplitude is obtained by summing the so-called exclusion-principle-violating (EPV) corrections in the denominators of the second-order energy.[11] (For more detail see the Appendix.) These corrections lead to a revised evaluation of the coefficient C of the inter-Bond CT excited determinant and of the inter-Bond delocalization energy. When $t' = t$, $C = 4/19 = 0.210$ and the delocalization energy between two adjacent Bonds becomes $\varepsilon_{ij} = (8/19)t$, which gives a total energy for the π electrons

$$E(0 + 2_{(\mathrm{EPV})}) = 2tN + (8/19)tn_{\mathrm{b}} \tag{18}$$

For an open chain with N Bonds the number of bonds (i.e., non-Bonds) is $n = N - 1$, whereas it is $n = N$ in a $2N$-membered

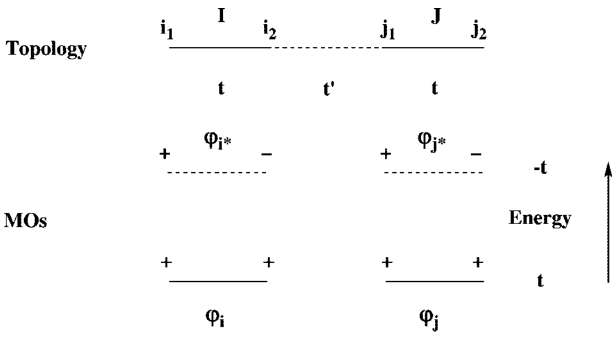


Figure 1. Definition of Bonds and of their bond MOs.

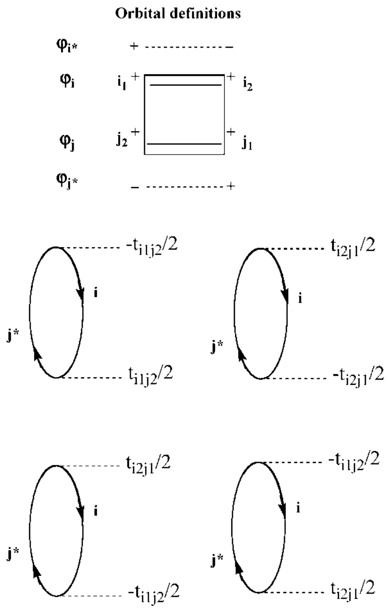


Figure 2. MO definitions of cyclobutadiene. Feynman diagrams describing back-and-forth (upper part) and cyclic (lower part) contributions.

ring. At this stage the energy difference between hexatriene and benzene is already $8t/19 = 0.42t$, owing to the fact that $n = 2$ in hexatriene and 3 in benzene (i.e., simply to the difference in the number of C−C bonds), and does not reflect any cyclic movement of the electrons. The statement is valid for any ring, so that the estimate of the cyclic energy of a ring from comparison with the π electron energy of its open-chain parent, as proposed in the popular Breslow formula,[7] overestimates this quantity by including a purely local short-range delocalization energy, as already discussed.[6]

It is also important to consider the case where two Bonds interact through more than one bond. Two cyclic cases are possible: the arrangements found in cyclobutadiene and methylene cyclopropene.

In the former (Figure 2), the second-order CT contribution is

$$\langle\phi_0|H|\phi_{ij^*}\rangle^2/(\varepsilon_i - \varepsilon_{j^*}) = (1/2(t_{i_1j_2} - t_{i_2j_1}))^2/2t = (t_{i_1j_2}{}^2 + t_{i_2j_1}{}^2 - 2t_{i_1j_2}t_{i_2j_1})/(8t) \quad (19)$$

In the first two contributions the electron hops twice through the same bond in a back-and-forth movement, while in the last two terms it hops through the bond i_1j_2 to reach ϕ_{ij^*} and returns to ϕ_0 through the bond i_2j_1, in a cyclic movement. These four terms are pictured in the Feynman diagrams of Figure 2.[12]

The cyclic effect cancels the back-and-forth movements. Its amplitude is (t/8) × (2 × 2 × 2) (two diagrams, α and β electrons, $i \rightarrow j^*$ and $j \rightarrow i^*$ CT) i.e. $E^{(2)}$ cyclic $= -t$, which represents the antiaromatic (positive) cyclic energy of cyclobutadiene. There is negative interference between the movements through the upper and the lower bonds in the sense that the electron starting from Bond 1 arrives in the antibonding orbital with a different phase depending on the single bond followed in the CT pathway.

For the other two-Bond cyclic structure (cf. Figure 3) Bond J interacts through the same atom j_1 with i_1 and i_2. The $j \rightarrow i^*$ CT is zero for symmetry reasons, but the $i \rightarrow j^*$ CT is nonzero. Cyclic contributions are present in both processes, but they cancel, so that there is no cyclic contribution in this molecule. So far our analysis coincides with the double-cut approach.[6]

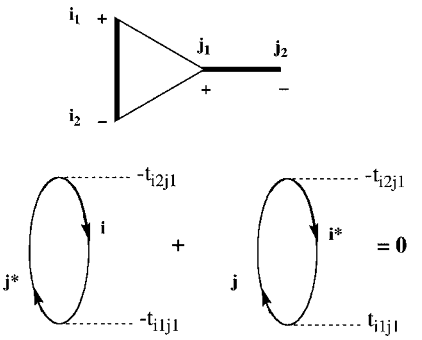


Figure 3. MO definitions of methylene cyclopropene and the Feynman diagrams describing the cyclic contributions.

II.B.3. The Third-Order Cyclic Corrections and the Aromaticity of Benzene. We now move on to consider the third-order correction, which is expressed as

$$E^{(3)} = \sum_i \sum_{j^*} \sum_k \sum_{l^*} \langle\phi_0|H|\phi_{ij^*}\rangle\langle\phi_{ij^*}|H|\phi_{kl^*}\rangle \langle\phi_{kl^*}|H|\phi_0\rangle/(E_0 - E_{ij^*})(E_0 - E_{kl^*}) \quad (20)$$

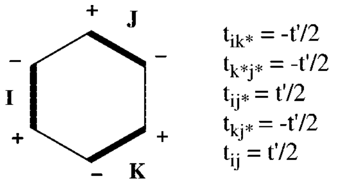
The determinants ϕ_{ij^*} and ϕ_{kl^*} do not interact, except if $i = k$ or $j^* = l^*$, according to the assumed strong localization of the MOs and to the tight-binding character of the Hamiltonian. This means that (i) I interacts with both J and K, *and* (ii) J and K interact, which implies that I, J and K are involved in a ring. Depending on how many of the three Bonds participate through one or two atoms in the ring, this may be a six-, five-, four- or three-membered ring.

The third-order correction becomes

$$E^{(3)} = \sum_i \sum_{j^*} \sum_{k^*} \langle\phi_0|H|\phi_{ij^*}\rangle\langle\phi_{ij^*}|H|\phi_{ik^*}\rangle \langle\phi_{ik^*}|H|\phi_0\rangle/(E_0 - \mathrm{E}_{ij^*})(E_0 - E_{ik^*}) + \sum_i \sum_{j^*} \sum_k \langle\phi_0|H|\phi_{ij^*}\rangle\langle\phi_{ij^*}|H|\phi_{kj^*}\rangle\langle\phi_{kj^*}|H|\phi_0\rangle/(E_0 - E_{ij^*})(E_0 - E_{kj^*}) \quad (21)$$

The diagrams of Figure 4 show that all these contributions introduce cyclic movements of the electrons. For a set of three interacting Bonds, one may reverse the order of ϕ_{ij^*} and ϕ_{ik^*} or of ϕ_{ij^*} and ϕ_{kj^*} in the diagrams of Figure 4, which changes the clockwise circulation into an anticlockwise circulation.

We now specify the third-order correction for benzene and its conjugated isomers. For benzene all contributions have equal values. Fixing the signs of the antibonding MO coefficients, we find that each of them brings an energy lowering of $(t'/2)^3/2t^2 = t'^3/(32t^2)$.



The number of contributions is 24 (three Bonds, two spins, two types of diagrams, clockwise and anticlockwise movements) so that the cyclic energy is $E^{(3)} = 0.75t'^3/t^2$, i.e., $0.75t$ if $t' = \mathrm{t}$. Added to the previously calculated value of $E(0 + 2_{(\mathrm{EPV})})$, this gives a total π energy

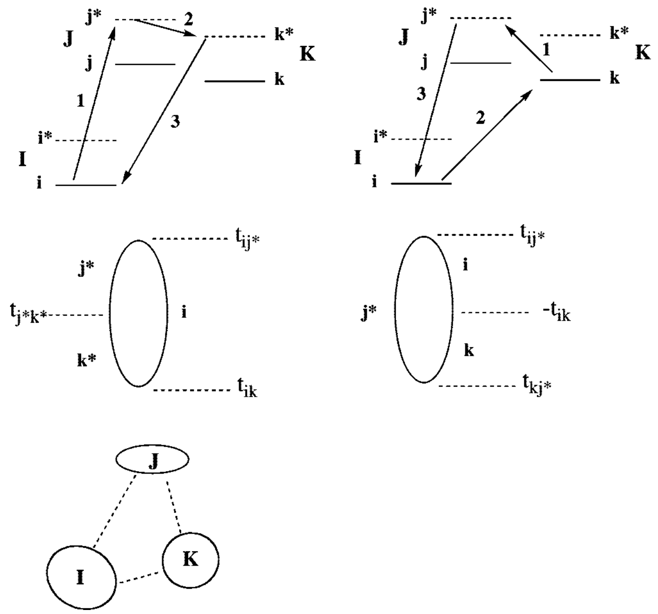


Figure 4. General picture of the third-order cyclic effects. The numbers 1, 2, 3 refer to the ordering of the hoppings. The bonding MOs are in full lines, the antibonding ones in dotted lines.

$$E(0+2_{(EPV)}) + E^{(3)} = 8.01t$$

This is an accurate estimate, since the exact energy is 8.0t, although this accuracy is somewhat fortuitous. In fact, each term of $E^{(3)}$ can be calculated more rigorously as $(C)^2t'/2$. Using the EPV corrected value of C (= 4/19),

$$E^{(3)}=E_{\mathrm{cycl}} = 0.532t$$

which reduces the total energy to 7.8t. As will be seen below, the missing energy (0.20t) is due to fourth-order back-and-forth noncyclic delocalization effects.

At this stage, it is worth considering other ring-containing isomers of benzene. The 3,4-dimethylene cyclobutene isomer presents a four-membered ring and is expected to exhibit a degree of antiaromaticity. Using the Bond labeling of Figure 5, and considering the possible third-order cyclic corrections, one sees that partial cancelation occurs.

The final correction is

$$E^{(3)}=E_{\mathrm{cycl}}=8(-t'^3/32t^2) = -0.25t$$

i.e., antiaromatic. Its amplitude is one-third of the aromatic contribution of benzene (in absolute value). Consideration of EPV corrections reduces it to $-0.18t$. This quantity is significantly smaller than the antiaromatic contribution for cyclobutadiene, and this example shows that the cyclic corrections do not depend solely on ring size, but also on the environment.

Now consider the 3-membered ring isomer of benzene ([3]radialene). A strict cancelation occurs between the interactions through bonding and through antibonding MOs, $E_{\mathrm{cycl}} = 0$ (Figure 6).

The same type of cancelation occurs in fulvene, the 5-membered ring isomer, as illustrated in Figure 7.

II.B.4. Fourth-Order Back-and-Forth and Four-Body Cyclic Delocalization Effects. The fourth-order corrections are of three types: EPV corrections, which have already been included in energy denominators; back-and-forth movements of the electrons that imply CT between next-nearest-neighbor (NNN) Bonds; cyclic fourth-order effects that occur between four Bonds in cyclic arrangement and involve a cyclic circulation of electrons.

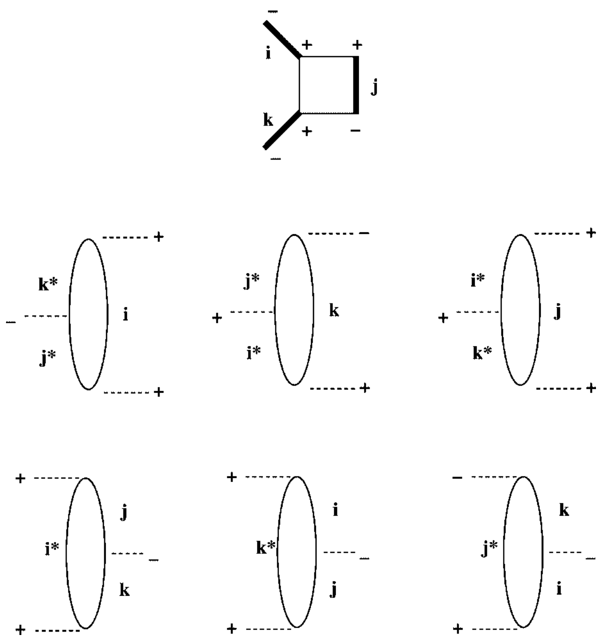


Figure 5. Bond labeling of 3,4-dimethylene cyclobutene and partial cancelation of third-order corrections. Only clockwise contributions are pictured. By convention, in this and the following figures, the downward (upward) arrows which should appear in the propagation lines labeled by bonding (antibonding) MOs are omitted.

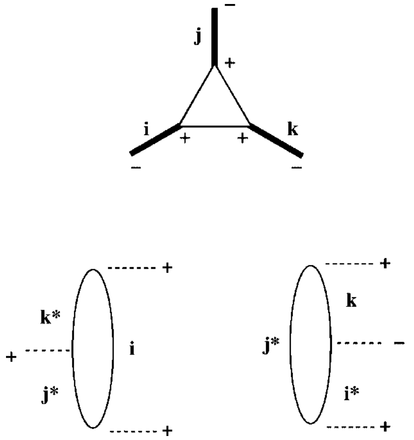


Figure 6. Strict cancelation of the third-order corrections in [3]radialene.

The NNN effects are present in 6-atom fragments and are pictured by four types of fourth-order diagrams. For a fragment $I{-}J{-}K$ the i→k* NNN CT is involved in the four diagrams pictured in Figure 8.

If the Bonds (and the bonds) are equivalent, each contribution (including in the denominator EPV relative to the i→k* NNN CT determinant) gives

$$(\pm)C^2(t'/2)^2/(2t+4t'^2/8t)$$

The sign depends on the relative topology of the Bonds. If the intermediate Bond J is connected to Bonds I and K by different atoms (I---j_1—j_2---K), all contributions are equal and, starting from I, the movement may be directed left or right, and may involve α or the β electrons, so there are six such corrections per triplet of Bonds. This leads to an energy $E_{\mathrm{NNN}} = 0.07t$ per internal Bond if $t' = t$. This three-Bond increment of energy

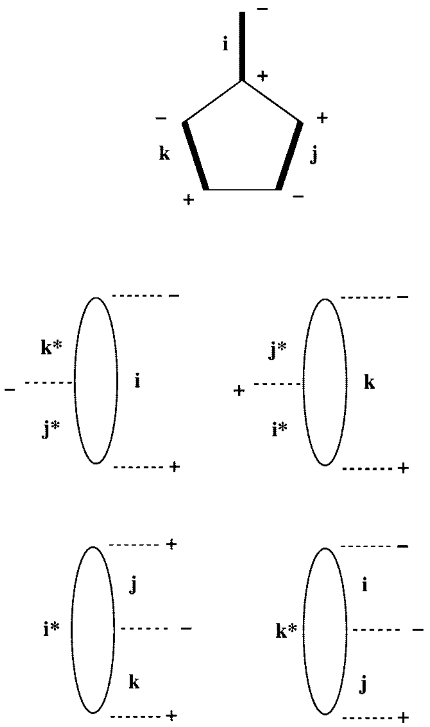


Figure 7. Strict cancelation of the third-order corrections in fulvene.

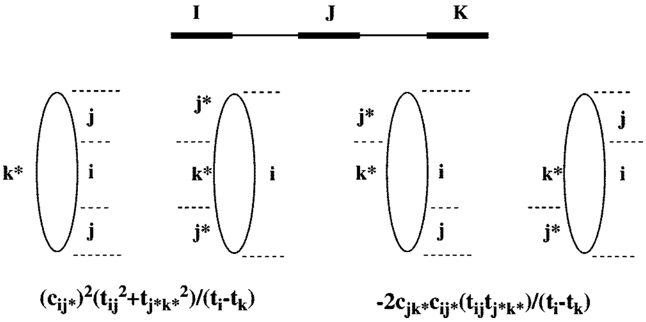


Figure 8. Fourth-order corrections involving CT between NNN Bonds.

reflects a back-and-forth delocalization of the electrons over three Bonds. It leads to a final value of $(2 + 0.43 + 0.07)t = 2.50t$ for the energy per internal Bond in a chain or in a ring free from bond-length alternation. This value compares well with the exact value $8t/\pi = 2.54t$ for the infinite 1-D chain, showing that delocalization beyond NNN Bonds is only responsible for 2 % of the cohesive energy. Three such delocalization processes are present in benzene. Adding the corresponding energy to the previous estimate for the benzene energy (to third order) leads to $8.0t$, i.e., the exact π energy. This agreement illustrates the excellent convergence of the perturbation expansion.

If the intermediate Bond J is connected to bonds I and K by the same atom, the NNN CT $I \rightarrow K^*$ is zero, as in the right-side diagrams of Figure 9, and the integral $t_{j^*k^*}$ changes its sign. If we call $E_{\mathrm{N(N)N}}$ the three-body correction for such a topology, $E_{\mathrm{N(N)N}} = 0$.

Finally, the third type of correction, arising from cyclic fourth-order effects occurring between four Bonds in a cyclic arrangement (cf. Figure 10), involves a cyclic circulation of electrons.

The various fourth-order cyclic corrections can be calculated as

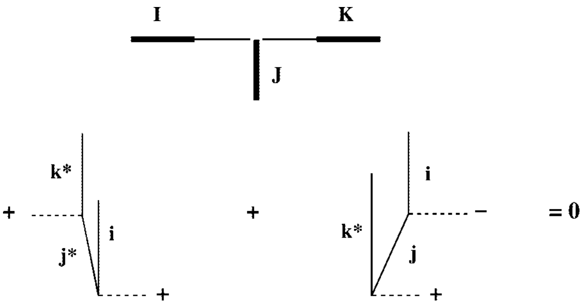


Figure 9. Cancelation of CT between NNN Bonds in branched chains.

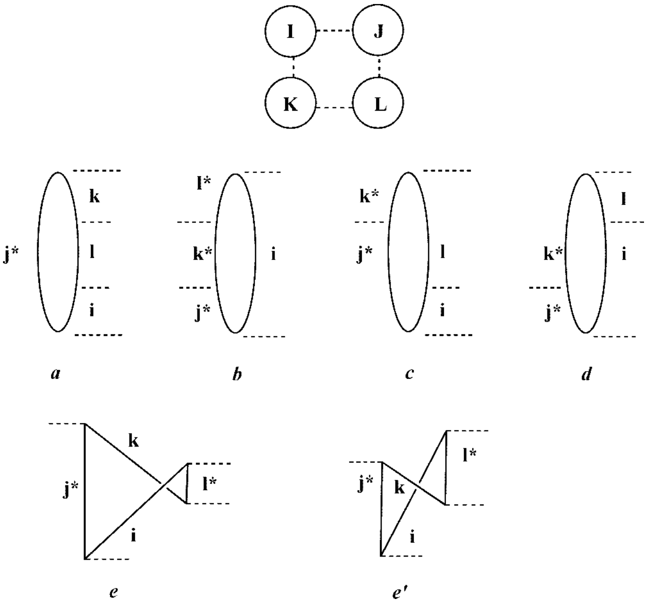


Figure 10. Fourth-order cyclic circulation corrections between 4 Bonds. The diagrams concern clockwise circulation with an i to j^* initial CT.

$$a = C_{kj^*}t_{kl}t_{il}C_{ij^*}/(t_l - t_{j^*}) \tag{22}$$

$$b = C_{il^*}t_{l^*k^*}t_{k^*j^*}C_{ij^*}/(t_i - t_{k^*}) \tag{23}$$

$$c + d = -C_{lk^*}t_{k^*j^*}t_{il}C_{ij^*}[(t_l - t_{j^*})^{-1} + (t_i - t_{k^*})^{-1}] \tag{24}$$

$$e + e' = -(C_{kj^*}t_{il^*}t_{kl^*} + C_{il^*}t_{kj^*}t_{kl^*})C_{ij^*}/(-t_i + t_k - t_{j^*} - t_{l^*}) \tag{25}$$

Each contribution is of order $C^2(t'/2)^2/2t$, and for equal bond lengths

$$|a| = |b| = |c| = |d| = |e + e'| = |C^2t/8|$$

The sign of each contribution depends on both the molecular graph and the Feynman diagram and ultimately on the nature of the $i \rightarrow j^*$ first excitation.

The simplest case concerns the 8-membered ring, i.e., cyclooctatetraene. It may be noted that in this ring the NNN CTs $i \rightarrow k^*$ have a zero coefficient. This may be seen as an effect of symmetry since ϕ_{ik^*} is antisymmetrical with respect to the plane passing through the middle of Bonds I and K, as already noticed by Hiberty and Shaik.[13] One may also see this cancelation as an interference between clockwise $i \rightarrow j^* \rightarrow k^*$ and anticlockwise $i \rightarrow l^* \rightarrow k^*$ movements, i.e., between the two trajectories of the electron leaving Bond I to reach the antibonding MO of Bond K as seen in Figure 11.

It is easy to check that all corrections ($a = b = c = d = e + e'$) have the same sign ($-C^2t/8$), i.e., are positive. There are

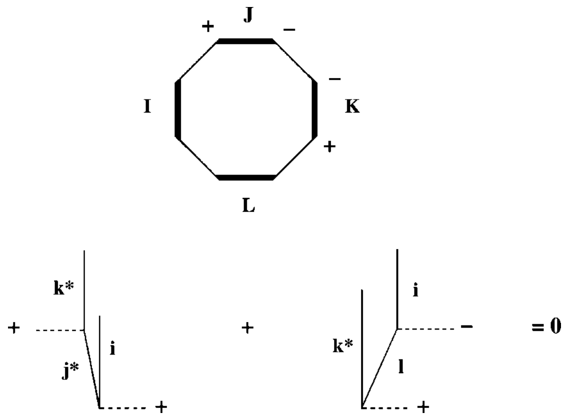


Figure 11. Cancelation of NNN-CT in cyclooctatetraene.

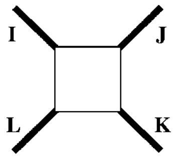


Figure 12. [4]Radialene.

90 terms: 4 (first Bond) × 2 (spin) × 2 (directions of circulation) × 5 (contributions). As $C = 4/19$, the total cyclic correction of cyclooctatetraene is antiaromatic, $E^{(4)}_{\mathrm{cycl}} = 0.499t$, i.e., half of the antiaromatic effect in cyclobutadiene.

Another highly symmetric structure is the [4]radialene (Figure 12) for which all molecular integrals are equal to $t/2$. The crossing of propagation lines in diagrams *e* and *e′* (Figure 10) introduces a negative sign. The same sign occurs in diagrams *c* and *d*, which will cancel with diagrams *a* and *b*. The final result will be $-C^2t/8$ (4 × 2 × 2) = $-0.09t$. This is a weakly antiaromatic correction, less than 10 % of the contribution in cyclobutadiene. This example again shows that the cyclic correction is not specific to ring size, but depends strongly on the bonds in which the atoms of the ring are engaged.

III. A General Estimate of the Properly Cyclic Delocalization Energy of a Ring-Containing Conjugated Hydrocarbon: Additive Evaluation of the Delocalization Energy

III.A. The Multiple-Cut Expression for the Cyclic Delocalization Energy. As a direct generalization of the previous section, it is clear that one may evaluate the energy of a delocalized system starting from a strongly localized function, associated with a Kekulé structure. For a molecular graph that does not contain rings, the delocalization energy will be obtained as a sum of (i) intra-Bond energies E_I, appearing at zeroth order; (ii) inter-Bond delocalization energies Δ_{IJ} between adjacent Bonds *I* and *J*, appearing at second order; (iii) noncyclic three-Bond delocalization energies Δ_{IJK} including back-and-forth movements of the electrons, appearing at fourth order; (iv) and so on, according to an incremental scheme of additive contributions involving *N* Bonds.

Consider a ring-free molecule built from the Bonds *I*, *J*, *K*, *L*, *M*. Its energy can be written as

$$E_{IJKLM} = \sum_I E_I + \sum_{\langle IJ\rangle} \Delta_{IJ} + \sum_{\langle IJK\rangle} \Delta_{IJK} + \sum_{\langle IJKL\rangle} \Delta_{IJKL} + \Delta_{IJKLM} \quad (26)$$

where the subsets ⟨*IJK*⟩ are chemically connected and the last term represents the specific collective effect of the whole set of Bonds *I*, *J*, *K*, *L*, *M*, in the molecule *IJKLM*. This latter contribution results from perturbative contributions that depend on all the Bonds of the molecule.

In this approach one may define the quantities E_I from the π energies of isolated Bonds *I*. The quantity Δ_{IJ} reflects the effect of delocalization between Bonds *I* and *J* and is obtained as

$$\Delta_{IJ} = E_{IJ} - E_I - E_J \quad (27)$$

where E_{IJ} is the π energy of the conjugated molecule that contains only the Bonds *I* and *J* with the same interaction as in the IJKLM molecule.

Similarly the three-Bond increment is

$$\Delta_{\mathrm{IJK}} = E_{\mathrm{IJK}} - E_{\mathrm{I}} - E_{\mathrm{J}} - E_{\mathrm{K}} - \Delta_{\mathrm{IJ}} - \Delta_{\mathrm{IK}} - \Delta_{\mathrm{JK}} \quad (28)$$

Combination of equations (27) and (28) gives:

$$\Delta_{IJK} = E_{IJK} - E_{IJ} - E_{IK} - E_{JK} + E_I + E_J + E_K \quad (29)$$

Two cases have to be considered:

(a) If the *I*−*J*−*K* system is acyclic, i.e., without connection between *I* and *K*, then $E_{IK} = E_I + E_K$ and the noncyclic three-Bond delocalization effect centered on Bond *J* is

$$\Delta_{I-J-K} = E_{IJK} - E_{IJ} - E_{JK} + E_J \quad (30)$$

which reflects the specific back-and-forth delocalization effects centered on Bond *J*.

(b) If the three Bonds *I*, *J* and *K* define a ring, with a connection between *I* and *K*, the three-Bond correction Δ_{IJK} involves both (i) noncyclic corrections Δ_{I-J-K}, Δ_{J-K-I} and Δ_{K-I-J}, centered on Bonds *J*, *K* and *I* respectively, and (ii) a purely cyclic correction $E_{\mathrm{cycl},IJK}$, which will be given by

$$E_{\mathrm{cycl},IJK} = \Delta_{IJK} - \Delta_{I-J-K} - \Delta_{J-K-I} - \Delta_{K-I-J} \quad (31)$$

The desired cyclic energy is therefore equal to the global three-bond correction (Δ_{IJK}) *minus* the sum of the noncyclic three-Bond contributions ($\sum_{\langle IJK\rangle}\Delta_{I-J-K}$) which are the same in the cyclic molecule as in the moieties resulting from a single cut, i.e., cutting a single bond appearing in the Kekulé graph of the ring. Returning to the definitions of the four three-Bond quantities as listed above, one obtains

$$E_{\mathrm{cycl},IJK} = E_{IJK} - E_{I-J-K} - E_{J-K-I} - E_{K-I-J} + E_{IJ} + E_{IK} + E_{JK} \quad (32)$$

This formula may be generalized easily to rings involving more than three Bonds. Let us call $E_{\mathrm{K|-L}}$ the energy of the open system where the single bond between the Bonds *K* and *L* has been cut, and $E_{(-K)}$ the energy of the system in which the Bond *K* has been removed. Then

$$E_{\mathrm{cycl},IJK\ldots N} = E_{IJK\ldots N} - \sum_{\langle KL\rangle} E_{K|-L} + \sum_K E_{(-K)} \quad (33)$$

where the first sum runs over the pairs of adjacent Bonds and the last sum on the various Bonds. One may check that in this equation all the Bond energies E_J, all the two-Bond energies Δ_{IJ}, all the noncyclic three-Bond increments Δ_{I-J-K}, etc... strictly cancel.

This relation may be formulated as follows:

"The properly cyclic delocalization energy of a ring built from *N* double Bonds is obtained from the energy of the ring by subtracting the energies of the *N* open systems in which one single bond has been cut and adding the energies of the *N* subsystems in which one double bond has been removed".

Let us summarize the logic of our approach in a more formal manner:

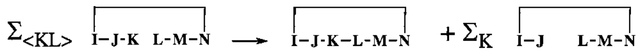


Figure 13. Chemical scheme for the evaluation of ACE_{MC} of a cyclic molecule.

(1) A fully localized zero-order wave function, built from strongly localized Bond MOs according to a Kekulé structure, is defined. On each Bond an antibonding MO is also defined.

(2) One may calculate the exact energy of the molecule through a perturbative expansion, starting from the strongly localized zero-order wave function, the hopping integrals between the atoms of adjacent Bonds defining the perturbation operator. The energy is a sum of contributions of various orders. Each of these contributions can be pictured as a Feynman diagram, where each propagation line is labeled by a Bond bonding or antibonding MO.

(3) For a tight-binding Hamiltonian each interaction line changes a label of a Bond into the label of an adjacent Bond (through bonding−bonding, antibonding−bonding, antibonding−antibonding couples).

(4) The only contributing diagrams are linked, in the sense of the linked cluster theorem,[14] which implies that each contribution of the energy involves a connected subset of Bonds, and that it reflects a process in which electrons circulate over the entire subset of Bonds. It therefore represents a delocalization effect on this subset of Bonds.

(5) The sum of all-order contributions involving all Bonds of a subset of connected Bonds represents their specific collective increment, corresponding to the specific electronic delocalization on this entire subset. This increment does not depend on the existence of other Bonds connected to this subset,

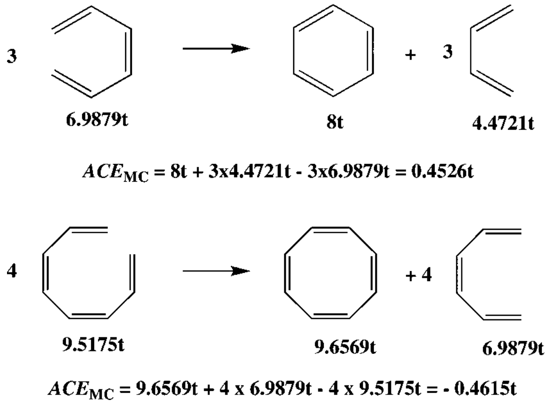
(6) The energy of a molecular graph constituted of N Bonds is the sum of Bond energies, two-Bond increments, three-Bond increments, etc., relative to all the connected subsets appearing in the graph, and of a graph-specific N-Bond increment. This increment is the difference between the total energy of the graph minus the sum of the Bond energies and of all the ($k < N$)-Bond increments.

(7) The properly cyclic energy of a ring containing N-Bonds is the difference between the N-Bond increment of the ring and the sum of all N-Bond increments of the N-open graphs obtained by cutting a bond between adjacent Bonds in the ring.

III.B. Aromatic Cyclic Energy from the Multiple Cut Evaluation: ACE_{MC}. We now turn to the practical application of eq (33). It may be translated into a hyperhomodesmotic reaction,[2d] by relating each entity $E_{K|-L}$ and $E_{(-K)}$ to a conjugated molecule where the dangling valencies resulting from the broken bonds are unambiguously terminated by hydrogen atoms (Figure 13). There are equal numbers of CH bonds, type by type, on each side of the proposed hyperhomodesmotic equation that appears in Figure 13. The desired cyclic energy ACE_{MC} is thus the enthalpy change in a chemical scheme illustrated in Figure 14 for benzene and cyclooctatetraene, using a single Hückel hopping integral t for reactants and products. As long as one stays within the framework of simple Hückel theory, the sigma bonds do not play a role and geometry optimizations need not be considered.

Equation (33) and Figure 13 give the ACE_{MC} estimate of the aromatic cyclic energy of a ring. In the case of [N]annulenes, the general expression of ACE_{MC} is

$$ACE_{MC}(N) = E_{cyc}(N) - (N/2)E_{acyclic}(N) + (N/2)E_{acyclic}(N-2) \text{ for even } N$$



$ACE_{MC} = 8t + 3x4.4721t - 3x6.9879t = 0.4526t$

$ACE_{MC} = 9.6569t + 4 \times 6.9879t - 4 \times 9.5175t = - 0.4615t$

Figure 14. Evaluation of ACE_{MC} of benzene and cyclooctatetraene.

TABLE 1: Comparison of BRE and ACE-Type Values to the Cyclic Contribution to the Delocalization Energy Extracted from the Perturbative Approach E_P (All in t Units) for the First [N]Annulenes, $N = 4-22$, and Some Selected Isomers[a]

compound	BRE/t	ACE_{DC}/t	ACE_{MC}/t	E_P/t
[N]annulene C_NH_N[b]				
C_4H_4	−0.472	−0.944	−0.944	−1.000
C_6H_6	1.012	0.496	0.453	0.532
C_8H_8	0.139	−0.390	−0.462	−0.499
$C_{10}H_{10}$	0.891	0.355	0.265	
$C_{12}H_{12}$	0.336	−0.203	−0.306	
$C_{14}H_{14}$	0.842	0.301	0.188	
$C_{18}H_{18}$	0.816	0.273	0.146	
$C_{22}H_{22}$	0.799	0.255	0.119	
C_4H_4 isomers				
$C_3H_2(CH_2)$ (methylene cyclopropene)	0.490	0.018	0.018	0.000
C_6H_6 isomers				
$C_5H_4CH_2$ (fulvene)	0.478	−0.038	0.006	0.000
$C_4H_2(CH_2)_2$ (3,4-dimethylene cyclobutene)	0.308	−0.208	−0.164	−0.210
$C_4H_3(CHCH_2)$ (vinyl-cyclobutadiene)	−0.298	−0.814	−0.814	–
$C_3(CH_2)_3$ (3-radialene)	0.400	−0.028	0.016	0.000
C_8H_8 isomers				
$C_4(CH_2)_4$ ([4]radialene)	0.324	−0.084	−0.072	−0.09
$C_7H_6CH_2$ (methylene cycloheptatriene)	0.470	−0.062	0.010	0.000
o-xylene[c]	0.440 0.624 0.548	0.049 0.080	0.068	0.061 0.066
p-xylene	0.516	0.051	0.068	0.061

[a] The perturbative values include EPV corrections. [b] Values extracted from the analytical expressions for BRE, ACE_{DC}, ACE_{MC}. [c] Three possible single cuts (BRE) and two possible double cuts (ACE_{DC}) can be considered.

ACE_{MC} values estimated for neutral [N]annulenes and selected isomers are given in Table 1. The good agreement of these ACE_{MC} values with the perturbative evaluations of the 2-, 3- and 4-Bond systems performed in the previous section accounts for the fast convergence of the perturbation expansion. Of course, the use of eq (33) is much easier, for the Hückel Hamiltonian, than the perturbative expansion, especially if the ring involves $N > 4$ Bonds, since the perturbative approach would require consideration of an Nth-order expansion. Equation (33) also incorporates higher-order corrections, and should be considered as more reliable.

IV. Comparison of ACE_{MC} with Previous Estimates of the Cyclic Contribution to the Delocalization Energy

ACE_{DC}, based on a double cut of the ring, has been shown to perform better than Breslow resonance energies (BRE), which

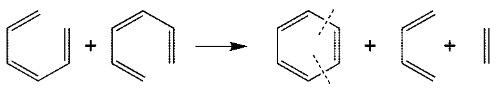


Figure 15. Chemical scheme for the evaluation of ACE$_{DC}$ of benzene.

estimate the cyclic energy as the difference between the π-energy of the ring and the π-energy of the acyclic reference resulting from a single cut.[6] BRE includes in the cyclic energy a short-range (second-order) delocalization effect between the two Bonds separated by the cut bond. This spurious contribution is close to $0.5t$.

We now compare the multiple-cut (ACE$_{MC}$) and the double-cut evaluations (ACE$_{DC}$), taking the case of benzene for illustration. The double-cut formula evaluates the cyclic energy as (Figure 15)

$$\mathrm{ACE_{DC}}(C_6H_6) = E(C_6H_6) - 2E(C_6H_8) + E(C_4H_6) + E(C_2H_4)$$

The Bond energies and the two-Bond energies cancel exactly in this expression, but there are three three-Bond noncyclic delocalization increments in C_6H_6, and only one in each of the two open chains C_6H_8. Consequently the double-cut evaluation incorrectly attributes one three-Bond noncyclic delocalization increment to the cyclic energy. Of course this error is very small, as it is a fourth-order correction, of size about $0.07t$, as calculated in section II. Nevertheless, this error is expected to prevent this estimate from converging to zero when the size of the ring tends to infinity.

Analytical expressions of BRE, ACE$_{DC}$ and ACE$_{MC}$ have been derived for $[4n + 2]$ and $[4n]$annulenes. (See Supporting Information for details.) It is found that the Breslow resonance energies are

$$\mathrm{BRE}(4n+2) = 2t\left[\frac{2}{\sin\frac{\pi}{4n+2}} - \frac{1}{\sin\frac{\pi}{8n+6}} + 1\right]$$

$$\mathrm{BRE}(4n) = 2t\left[2\cot\frac{\pi}{4n} - \frac{1}{\sin\frac{\pi}{8n+2}} + 1\right]$$

with the same nonzero asymptote as n tends to infinity: $\mathrm{BRE}_\infty = 12 - 4/\pi]t = 0.7268t$.

The estimate based on the double cut strategy gives an expression for the cyclic contribution ACE$_{DC}$:

$$\mathrm{ACE_{DC}}(4n+2) = 2t\left[\frac{2}{\sin\frac{\pi}{4n+2}} + \frac{1}{\sin\frac{\pi}{8n+2}} - \frac{2}{\sin\frac{\pi}{8n+6}} + 2\right]$$

$$\mathrm{ACE_{DC}}(4n) = 2t\left[2\cot\frac{\pi}{4n} + \frac{1}{\sin\frac{\pi}{8n-2}} - \frac{2}{\sin\frac{\pi}{8n+2}} + 2\right]$$

which both give the significantly smaller, but still nonzero, asymptote of

$$\mathrm{ACE_{DC\infty}} = \left[4 - \frac{12}{\pi}\right]t \approx 0.1803t$$

The full multiple-cut approach yields the expressions:

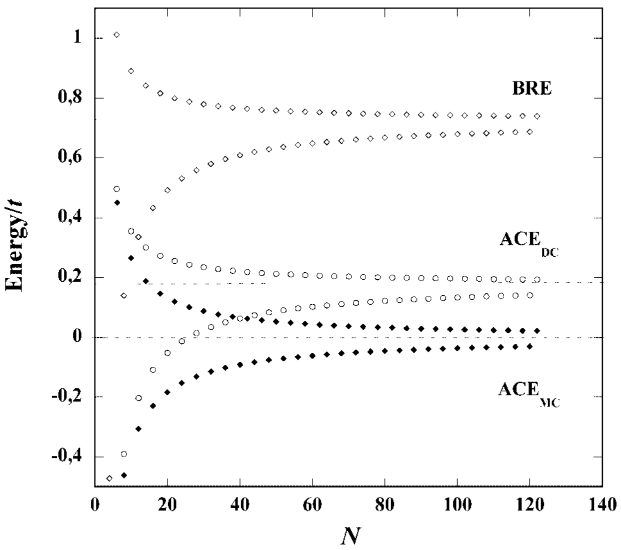


Figure 16. Comparison of the various estimates of the cyclic contribution to the delocalization energy for $[4n + 2]$ and $[4n]$annulenes.

$$\mathrm{ACE_{MC}}(4n+2) = 2t\left(\frac{2}{\sin\frac{\pi}{4n+2}} + (2n+1)\left[\frac{1}{\sin\frac{\pi}{8n+2}} - \frac{1}{\sin\frac{\pi}{8n+6}}\right]\right)$$

$$\mathrm{ACE_{MC}}(4n) = 2t\left(2\cot\frac{\pi}{4n} + 2n\left[\frac{1}{\sin\frac{\pi}{8n-2}} - \frac{1}{\sin\frac{\pi}{8n+2}}\right]\right)$$

which both tend to zero as $\pi/8n$ and $-7\pi/24n$ respectively, when n tends to infinity, and hence show the correct asymptotic behavior for a cyclization energy. It can be seen that the absolute decay to zero is faster for $[4n + 2]$annulenes than for $[4n]$annulenes. More detailed analysis shows that all three estimates tend to their asymptotes as a multiple of $1/n$ from above, for aromatic $4n + 2$ systems, and from below for antiaromatic $4n$ systems. These trends are illustrated in Figure 16, which makes apparent the superiority of the multiple-cut ACE$_{MC}$ approach.

The *o*-xylene case illustrates another advantage of the present approach. The three possible single cuts yield three possible values of BRE. Similarly, two possible values of ACE$_{DC}$ are available (Table 1), whereas ACE$_{MC}$ is univocally defined.

V. Extensions

V.A. Cycles with One or Several Conjugated Side Chains. One may generalize the application of eq (33) to cycles with one or several conjugated side chains. In a simpler formulation, Bonds of the side chain can be gathered up with the Bond of the ring bearing this substituent. Thus, the styrene molecule is divided into three parts: two double bonds A and B, and a butadiene moiety C connected to A by one unsubstituted carbon atom and to B by a substituted carbon atom (Figure 17). The corresponding scheme for the evaluation of ACE$_{MC}$(styrene) for the simplified approach involving three moieties A−C is given at the top, while the equivalent scheme corresponding to the fragmentation into four moieties A−D is given at the bottom of Figure 17, which illustrates the equivalence of the two fragmentations.

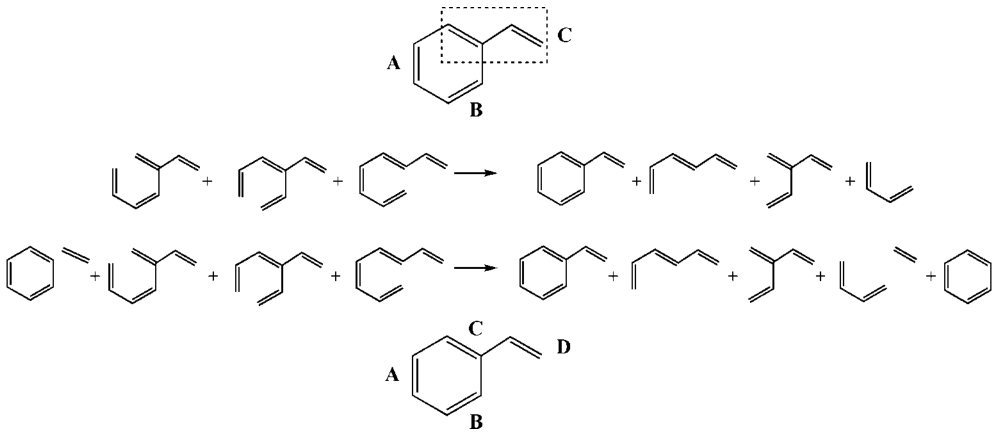


Figure 17. Illustration of equivalence of the simplified (top) and complete (bottom) evaluation of ACE_{MC} of styrene.

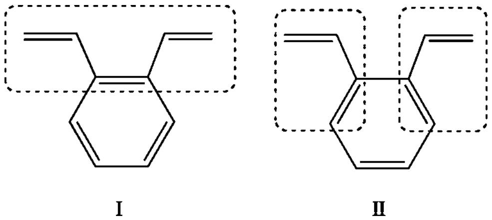


Figure 18. Two Kekulé structures for *o*-divinylbenzene.

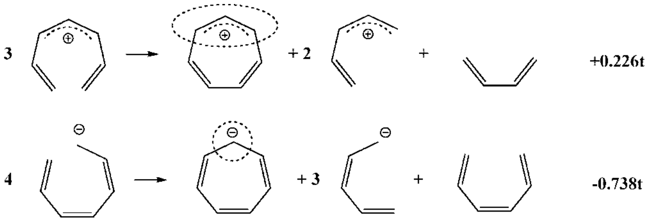


Figure 19. Evaluation of ACE_{MC} of C_7H_7 cation and anion.

When two side chains are attached on adjacent carbon atoms, they may be either gathered to the same Bond or with two different adjacent Bonds, depending on the underlying Kekulé picture. This is illustrated below for *o*-divinylbenzene (Figure 18).

The best partition into Bonds, or Bonds with their conjugated tails, is the one giving the lowest sum of the energies of these blocks. As an alternative criterion one may select the Kekulé fully localized function which has the greatest overlap with the variational solution, or the one whose bond indices have the greatest similarity to those of the variational solution. In practice, in the cases we have examined, all these criteria coincide. For instance, in the above *o*-divinylbenzene, it is preferable to use the Kekulé structure I. ACE_{MC} values estimated from structure I and structure II, namely $0.400t$ and $0.370t$, respectively, are, however, not very different in this case.

V.B. Ionic Closed-Shell Conjugated Hydrocarbons. For cationic conjugated hydrocarbons one must consider a two-electron unit A^+ spread over three adjacent carbon atoms. In anions, one of the units, namely A^-, is a negatively charged single carbon atom. This is illustrated in Figure 19 for the C_7H_7 case. The cation is moderately aromatic (as is $C_5H_5^-$ ($ACE_{MC} = 0.208t$)) whereas the anion is strongly antiaromatic.

The general formula for cationic (anionic) $[2N + 1]$annulenes is given below:

$$ACE_{MC}(2N+1)^+ = E_{cyc}(2N+1)^+ - NE_{acyc}(2N+1)^+ + (N-1)E_{acyc}(2N-1)^+ + E_{acyc}(2N-2)$$

$$ACE_{MC}(2N+1)^- = E_{cyc}(2N+1)^- - (N+1)E_{acyc}(2N+1)^- + (N)E_{acyc}(2N-1)^- + E_{acyc}(2N)$$

V.C. Heterocycles. So far we have only used the simplest Hückel Hamiltonian, with equal on-site monoelectronic energies and equal bond lengths. Our approach may be straightforwardly extended to heterocyclic molecules, for instance to cycles containing nitrogen atoms either involved in an imine or amine function. The former group introduces a C=N Double Bond, the latter plays the role of a two-electron Bond since they bring 2 electrons to the π system. In the latter case, the electron pair does not possess a virtual valence MO. Therefore, in a pyrrole ring for instance, the lone pair can only appear as a hole in the third-order cyclic diagrams which were presented in the section devoted to benzene. One may see that one looses half of the cyclic contributions. If the energy of the lone pair is t (i.e., equal to the energy of the bonding MOs), application of eq (33) gives a cyclic energy of $0.28t$, approximately half that of benzene. The substitution of a Bond by a lone pair in an aromatic ring does not suppress the aromaticity but does significantly reduce it. An even larger aromaticity loss is expected for the true geometry that would be described using various t parameters over the heterocycle.

V.D. Role of the Cyclic Correction in the Distortivity of the π-Delocalization Energy. ACE_{MC} may be also estimated for conjugated systems exhibiting bond-length alternations. Two different resonance integrals t and t' ($t' < t$) are therefore required to describe intra-Bond and inter-Bond overlap respectively.

The case of distorted benzene rings is considered below. Figure 20 plots the cyclic energy contribution of a 6-membered ring as a function of the distortion parameter δ, where the resonance integrals are $t(1+\delta)$ and $t(1-\delta)$ for short Bonds and long bonds, respectively.

It is interesting to see that a sizable cyclic contribution survives in a distorted benzene ring. This is in agreement with the robustness of ring currents in distorted 6-membered rings.[15] This cyclic correction decreases when the bond alternation increases and so acts against the distortion. This result is not contradictory with the famous statement of Hiberty and Shaik[16] that the π electron delocalization energy is distortive, i.e., increases in absolute value with bond length alternation. These authors established that the equality of the bond lengths of benzene is driven by the σ system. The leading term of π-delocalization energy is of second order, coming from the delocalization between adjacent Bonds, and is distortive. The properly cyclic contribution works in the opposite direction, but

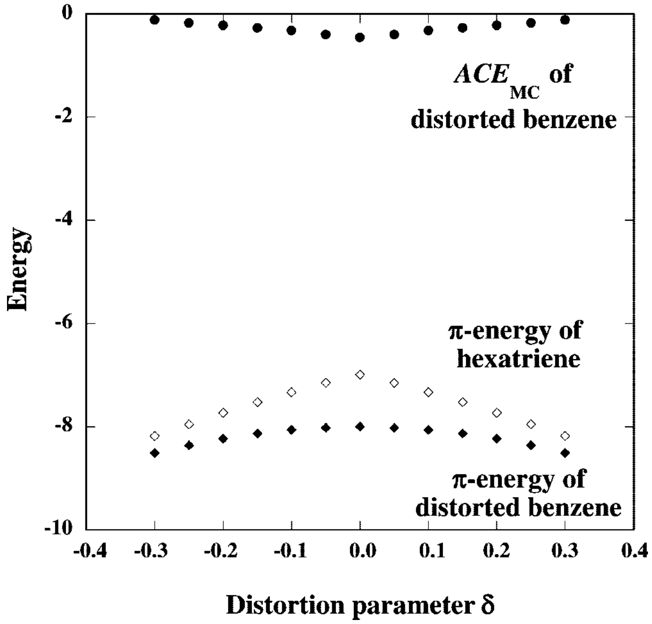


Figure 20. Various energy contributions ($-t$ units) of distorted benzene as a function of the distortion parameter δ.

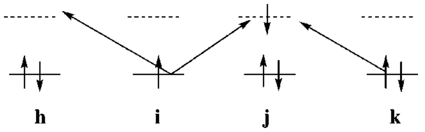


Figure 21. Exclusion principle violating processes for the $\phi_{i\rightarrow j^*}$ CT determinant.

is of higher order and is smaller in magnitude (Figure 20). It seems that this observation, which extends and confirms related work on periodic systems,[8] makes the question somewhat more subtle and reconciles the analysis of Hiberty and Shaik with the intuition that the circulation around the ring should be greater for equal bond lengths. In contrast, the positive cyclic circulation energy goes through a maximum for equal bond length in antiaromatic systems, and acts in favor of distortion and increases the barrier between the two Kekulé structures, since it goes from $-0.06t$ for $\delta = 0.3$ to $-0.50t$ for $\delta = 0$ in cyclooctatetraene.

V.E. *Ab Initio* Transposition. One should finally consider whether one can extend our approach to more sophisticated Hamiltonians. Extension to Pariser−Parr−Pople or similar semiempirical Hamiltonians would be straightforward, as cutting of a bond simply consists in canceling the hopping integral on that bond. For *ab initio* calculations, one may consider the energies of the various molecules appearing on both sides of the hyperhomodesmotic reaction in a DFT or strict *ab initio* computation. This approach has been applied to benzene in ref 6. It gives a value of -19.9 kcal$\cdot$mol^{-1} without zero-point energy correction (-20.0 kcal$\cdot$mol^{-1} with zero-point energy correction) at the B3PW91/6-31G** level of calculation. These values are consistent with the Hückel estimate ($0.45t$), since they suggest a reasonable value of t close to 2 eV. Note, however, that in this approach the relaxed geometries of the fragments are different from those that they would have in the ring, affecting the corresponding π-energies. In order to avoid this difficulty, one could consider the ring only and suppress the integrals involving the overlap distribution between the π atomic orbitals of the two atoms of the cut bonds (overlap, monoelectronic and bielectronic integrals), which would interrupt the delocalization through these bonds. A forthcoming paper[17] will employ a more rigorous strategy using the optimized π valence molecular orbitals furnished by a CASSCF calculation, defining Bond MOs and following the perturbative scheme of section II. It will be shown that the results are perfectly consistent with those of the Hückel Hamiltonian.

VI. Conclusion

The present paper has proposed an improved evaluation of the properly cyclic delocalization energy in ring-containing molecules. The Breslow estimate is based on a single cut of the ring. Previous work has shown the logical superiority of an evaluation based on a double-cut of the ring. The present proposal takes this logic further, and gives the ultimate multiple-cut formula. As shown analytically, and confirmed by the asymptotic behavior of the cyclic energy contribution when the ring size tends to infinity, the present formulation is free from high-order noncyclic many-Bond contributions, avoiding the (small) bias introduced through a noncyclic three-Bond contribution in the double-cut estimate. ACE$_{\mathrm{MC}}$ performs better than ACE$_{\mathrm{DC}}$, but a similar linear correlation with ELFπ is expected.[6] The domain of application of this approach is broad. An interesting theoretical feature is that it shows that the properly cyclic energy contribution of aromatic rings fights against bond alternation but cannot overcome the trend of the short-range delocalization effects, which dominates the π electron energy and prefers bond alternation, as shown by Hiberty and Shaik. Future work will describe an *ab initio* implementation of the present analysis.

From an epistemological point of view, this work suggests a few remarks:

(i) To identify and quantify the impact of a collective phenomenon, it is important to start from localized elements, free from collective effects. The use of SCF localized MOs for instance would be incorrect since they already incorporate the cyclic delocalization. This statement may seem paradoxical, but is logical.

(ii) Analysis of the eigenenergy of the ultrasimplified Hückel Hamiltonian made use of a high-order perturbative expansion expressed in terms of Feynman diagrams, and the linked cluster theorem. Although the hyperhomodesmotic reaction proposed for the evaluation of the cyclic energy is acceptable on intuitive grounds, its rigorous justification rests on techniques that are in danger of disappearing from quantum chemistry course and textbooks.

Acknowledgment. One author (J.-P.M.) dedicates this work to his friend Sason Shaik. His fight in favor of the conceptual dimension of quantum chemistry, his taste for images and for qualitative interpretations, and his sense of poetry have been an encouragement for decades. He thanks Vincent Robert and Iberio de P. R. Moreira for their interest in the early stages of this work. The authors also thank Bruno Lepetit for helpful discussion. P.W.F. thanks the Royal Society/Wolfson Scheme for a Research Merit Award.

Appendix. Introduction of EPV Corrections in the Evaluation of the Inter-Bond Charge Transfer Energy

The quantity EPV(ij^*) relative to the determinant ϕ_{ij^*} is the sum of the second-order corrections that results from those CT excitations that are possible on ϕ_0 and impossible on ϕ_{ij^*}

$$\mathrm{EPV}(ij^*) = \sum_{kl^*} \frac{{t'_{kl^*}}^2}{t_k - t_l} \text{ such as } a^+_{l^*} a_k \phi_{ij^*} = 0$$

$$= \sum_{l^*} \frac{{t'_{il^*}}^2}{t_i - \mathrm{t}_l} + \sum_k \frac{{t'_{kj^*}}^2}{t_k - t_j} - \frac{{t'_{ij^*}}^2}{t_i - t_j}$$

For the determinant ϕ_{ij^*} three such processes are ruled out in a 1D chain, as seen in Figure 21, namely, the excitations (i) $i \rightarrow j^*$, (ii) $i \rightarrow h^*$, and (iii) $k \rightarrow j^*$. When the Bonds (and the bonds) are equivalent

$$\mathrm{EPV}(ij^*) = \frac{3t'^2}{8t}$$

The energy denominators $E^0 - E^0_{ij^*}$ should be replaced by

$$\Delta E_{ij^*} = 2t + 3\mathrm{t}'^2/(8t)$$

The corrected first order coefficients of the CT determinants are then

$$C = (t'/2)/(2t + 3t'^2/(8t))$$

and the second-order energy introduced by the CTs between two adjacent Bonds becomes

$$\varepsilon_{ij} = t'^2/(2t + 3t'^2/8t)$$

Supporting Information Available: Total π energies of [*N*]annulenes and [*N*]polyene chains, analytical expression and asymptotic behavior for [$4n + 2$] and [$4n$]annulenes of Breslow resonance energies (BRE), aromatic cyclic energy resulting from a double cut ($\mathrm{ACE_{DC}}$) and aromatic cyclic energy resulting from a multiple cut ($\mathrm{ACE_{MC}}$). This material is available free of charge via the Internet at http://pubs.acs.org.

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JP802839N