Why Is the Delocalization Energy Negative and Why Is It Proportional to the Number of π Electrons?

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Abstract: The delocalization energy of conjugated hydrocarbons is almost always negative and proportional to the number of π electrons. A theoretical deduction is given for these properties and a physical interpretation is obtained using localized π orbitals. The delocalization energy is found to be negative because, with rare exceptions, *each localized* π orbital is still more delocalized than the ethylene π orbital, a phenomenon termed "local delocalization." The proportionality to the number of π electrons obtains because most *localized* π orbitals have nearly the same energy which, moreover, is nearly molecule independent among similar molecules. The latter observation motivates the definition of a new set of localized molecular orbitals, called *homogeneous* localized orbitals, whose orbital energies are exactly equal. It is shown that, in conjugated hydrocarbons, homogeneous localized orbitals closely resemble maximally localized π orbitals.

1. The Delocalization Energy and Its Two Basic Properties

Systems of conjugated double bonds are especially stable and it is generally accepted that this is due to the delocalization of π electrons. In the Hückel or Wheland approximations,[1] this stability is related to the sum of the occupied π orbital energies. The fact that this sum is less than the sum of the orbital energies of an equal number of ethylenic π orbitals is associated with "resonance stabilization." The *delocalization energy* is defined to be the difference between these energies

$$\mathrm{DE} = \sum_i g_i\epsilon_i - Ne$$

where N is the number of π electrons, $\epsilon_1, \epsilon_2, \ldots$ are the occupied π orbital energies, and *e is the π orbital energy of ethylene*. The summation in eq 1 includes only the occupied orbitals with occupation numbers

$$g_i = \begin{array}{c} 1, \text{ if orbital } i \text{ is singly occupied} \\ \text{or} \\ 2, \text{ if orbital } i \text{ is doubly occupied} \end{array} \qquad (2)$$

The relation between DE and experimental resonance energies is discussed in various texts.

The delocalization energy has two fundamental properties. First, it is almost always negative, *i.e.*

$$\mathrm{DE} < 0 \qquad (3)$$

and second, it is often roughly proportional to the number of π electrons, *i.e.*

$$\mathrm{DE} \sim \text{constant} \times N \qquad (4)$$

Equation 3 expresses resonance stabilization. Although it is well known, its origin has not been fully understood, for in all conjugated systems one finds that $\epsilon_i < e$, for the lowest occupied orbital, and $\epsilon_i > e$, for the highest occupied orbital. It is therefore not clear why the *sum over all* occupied orbital energies should always be less than the sum of an equal number of ethylenic orbital energies. Intuitively, it seems that this has something to do with delocalization. Equation 4 is less widely appreciated, although it was noted by Scherr.[2] Reasons for its validity are also unclear. The object of this paper is to elucidate the reasons for and the significance of the relations in eq 3 and 4.

2. Validity of the Two Basic Properties in (3) and (4)

General Formula. The theoretical derivation of the empirically observed relations 3 and 4 will be based on the orbital energy for a π electron system, namely

$$\epsilon_i = \text{Coulomb integral} + x_i \times \text{resonance integral} \qquad (5)$$

where

$$x_i = m_i/(1 + Sm_i) \qquad (6)$$

The m_i are the eigenvalues of the topological matrix[3] of the system and S is the nearest neighbor overlap integral: $S = 0$ for Hückel orbitals; $S \approx 0.25$ for Wheland orbitals. When $S = 0$ we shall call the x_i "Hückel numbers" and give them the symbol m_i. When $S \neq 0$, the x_i will be referred to as "Wheland numbers." *For ethylene* one finds

$$m = 1 \qquad (7)$$

$$x = 0.8 \qquad (8)$$

The delocalization energy of eq 1 can now be written

$$\mathrm{DE} = (\mathrm{de}) \times N \times \text{resonance integral} \qquad (9)$$

where (de), the "delocalization energy per electron" in units of the resonance integral, is given by

$$(\mathrm{de}) = \bar{m} - m = \bar{m} - 1 \qquad (10)$$

for Hückel orbitals and

$$(\mathrm{de}) = \bar{x} - x = \bar{x} - 0.8 \qquad (11)$$

for Wheland orbitals. The quantities

$$\bar{m} = N^{-1}\sum_i g_i m_i \qquad (12)$$

and

$$\bar{x} = N^{-1}\sum_i g_i x_i \qquad (13)$$

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[1] R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry," Interscience, New York, N. Y., 1959, Chapter 4.

[2] C. W. Scherr, *J. Chem. Phys.*, **21**, 1413 (1953); reprinted in "Free-Electron Theory of Conjugated Molecules," Wiley, New York, N. Y., 1964.

[3] K. Ruedenberg, *J. Chem. Phys.*, **34**, 1884 (1961); reprinted in text cited in ref 2.

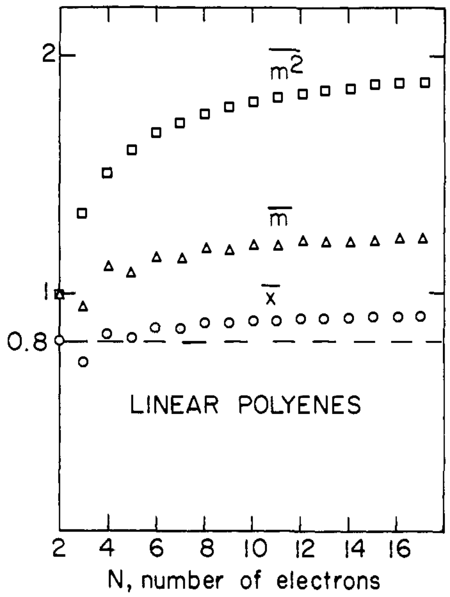

Figure 1. Average Hückel and Wheland numbers in linear polyenes.

are the *average* Hückel and Wheland numbers, respectively, of the molecule in question.

We shall now show that the Hückel and Wheland numbers each have the following properties, which are equivalent to the basic properties of the delocalization energy: (1) they are usually larger than the ethylene numbers, so that DE is *usually negative* (the resonance integral being negative); (2) they are nearly *molecule independent* within certain classes of conjugated molecules.

In order to readily assess the behavior of the Wheland numbers, we shall make some judicious approximations. The denominator in eq 6 can be rewritten

$$(1 + m_iS)^{-1} = (1 + {}^3/_2S)^{-2}(1 + 3S - m_iS)/(1 - \delta^2) \quad (14)$$

with

$$\delta = ({}^3/_2 - m_i)S/(1 + {}^3/_2S) \quad (15)$$

Moreover, it can be shown that[4]

$$-3 \leq m_i \leq 3 \quad (16)$$

for *all* π systems, and in *most* systems the m_i for occupied orbitals are positive. Consequently

$$\delta^2 < 9/121 = 0.074 \quad (17)$$

and the expansion of $(1 - \delta^2)^{-1}$ in powers of δ^2 is rapidly convergent. A good approximation is obtained by neglecting δ^2 altogether. Thereby, insertion of eq 14 into eq 6 yields the expression

$$\bar{x} = [(1 + 3S)\bar{m} - S\bar{m}^2]/(1 + {}^3/_2S)^2 \quad (18)$$

$$= 0.9256\bar{m} - 0.1322\bar{m}^2 \quad (18')$$

where

$$\bar{m}^2 = N^{-1}\sum_i g_i m_i^2 \quad (19)$$

is the average of the squares of the Hückel numbers.

We will now calculate the Hückel and Wheland numbers for some important classes of conjugated hydrocarbons and use our results to verify the two basic properties.

Linear Polyenes. Here[5]

$$m_i = 2 \cos [i\pi/(N + 1)] \quad (20)$$

so that $\bar{m}$ and $\bar{m}^2$ have the analytic forms (all subsequent summations are readily obtained using the identity $1 + 2\Sigma_{n=1}{}^M \cos n\alpha = [\sin (M + {}^1/_2)\alpha/(\sin {}^1/_2\alpha)]$)

$$N\bar{m} = 2 \cos [\pi(2 - g_M)/2(N + 1)]/\sin [\pi/2(N + 1)] - 2 \quad (21)$$

and

$$N\bar{m}^2 = 2(N - 1) \quad (22)$$

respectively. The integer M is defined as

$$M = \begin{matrix} N/2, \text{ even } N \\ \text{or} \\ (N + 1)/2, \text{ odd } N \end{matrix} \quad (23)$$

Values of $\bar{m}$, $\bar{m}^2$, and $\bar{x}$ are plotted *vs.* N in Figure 1. Except for allyl (N = 3), all average Hückel and Wheland numbers are larger than ethylene's (N = 2), so all systems having $N \geq 4$ will have a negative delocalization energy. Moreover, after the first few systems the results are independent of N. This can be demonstrated explicitly by taking the limits $N \gg 1$, $M/N \rightarrow {}^1/_2$

$$\lim \bar{m} = 4/\pi = 1.27 \quad (24)$$

$$\lim \bar{m}^2 = 2 \quad (25)$$

and hence

$$\lim \bar{x} = 0.92 \quad (26)$$

Alternatively, one can get the same results by averaging eq 20

$$\bar{m} = (2/\pi)\int 2 \cos \theta \, d\theta = 4/\pi = 1.273 \quad (27)$$

$$\bar{m}^2 = (2/\pi)\int 4 \cos^2 \theta \, d\theta = 2 \quad (28)$$

The integration range $0 \leq \theta \leq \pi/2$ is chosen because the m_i for occupied orbitals in linear polyenes are nonnegative.

Cyclic Polyenes. The orbital energies are given by[5]

$$m_i = 2 \cos i2\pi/N \qquad i = 0, 1, 2, \ldots \quad (29)$$

and, whereas m_0 is nondegenerate, all other m_i ($i \geq 1$) are doubly degenerate. Consequently, there are four types of cyclic polyenes depending upon the occupation of the highest filled orbital. The four types can be distinguished by the index

$$j = -1, 0, 1, 2 \quad (30)$$

in the formula

$$N = 4\mu + j \quad (31)$$

where N denotes the number of electrons, μ denotes the index of the highest filled orbital, and the occupation

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[4] K. Ruedenberg, *J. Chem. Phys.*, **22**, 1878 (1954); reprinted in text cited in ref 2.

[5] C. A. Coulson, *Proc. Cambridge Phil. Soc.*, **46**, 202 (1950); C. A. Coulson and A. Streitweiser, "Dictionary of π-Electron Calculations," Pergamon Press, New York, N. Y., 1965.

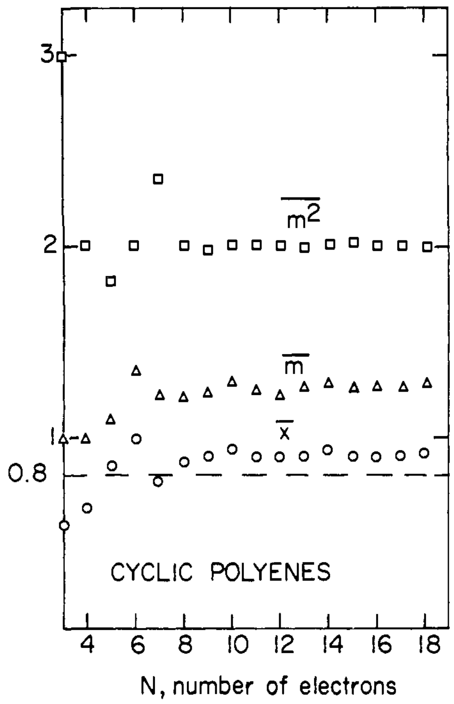

Figure 2. Average Hückel and Wheland numbers in cyclic polyenes.

number of this orbital is given by

$$g_\mu = (2 + j) \tag{32}$$

Summing over the occupied orbitals, one obtains

$$N\bar{m} = 4\cos[\pi(1 - j/2)/N]/\sin(\pi/N) - (2 - j)m_\mu \tag{33}$$

and

$$N\bar{m}^2 = -4\sin[2\pi(1 - j/2)/N]/\sin(2\pi/N) + 8(\mu + {}^1\!/_2) - (2 - j)m_\mu{}^2 \tag{34}$$

Plots of $\bar{m}^2$ and the average Hückel and Wheland numbers in Figure 2 are similar to those in Figure 1. Beyond the first few members our assertions about the Hückel and Wheland numbers hold here also. The limiting cases are again described by eq 24–28. It is interesting that the $4\mu + 2$ systems approach the limits from above and all others approach from below.

Linear Polyacenes. The analysis is more complicated here, since[5]

$$\begin{aligned} m_0 &= 1 \\ m_i &= {}^1\!/_2\{1 + [9 + 8\cos(i\pi/(\nu + 1))]^{1/2}\} \quad i = 1, 2, \ldots \nu \\ m_i' &= {}^1\!/_2\{-1 + [9 + 8\cos(i\pi/(\nu + 1))]^{1/2}\} \quad i = 1, 2, \ldots \nu \end{aligned} \tag{35}$$

where

$$N = 4\nu + 2 \text{ and } \nu = \text{number of rings} \tag{36}$$

For $\bar{m}^2$, one finds straightforwardly that

$$N\bar{m}^2 = 10\nu + 2 \tag{37}$$

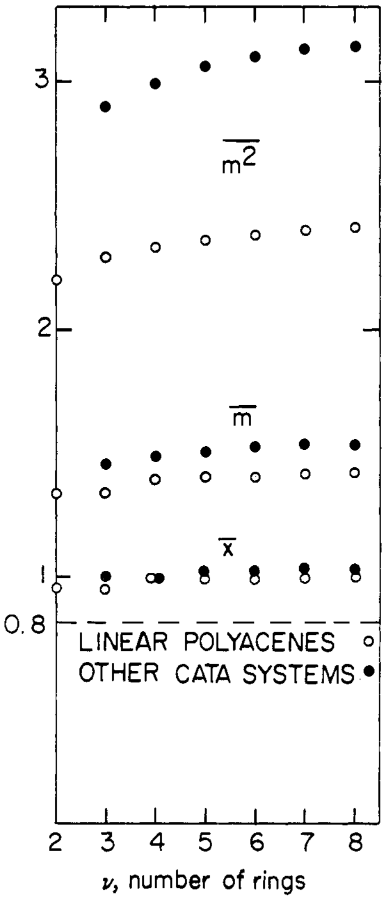

Figure 3. Average Hückel and Wheland numbers in catacondensed hydrocarbons.

by summing over the occupied orbitals. For $\bar{m}$ one obtains

$$\begin{aligned} N\bar{m} &= 2m_0 + 2\sum_{i=1}^{\nu}(9 + 8\cos[i\pi/(\nu + 1)])^{1/2} \\ &= 2\sum_{i=1}^{\nu+1}(9 + 8\cos[i\pi/(\nu + 1)])^{1/2} \end{aligned} \tag{38}$$

$$N\bar{m} = 2\sum_{i=1}^{\nu+1}\{1 + 16\cos^2[i\pi/2(\nu + 1)]\}^{1/2}$$

which can be fairly closely approximated by

$$N\bar{m} = 2\sum_{i=1}^{\nu+1}\{1 + 3\cos[i\pi/2(\nu + 1)]\} \tag{39}$$

Execution of the summation yields

$$N\bar{m} = 2(\nu + 1) + 3\{\cot[\pi/4(\nu + 1)] - 1\} \tag{40}$$

whence, by virtue of eq 37

$$N\bar{m} = {}^1\!/_2 N - 2 + 3\cot(\pi/N + 2) \tag{41}$$

Results using eq 37 and 41 are shown in Figure 3. The values of $\bar{m}$ and $\bar{x}$ are substantially larger than the ethylenic values. Since N has at least the value 6 and increases rapidly with the number of rings, $\bar{m}$ and $\bar{x}$ approach the limiting values quickly. The latter are

$$\lim \bar{m} = {}^1\!/_2 + 3/\pi = 1.455 \tag{42}$$

$$\lim \bar{m}^2 = 2.5 \tag{43}$$

$$\lim \bar{x} = 1.016 \tag{44}$$

The limiting value of eq 42 is also obtained by the integral averaging

$$N\bar{m} = [4(\nu + 1)/\pi]\int_0^{\pi/2} d\theta(1 + 3\cos\theta)$$

$$\lim \bar{m} = \pi^{-1}\int_0^{\pi/2} d\theta(1 + 3\cos\theta) = {}^1/_2 + 3/\pi$$

Condensed Benzenoid Hydrocarbons. It is known[4] that in systems with condensed rings, one has

$$m_i = 3\cos k_i \tag{45}$$

where k_i is determined from an eigenvalue problem. Hence we cannot employ summation techniques to obtain the average Hückel and Wheland numbers. This being the case, we shall use a simple procedure based on the ratio of joint atoms (common to more than one ring) to nonjoint atoms. The $\bar{m}$ and $\bar{m}^2$ for nonjoints are assumed to be given by eq 27 and 28, while the values

$$\bar{m} = (2/\pi)\int_0^{\pi/2} 3\cos\theta\, d\theta = 6/\pi = 1.91 \tag{46}$$

$$\bar{m}^2 = (2/\pi)\int_0^{\pi/2} 9\cos^2\theta\, d\theta = 4.5 \tag{47}$$

are used for joint atoms. The latter are obtained by averaging eq 45. Thus, if N is the total number of atoms and J is the number of joint atoms, we assume that, approximately

$$\bar{m} = (6/\pi)(J/N) + (4/\pi)[(N - J)/N] = (4/\pi) + (2/\pi)(J/N) \tag{48}$$

$$\bar{m}^2 = (9/2)(J/N) + 2[(N - J)/N] = 2 + 2.5(J/N) \tag{49}$$

Substitution in eq 18′ yields

$$\bar{x} = 0.9141 + 0.2588(J/N) \tag{50}$$

which shows a relatively weak dependence on N. For example, in the case of *catacondensed* systems (no ring is common to more than two other rings) one has

$$J = (N - 6)/2 \text{ (cata systems)} \tag{51}$$

and thus

$$\bar{m} = 1.59 - 1.91/N \tag{52}$$

$$\bar{m}^2 = 3.35 - 6.50/N \tag{53}$$

$$\bar{x} = 1.055 - 0.7763/N \tag{54}$$

The quick approach to limiting $\bar{m}$ and $\bar{x}$ values is shown in Figure 3. Moreover, the behavior is similar to that shown for the linear polyacenes. Since the latter are special types of cata systems, this provides evidence for the validity of our approximations.

Exact and Approximate Hückel and Wheland Numbers. Tables I–III compare the approximate Hückel and Wheland numbers with exact values. Since our polyene $\bar{m}$ are exact, Table I shows only the polyene $\bar{x}$. The row labels are the number of π electrons. Agreement between exact and approximate values is typically excellent. Table II lists the results for catacondensed molecules. The first seven rows describe linear polyacenes, and we see that their $\bar{m}$ are more accurate than those of the other cata systems. However, the $\bar{x}$ are little affected by the different averaging schemes em-

Table I. Average Wheland Numbers in Polyenes

	Linear		Cyclic	
N	Exact[a]	Approx	Exact[a]	Approx
2	0.8021	0.80		
3	0.6989	0.70	0.4502	0.54
4	0.8463	0.85	0.6695	0.67
5	0.8062	0.81	0.8574	0.85
6	0.8673	0.86	0.9811	0.98
7	0.8460	0.85	0.8560	0.77
8	0.8794	0.88	0.8589	0.87
9	0.8663	0.87	0.8983	0.90
10	0.8873	0.88	0.9448	0.94
11	0.8784	0.88	0.8987	0.90
12	0.8928	0.89	0.8950	0.90
13	0.8863	0.89	0.9107	0.91
14	0.8969	0.89	0.9347	0.93
15	0.8920	0.89	0.9109	0.91
16	0.9000	0.90	0.9077	0.91
17	0.8962	0.90	0.9159	0.91
18			0.9305	0.93

[a] Calculated in this laboratory with $S = 0.2468$.

Table II. Average Hückel and Wheland Numbers in Catacondensed Hydrocarbons

	$\bar{m}$		$\bar{x}$	
Molecule	Exact[a]	Approx	Exact[b]	Approx
Naphthalene	1.3683	1.3308	0.9898	0.95
Anthracene	1.3795	1.3429	0.9898	0.95
Naphthacene	1.3850	1.3851	0.9891	0.99
Pentacene	1.3884	1.3956	0.9884	0.99
Hexacene	1.3905	1.4025	0.9879	0.99
Heptacene	1.3923	1.4051	0.9875	1.00
Octacene	1.3935	1.4109	0.9872	1.00
Phenanthrene	1.3892	1.45	0.9989	0.98
Chrysene	1.3994	1.48	1.0029	1.01
3,4-Benzophenanthrene	1.3993	1.48	1.0027	1.01
Benzanthracene	1.3945	1.48	0.9982	1.01
Picene	1.4065	1.50	1.0057	1.01
Pentaphene	1.3983	1.50	0.9980	1.01
3,4:5,6-Dibenzophenanthrene	1.4062	1.50	1.0019[a]	1.01
1,2:5,6-Dibenzanthracene	1.4037	1.50	1.0030	1.01
1,2:7,8-Dibenzanthracene	1.4027	1.50	0.9884	1.01

[a] Taken from "Dictionary of Values of Molecular Constants (Wave Mechanical Methods)," C. A. Coulson and R. Daudel, Ed. [b] Calculated in this laboratory with $S = 0.2468$.

Table III. Average Hückel and Wheland Numbers in Pericondensed Hydrocarbons

	$\bar{m}$		$\bar{x}$	
Molecule	Exact[a]	Approx	Exact[d]	Approx
Triphenylene	1.4041	1.47	1.0072	1.01
1,2:3,4-Dibenzanthracene	1.4065	1.49	1.0057	1.01
Pyrene	1.4066	1.49	1.0044	1.01
Perylene	1.4123	1.49	1.0065	1.01
1,2-Benzpyrene	1.4111[b]	1.52	1.0055	1.02
4,5-Benzpyrene	1.4168[b]	1.52	1.0073[b]	1.02
Anthanthrene	1.4206[c]	1.54	1.0077	1.03
1,12-Benzoperylene	1.4284	1.54	1.0115	1.03
Coronene	1.4405	1.58	1.0174	1.04
Ovalene	1.4530[b]	1.63	1.0214[b]	1.07

[a] Table II, footnote *a*. [b] Taken from ref 5 of text. [c] Taken from "Supplemental Tables of Molecular Orbital Calculations," A. Streitweiser and J. Brauman, Ed., Pergamon Press, New York, N. Y., 1965. [d] Calculated in this laboratory with $S = 0.2468$.

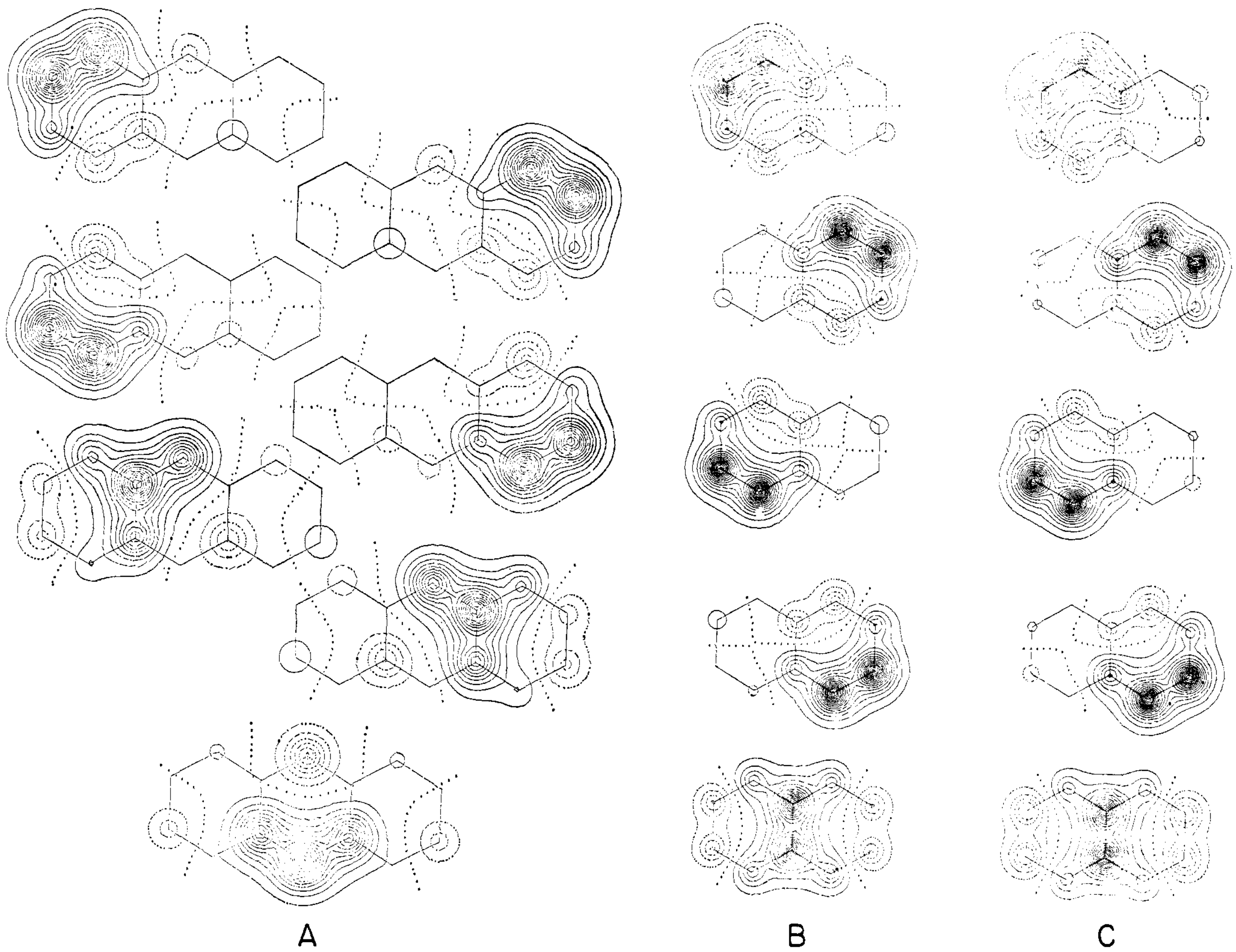

Figure 4. Localized molecular orbitals in anthracene and naphthalene. A and B show maximally localized orbtials. C shows homogeneously localized orbitals. Solid lines are positive contours, dashed lines are negative contours, and dotted lines show the nodes.

ployed. Finally, in Table III we show some results for pericondensed systems. The first group contains molecules in which one ring fuses with no more than four neighboring rings, and the second group lists some molecules with even greater ring sharing.

Note that almost all of the Hückel and Wheland numbers in these tables are greater than the ethylene values (see eq 7 and 8) and in each class are approximately independent of N. This explicitly illustrates the two basic properties of the delocalization energy and the validity of our demonstration. Note also that the approximations closely reproduce the observed trends in the delocalization energy per π electron. For example, the stabilization is largest for the peri systems, somewhat less for the cata, and, except for benzene, least of all for the polyenes.

3. Delocalization Energy Explained by Local Delocalization

Localized π Orbitals in Conjugated Hydrocarbons. Considerable freedom exists regarding the choice of the orthogonal molecular orbitals (MO's) in a molecule. This freedom can be exploited to choose the MO's in localized form (LMO's).[6] In recent applications[7,8] of this technique we have shown that localization of the canonical Hückel or Wheland MO's of an aromatic system provides a set of LMO's with interesting properties. As examples of our results, contour maps of the π LMO's of anthracene and naphthalene are shown in Figures 4A and 4B, respectively. Four different *types* of LMO's are seen to occur. In fact, these four localized bond types are essentially the *only ones* we found in a detailed examination of 18 benzenoid hydrocarbons.[7,8]

Figure 5 shows some examples of Wheland π LMO's for the other classes of molecules we have been considering. Pairs of equivalent LMO's occur in cyclobutadiene and butadiene. One member of each set is shown in Figures 5A and 5B, respectively. Figure 5C shows one member of a possible set of three equivalent Kekulé-type LMO's in benzene, while Figure 5D shows one member of a similar set of four equivalent cyclooctatetraene LMO's.

In sharp contrast with the canonical π MO's, the LMO's have two obvious characteristics: (1) they are all about the same size, and (2) with the exception of cyclobutadiene (Figure 5A), positive contours extend at least

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[6] C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963).

[7] W. England, L. S. Salmon, and K. Ruedenberg, *Fortschr. Chem. Forsch.*, **23**, 31 (1971).

[8] W. England and K. Ruedenberg, *Theor. Chim. Acta*, **22**, 196 (1971).

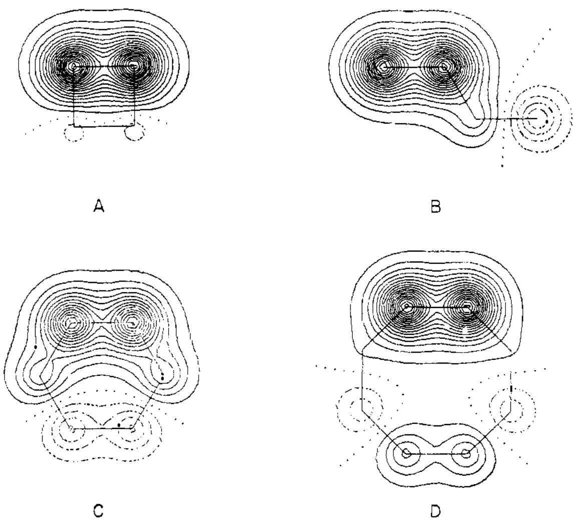

Figure 5. Localized molecular orbitals in butadiene, cyclobutadiene, benzene, and cyclooctatetraene. Solid lines are positive contours, dashed lines are negative contours, and dotted lines show the nodes.

over three atoms. (On Figures 4 and 5 the largest orbital lobes are drawn as the positive contours.) Now, it is well known that the energy of any individual π-electron orbital *decreases* (becomes more negative) when the *size* of its *largest* lobe *increases*, a fact which is mainly due to the decrease in the kinetic energy.[9] Accordingly we find the following behavior for the LMO orbital energies. (1) For a given *class* of conjugated hydrocarbons, most localized orbitals have nearly the same value of the orbital energy, and (2) these orbital energies almost always lie lower than ethylene's orbital energy. This leads to simple physical interpretations of the two basic properties of the delocalization energy.

Local Delocalization and the Physical Interpretation of the Delocalization Energy. The sum of the orbital energies is invariant against orthogonal orbital transformations, *i.e.*

$$\sum_i g_i\epsilon_i = \sum_i g_i\eta_i \tag{55}$$

where the ϵ_i are the canonical Hückel–Wheland orbital energies and the η_i are the localized orbital energies. Hence, the delocalization energy of eq 1 can be expressed as

$$\mathrm{DE} = \sum_i g_i\eta_i - Ne \tag{56}$$

Now, the positive contours of the *ethylene* π orbital are perfectly confined to two atoms. Hence, whenever the LMO positive contours extend over more than two atoms, the η_i will be *more negative* than e because of a greater contribution from the resonance integral (the contribution from the Coulomb integral is unchanged). *It is now apparent why the delocalization energy is almost always negative. Every one of the maximally localized π orbitals is still more delocalized than the ethylene π orbital.* In other words, resonance stabilization of conjugated systems is due to the "*local delocalization*" of the π LMO's onto more than two atoms. We can see from cyclobutadiene in Figure 5A that when the LMO's extend only over two atoms, the resonance energy is zero (Hückel case) or positive (Wheland case).

4. Homogeneous Localization and the Proportionality of the Delocalization Energy to the Number of π Electrons

We mentioned in the preceding section that the maximally localized orbitals in these molecules have nearly the same energy. In view of this, it is natural to define a new type of localized orbital in a conjugated system by the additional constraint that all localized π orbitals have the same orbital energy. Of course, these orbitals may not be as localized as the maximally localized ones, but it is expected that the two types will not differ too much from each other. We choose the name *homogeneous localization* for this method of constructing localized orbitals.

It is apparent that the orbital energy of each of the homogeneously localized molecular orbitals (HLMO's) in a molecule will be the average

$$\bar{\eta} = N^{-1}\sum_i g_i\epsilon_i \tag{57}$$

By virtue of eq 5, 12, and 13, this becomes

$$\bar{\eta} = \text{Coulomb integral} + \bar{y} \times \text{resonance integral} \tag{58}$$

where $\bar{y}$ is the average Hückel or Wheland number for the molecule in question. We have already seen that as the number of π electrons increases, the $\bar{y}$ rapidly become constant in many classes of conjugated hydrocarbons. Hence, if we rewrite the delocalization energy as

$$\begin{aligned}\mathrm{DE} &= (\bar{\eta} - e)N \\ &= (\bar{y} - y)N \times \text{resonance integral}\end{aligned} \tag{59}$$

where y is the Hückel or Wheland number of ethylene, we see that

$$(\mathrm{de})_0 = \bar{y} - y \tag{60}$$

is a "standard local delocalization energy" (in units of the resonance integral) *and is approximately molecule independent for many classes of conjugated hydrocarbons.* Since eq 59 becomes

$$\mathrm{DE} = (\mathrm{de})_0 \times N \times \text{resonance integral} \tag{61}$$

this makes it intuitively clear why the delocalization energy is proportional to the number of π electrons. The negative value of $(\mathrm{de})_0$ expresses the local delocalization of the HLMO's as compared with the two-center ethylene MO.

Examples of Homogeneous Localized Orbitals. The contour diagrams of the five naphthalene HLMO's are

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(9) The statement of this undisputable fact is often countered with the question: but what about the virial theorem, which states that the kinetic energy *increases* when the total energy decreases? There are two reasons why the virial theorem is not satisfied for the orbitals discussed here. First, in exact calculations the virial theorem holds only for the total energy, but not for individual orbitals, and not even approximately for valence orbitals. Secondly, in minimal basis set calculations with fixed orbital exponents the virial theorem is not even satisfied for the total energy. For example, in the classical Heitler–London calculation, H_2 has a lower energy than 2H, because the kinetic energy has dropped whereas the potential energy is raised. The calculations discussed here are quite analogous in character. Nonetheless, this type of calculation can and does give useful results. For more details on this question (which was raised by a referee), see M. J. Feinberg and K. Ruedenberg, *J. Chem. Phys.*, 54, 1495 (1971).

shown in Figure 4C. They differ only slightly from the optimal LMO's in Figure 4B. Since the latter are defined as maximizing the localization sum[6]

$$L(\phi) = \sum_i \int V_1 \int \mathrm{d}V_2 \phi_i{}^2(1)\phi_i{}^2(2)/r_{12} \qquad (62)$$

it is of interest to compare the numerical values of this criterion for the optimal LMO's, the homogeneous LMO's, and the canonical MO's. Using the naphthalene Wheland orbitals we find (in atomic units)

$$L(\text{canonical}) = 3.5623$$

$$L(\text{homogeneous}) = 5.3759$$

$$L(\text{optimal}) = 5.4634$$

showing that the HLMO's are very close to the LMO's by this criterion. Furthermore, as will always be the case when all LMO's are equivalent orbitals, each LMO shown in Figure 5 is simultaneously a HLMO. In view of these results, it can be safely predicted that it is possible to form conjugated hydrocarbon HLMO's that will be very similar to the optimal LMO's. One would also expect this to be true in simple crystals.

It should be appreciated that there are many sets of MO's with the property that all occupied MO's in the set have the same orbital energy. This is so because the equality of the orbital energies introduces fewer conditions than are necessary to specify an orthogonal transformation among all occupied MO's. The HLMO's should therefore be defined as those occupied MO's for which the localization criterion of eq 62 is maximized under the side condition that all orbital energies are equal. Their determination is thus more intricate than that of the usual LMO's.

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