# Hartree–Fock MO Theoretical Approach to Aromaticity. Interpretation of Hückel Resonance Energy in Terms of Kinetic Energy of π Electrons

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**Abstract:** In an attempt to obtain the physical picture of aromaticity/antiaromaticity, the total energies of cyclic and acyclic polyenes, obtained by the STO-3G method, were partitioned into one-electron potential, two-electron potential, kinetic, and nuclear repulsion energies. These energies are further partitioned into $\pi$- and $\sigma$-electron energies. It was found that the energy additivity holds in both $\sigma$ and $\pi$ kinetic energies in linear polyenes and that the total energy and the resonance energy by HMO can be correctly expressed in terms of the kinetic energy of $\pi$ electrons. Interpretations were given to those findings.

Ever since Kekule's intuitive idea in 1865,[1] aromaticity (and antiaromaticity) has been the most fascinating of problems not only conceptionally but also practically in organic chemistry.[2] Although aromaticity/antiaromaticity is not directly observable, experiments so far have only suggested existence of such characteristics in cyclic conjugated systems. The concept of aromaticity had originally developed as a means of characterizing a certain type of thermally stable organic molecule that was inclined to substitution rather than addition reaction as benzene is. In contrast to aromatic compounds, a cyclic conjugated compound is considered antiaromatic if it is chemically and thermally unstable; all synthetic approaches to the bare cyclobutadiene had been unsuccessfully carried out[3] until Watts et al. trapped it in a frozen matrix in 1965,[4] and Breslow et al.,[5] using the derivatives of cyclobutadiene, have reported experimental evidence in support of the antiaromaticity of cyclobutadiene.

In the theory of aromaticity, the Hückel aromaticity rule, the $(4n + 2)/4n$ rule,[6] has played the leading role. Although it is not perfect, the chemists' thinking about the problem of aromaticity has been apparently influenced by this magic rule. In an attempt to improve the Hückel rule, a large number of theoretical approaches have been carried out, resulting in various practical definitions of aromaticity.[7]

The modern definition of aromaticity may follow Dewar[8] in redefining the nonaromatic reference structure which may be taken from the conjugated single and double bonds in a finite or infinite linear polyene, and the difference between this reference energy ($E_{lin}$; in terms of the negative quantity) and the actual energy ($E_{cycl}$) of the cyclic conjugated system is defined as the resonance energy (RE ($=E_{cycl} - E_{lin}$)). It represents the positive (aromatic) and negative (antiaromatic) stability of the particular cyclic system relative to the reference structure.

Both MO theoretical and graph theoretical approaches so far show that such RE critically depends on the topology of the conjugated system. According to the modern theory,[9] almost quantitative treatment of RE is possible. However, we consider that the fundamental problem of aromaticity is why and what kinds of the $\pi$-electron energy produce aromaticity/antiaromaticity rather than the quantative prediction of RE. Conventional theories have inherent difficulties: the pertaining MO theories, Hückel and PPP MO methods, treat only $\pi$ electrons whose energies are largely dependent on the potentials from other electrons. Besides, due to simplified methods, the energy analysis is impossible.

Recently, ab initio calculations on RE have been performed.[10,11] Although ab initio MO theories take all electrons into account, previous calculations handled only total energies and estimated the $\pi$ RE in an indirect way.[11] And the results do no more than confirm and refine the Hückel results. Therefore, it is most necessary to develop the method that helps one understand the nature of $\pi$-electron systems without complications arising from the rigid stereochemistry of the $\sigma$ bonds.

In a previous report,[12] we have proposed an application of the energy partitioning technique[13] to the fundamental understanding of aromaticity where polygonal $H_n$ systems are used to show that the Hückel aromaticity rule can be reproduced in such systems. Although conceptionally workable, the difficulty of this model is that it cannot account for the actual compounds because of only the 1s orbital of hydrogen atoms being treated. In the present paper, we propose the energy partitioning method that handles $\pi$ and $\sigma$ electrons separately and new interpretations to the Hückel resonance energy and aromaticity/antiaromaticity which are obtained as the results of application of the method.

## Theory

We adopted the LCAO SCF MO theory based on the Hartree–Fock equation[14] since this theory is the only one that can be applied, with comprehensive accuracy, to the sizable systems of those treated here. The Hamiltonian of the molecular system is composed of operators referring to kinetic energy, potential energy between the electron and nucleus, and repulsion energy between electrons. The expectation value for each operator is considered to stand for the corresponding measured value. Thus, the electronic energy ($E^{el}$) in the molecule is composed of the kinetic ($E^K$) and potential energies. The latter is further partitioned into the attractive one-electron potential ($E^V$) (i.e., interactions between electrons and nuclei) and repulsive two-electron ($E^J$) energies. Since the wave function ($\Psi$) is expressed by the Fock matrix with the elements of molecular orbitals (MO's: $\Psi_i$), and since $\pi$ MO's, in most cases, do not mix with $\sigma$ MO's, $E^{el}$ and its partitioned energies can also be expressed as the sum of $\pi$-electron ($E_\pi$) and $\sigma$-electron ($E_\sigma$) energies. The plot in this study is to find out the role of these partitioned $\pi$-electron energies

(1) Kekule, A. *Bull. Soc. Chim. Fr.* **1865**, *3*, 98.

(2) (a) "Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity"; Bergmann, E. D., Pullmann, B., Eds.; Academic Press: New York, 1971. (b) *Spec. Publ.—Chem. Soc.* **1967**, *No. 21.* (c) Garratt, P. J. "Aromaticity"; McGraw-Hill: New York, 1971.

(3) Cava, M. P.; Mitchell, M. J. "Cyclobutadiene and Related Compounds"; Academic Press: New York, 1967.

(4) Watts, L.; Fitzpatrick, J. D.; Pettit, D. *J. Am. Chem. Soc.* **1965**, *87*, 3253.

(5) (a) Breslow, R.; Washburn, W. J. *J. Am. Chem. Soc.* **1970**, *92*, 427. (b) Breslow, R. Grubbs, R.; Muragashi, S.-I. *J. Am. Chem. Soc.* **1970**, *92*, 4137. (c) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393.

(6) (a) Armit, J. W.; Robinson, R. *J. Chem. Soc.* **1925**, 1604. (b) Robinson, R. *Spec. Publ.—Chem. Soc.* **1967**, *No. 21*, 47.

(7) (a) Dewar, M. J. S.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1952**, *A214*, 482. (b) Wheland, C. W. "Resonance Theory in Organic Chemistry"; Wiley: New York, 1955. (c) Wilcox, C. F., Jr. *Tetrahedron Lett.* **1968**, 795. (d) Herndon, W. C. *Tetrahedron* **1972**, *28*, 3675; **1973**, *29*, 3. (e) Graovac, I.; Gutman, I.; Trinajstic, N.; Zivkovic, T. *Theor. Chim. Acta* **1972**, *26*, 67. (f) Kaneko, C. *Tetrahedron* **1972**, *28*, 4915.

(8) Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789.

(9) (a) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305; **1972**, *94*, 3068. (b) Aihara, J.-I. *J. Am. Chem. Soc.* **1976**, *98*, 2750. (c) Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722.

(10) Haddon, R. C.; Starnes, J. J. *Adv. Chem. Ser.* **1978**, *No. 169*, 333.

(11) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7500.

(12) Ichikawa, H. *J. Am. Chem. Soc.* **1983**, *105*, 7467.

(13) Kollmar, H. *Theort. Chim. Acta* **1978**, *50*, 235.

(14) (a) Hall, G. G. *Proc. R. Soc. London, Ser. A* **1951**, *A205*, 541. (b) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.

**Table I.** Total Energies and Virial Ratios in Acyclic Polyenes[a]

$$CH_2=CH(CH=CH)_nCH=CH_2$$
$$\mathbf{1}$$

| n | E | ΔE | $-V/T$[b] |
|---|---|---|---|
| 0 | -153.020 366 |  | 2.006 747 |
| 1 | -228.967 961 | -75.947 595 | 2.007 076 |
| 2 | -304.915 814 | -75.947 853 | 2.007 246 |
| 3 | -380.863 730 | -75.947 916 | 2.007 353 |
| 4 | -456.811 651 | -75.947 921 | 2.007 417 |

[a] STO-3G in terms of atomic units).  [b] Virial ratio.

to the resonance energy of the system.

Since in LCAO MO theory each MO is expanded by a linear combination of atomic orbitals (AO's), the total energy ($E$) based on either the restricted[14] or unrestricted Hartree–Fock equation[15] is expressed by the sum of monocentric ($E_A$) and bicentric ($E_{AB}$) terms,

$$E = \sum_A E_A + \sum_{A>B} E_{AB} \tag{1}$$

These terms were further partitioned as

$$E_A = E_A{}^V + E_A{}^J + E_A{}^T \tag{2}$$

$$E_{AB} = E_{AB}{}^V + E_{AB}{}^J + E_{AB}{}^T + E_{AB}{}^N \tag{3}$$

where $E_{AB}{}^N$ is the nuclear repulsion energy between atoms A and B. The detailed method of calculation is shown in the Appendix section. By using this technique, one can study the energy balances in the molecular system. In the present study, we have used the GAUSSIAN 80[16] program to which new subroutines for the energy analyses were added.

As an MO method, we have adopted the STO-3G method.[17] All bond lengths and angles were optimized within the given symmetry.

## Results and Discussion

**Energy Additivity of Linear Polyenes.** The energy additivity of linear polyenes is the fundamental requirement in the definition of aromaticity.[8,9]

It has already been shown[10,11] that such an additivity holds in the all-electron ab initio calculations, supporting the original PPP[8] and HMO results.[9] We first investigated whether or not this linearity extends to the partitioned energies. Table I shows the total energies and the differences of the neighboring total energy ($\Delta E$) vs. $n$ in the linear polyene $CH_2=CH(CH=CH)_nCH=CH_2$ at the optimized geometry. The optimized geometries are shown in Table II.

Hess and Schaad showed[11] that in the 3-21G method,[18] the largest deviation of total energy from additivity is 0.17 kcal/mol. The present calculation shows the largest deviation being 0.08 kcal/mol, considerable improvement from the previous 3-21G results,[11] and the STO-3G calculation with deviation of 2.5 kcal/mol,[10] where only carbon–carbon bonds are optimized. The errors of additivity has been discussed in relation to the used basis function;[11] however, the present results suggest that such a deviation in the ab initio MO theories is not caused by the basis set but perhaps the condition of geometry optimization.

Table III shows the partitioned energies and their first- ($\Delta E$) and second-order differences ($\Delta^2 E$) between neighboring $n$'s, where $E^{HF}$ stands for the Hartree–Fock (HF) electronic energy. Firstly, both $\pi$ and total ($\pi + \sigma$) $\Delta^2 E$'s of electrostatic energies are not constant: the $E^V$, $E^J$, and $E^N$ terms nonlinearly increase their absolute values as $n$ increases, showing that $E^V$, $E^J$, and $E^N$ do not hold such a linear additivity as the total energy does. However, the sum of $\Delta^2 E^J$ and $\Delta^2 E^N$ cancels $\Delta^2 E^V$ to be almost zero. Since $\Delta^2 E$ of total energy is nearly zero, this indicates $\Delta^2 E^T$ being close to zero. Secondly, the $E^{HF}$ energies in both $\pi$ and $\sigma$ portions do not have any kind of linearity with $n$. This will be discussed in the next section.

As expected, the linearity is seen to be good for the kinetic energy ($E^T$). As far as total kinetic energy is concerned, such a linearity is a natural outcome since the total energy increases

(15) Pople, J. A.; Nesbet, R. K. J. Chem. Phys. **1954**, 22, 571.
(16) QCPE **1982**, No. 437.
(17) Collins, J. B.; Schleyer. P. v. R.; Binkley, J. S.; Pople, J. A. J. Chem. Phys. **1976**, 64, 5142.
(18) Binkley, J. S.; Pople, J. A.; Hehre, W. J. J. Am. Chem. Soc. **1980**, 102, 939.

**Table II.** Optimized Geometries of $C_{2h}$ Polyenes[a]



| | 1[c] | 2 | 3 | 4 |
|---|---|---|---|---|
| | | $n$[b] | | |
| | Bond Length, Å | | | |
| 1 | 1.0811 | 1.0811 | 1.0812 | 1.0812 |
| 2 | 1.0816 | 1.0816 | 1.0816 | 1.0815 |
| 3 | 1.3143 | 1.3145 | 1.3146 | 1.3146 |
| 4 | 1.0844 | 1.0844 | 1.0844 | 1.0844 |
| 5 | 1.4848 | 1.4840 | 1.4839 | 1.4838 |
| 6 | 1.0841 | 1.0841 | 1.0841 | 1.0841 |
| 7 | 1.3220 | 1.3233 | 1.3237 | 1.3237 |
| 8 | | 1.0842 | 1.0842 | 1.0841 |
| 9 | | 1.4799 | 1.4792 | 1.4787 |
| 10 | | | 1.0841 | 1.0841 |
| 11 | | | 1.3247 | 1.3251 |
| 12 | | | 1.0841 | 1.0842 |
| 13 | | | | 1.4778 |
| | Bond Angle, deg | | | |
| a | 122.0 | 122.0 | 121.9 | 122.0 |
| b | 116.0 | 116.0 | 116.0 | 116.0 |
| c | 120.1 | 120.1 | 120.1 | 120.1 |
| d | 124.1 | 124.1 | 124.2 | 124.1 |
| e | 116.0 | 116.1 | 116.1 | 116.0 |
| f | 124.0 | 123.9 | 124.0 | 124.0 |
| g | | 120.1 | 119.9 | 119.8 |
| h | | 124.0 | 124.1 | 124.1 |
| i | | | 116.2 | 116.1 |
| j | | | 124.0 | 124.0 |
| k | | | | 119.9 |
| l | | | | 124.0 |

[a] STO-3G.  [b] Corresponds to $n$ in Table I. The geometry for $n = 0$ was taken from the published data (Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive"; Carnegie-Mellon University Press: Pittsburgh, PA, 1981).  [c] Previous results are 1.319, 1.488, and 1.327 Å for 3, 5, and 7 (Haddon, R. C.; Starnes, W. H., Jr. Adv. Chem. Ser. **1978**, No. 169, 33).

linearly and since the virial theorem[19] generally holds independently of the basis functions of the MO method if the geometry is optimized with respect to the geometrical parameters. Satisfication to the virial requirement may be ascertained from the calculated virial ratios in Table I.

Finally, the convenient least-squares-fitted formulas to obtain STO-3G total energy and $\pi$ and total kinetic energies in structure **1** are given as follows.

total energy   $E = -75.94\,783n - 153.020\,24$ au   (4)

$\pi$ kinetic energy   $E_\pi{}^T = 2.51\,224n + 5.042\,57$ au   (5)

total kinetic energy   $E^T = 75.36\,315n + 151.995\,35$ au   (6)

**What Do Energies by HMO Represent?** Total HMO energies, calculated in the usual way, have been found to be linear functions of $n$;[9] i.e., the total energy of acyclic polyenes is simply a sum of these bond energy terms. It may be a common understanding that the energies by the $\pi$-electron MO theory must be concerned only with those of $\pi$ electrons in the potential fields of nuclei and inner and valence electrons. If this is true, those energies must correspond to $\pi$ portions of $E^{HF}$. The previous as well as the present all-electron ab initio calculations confirmed that the total

(19) (a) Eyring, H.; Walter, J.; Kimball, G. E. "Quantum Chemistry"; Wiley: New York, 1944; Chapter 18. (b) Löwdin, P. O. Mol. Spectrosc. **1959**, 3, 46.

*Hartree-Fock MO Approach to Aromaticity*

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**Table III.** Relationships between Partitioned Energies and $n$ in $\mathbf{1}^a$

|   | $E$ | $\Delta E$ | $\Delta^2 E$ |
|---|---|---|---|
| | $E^V$ | | |
| **0** | | | |
| $\pi$ | -45.475 82 | | |
| $\sigma + \pi$ | -564.508 83 | | |
| **1** | | | |
| $\pi$ | -79.673 00 | -34.197 18 | |
| $\sigma + \pi$ | -921.814 72 | -357.305 89 | |
| **2** | | | |
| $\pi$ | -117.787 44 | -38.114 44 | -3.917 26 |
| $\sigma + \pi$ | -1305.953 53 | -384.138 81 | -26.832 92 |
| **3** | | | |
| $\pi$ | -158.843 82 | -41.056 38 | -2.941 94 |
| $\sigma + \pi$ | -1710.337 40 | -404.383 87 | -20.245 06 |
| **4** | | | |
| $\pi$ | -202.285 88 | -43.442 06 | -2.385 68 |
| $\sigma + \pi$ | -2131.205 04 | -420.867 64 | -16.483 77 |
| | $E^J$ | | |
| **0** | | | |
| $\pi$ | 19.541 62 | | |
| $\sigma + \pi$ | 155.393 03 | | |
| **1** | | | |
| $\pi$ | 35.043 70 | 15.502 08 | |
| $\sigma + \pi$ | 271.208 95 | 115.815 92 | |
| **2** | | | |
| $\pi$ | 52.505 10 | 17.461 40 | 1.959 32 |
| $\sigma + \pi$ | 400.441 10 | 129.232 15 | 13.416 23 |
| **3** | | | |
| $\pi$ | 71.437 64 | 18.932 54 | 1.417 14 |
| $\sigma + \pi$ | 539.796 67 | 139.355 57 | 10.123 42 |
| **4** | | | |
| $\pi$ | 91.563 08 | 20.125 44 | 1.192 90 |
| $\sigma + \pi$ | 687.392 03 | 147.595 36 | 8.239 79 |
| | $E^T$ | | |
| **0** | | | |
| $\pi$ | 5.042 02 | | |
| $\sigma + \pi$ | 151.994 84 | | |
| **1** | | | |
| $\pi$ | 7.555 28 | 2.513 26 | |
| $\sigma + \pi$ | 227.359 15 | 75.364 31 | |
| **2** | | | |
| $\pi$ | 10.067 40 | 2.512 12 | -0.001 14 |
| $\sigma + \pi$ | 302.722 22 | 75.363 07 | -0.001 24 |
| **3** | | | |
| $\pi$ | 12.579 40 | 2.512 00 | -0.000 12 |
| $\sigma + \pi$ | 378.083 80 | 75.361 58 | -0.001 49 |
| **4** | | | |
| $\pi$ | 15.091 16 | 2.511 76 | -0.000 24 |
| $\sigma + \pi$ | 453.448 28 | 75.364 48 | 0.002 90 |
| | $E^{HF}$ | | |
| **0** | | | |
| $\pi$ | -20.892 18 | | |
| $\sigma + \pi$ | -257.120 96 | | |
| **1** | | | |
| $\pi$ | -37.074 08 | -16.181 90 | |
| $\sigma + \pi$ | -423.246 61 | -116.125 65 | |
| **2** | | | |
| $\pi$ | -54.614 92 | -17.540 84 | -1.358 94 |
| $\sigma + \pi$ | -602.790 21 | -179.543 60 | -13.417 95 |
| **3** | | | |
| $\pi$ | -74.826 78 | -20.211 86 | -2.671 02 |
| $\sigma + \pi$ | -792.456 94 | -189.666 73 | -10.123 13 |
| **4** | | | |
| $\pi$ | -95.631 74 | -20.804 96 | -0.593 10 |
| $\sigma + \pi$ | -990.364 72 | -197.907 78 | -8.241 05 |
| | $E^N$ | | |
| **0** | 104.100 59 | | |
| **1** | 194.278 65 | 90.178 06 | |
| **2** | 297.874 40 | 103.595 75 | 13.417 69 |
| **3** | 411.593 21 | 113.718 81 | 10.123 06 |
| **4** | 533.553 07 | 121.959 86 | 8.241 05 |

$^a$ STO-3G (in terms of atomic units).

energy is additive, but neither the $\pi$ portion nor total HF electronic energy is. This means that $\pi$-electron energies of the HMO (and
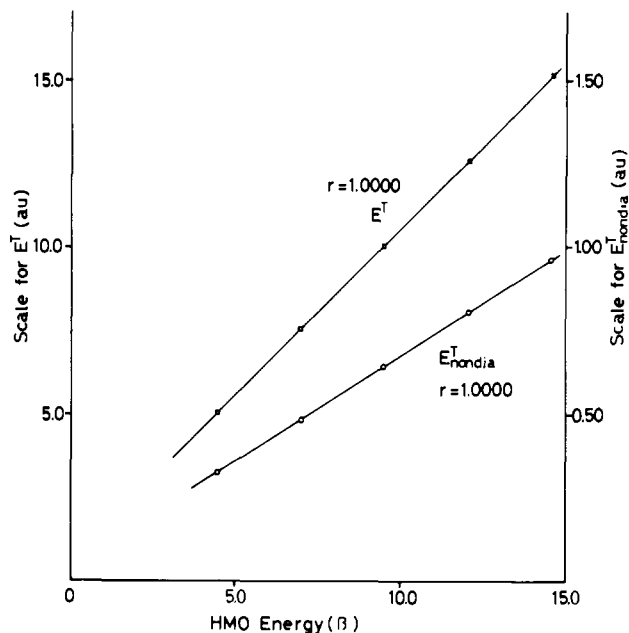


**Figure 1.** Plot of $\pi$ kinetic energies vs. HMO energies. The HMO energies are taken from ref 9a.

**Table IV.** Partitioned Bicentric $\pi$ Interactions in 1,3-Butadiene$^a$

| | $C_1$–$C_2$–$C_3$–$C_4$ | | | |
|---|---|---|---|---|
| | 1–2 | 1–3 | 1–4 | 2–3 |
| $E_\pi^V$ | -4.087 52 | 0.030 16 | 0.004 32 | 0.491 14 |
| $E_\pi^J$ | 1.713 96 | -0.012 74 | -0.006 30 | 0.218 16 |
| $E_\pi^T$ | 0.155 48 | 0.000 54 | 0.000 34 | 0.013 08 |

$^a$ STO-3G (in terms of atomic units).

also PPP) theory do not represent those in ab initio MO theories or actual $\pi$-MO energies. A problem arises; what do the energies by HMO theory represent? And the answer to this equation may give a clue to solve the problem of what causes aromatic stability and antiaromatic unstability.

The most significant result that we found in our energy analysis is that the linearity of the kinetic energy holds in both $\pi$ and $\sigma$ portions. This simply indicates that the energy by the $\pi$-electron MO theory corresponds to the negative value of the kinetic energy of $\pi$ electrons ($\pi$ KE) in ab initio theories. Figure 1 shows the correlation between the Hückel $\pi$ energies in $\beta$ and $\pi$ KE, where $E^T$ and $E_{nondia}^T$ stand for the $\pi$ KE and its nondiagonal part (i.e., sum of bicentric interactions). The correlation is perfect. Interestingly, the nondiagonal part also has a perfect correlation with Hückel energy.

This coincidence between kinetic energy and HMO energy may be understandable if one learns the following facts. In Table IV are shown partitioned $E_{AB}$ values for the $\pi$ electron ($E_{\pi AB}$) in butadiene. One- and two-electron potential energies, in absolute value, between $C_1$ and $C_2$ are 10-30 times larger than that of the kinetic energy. Moreover, such electrostatic interactions between nonbonding $C_1$ and $C_3$ still have enormous values (20-30 kcal/mol) while the kinetic energy for the interaction is only 0.34 kcal/mol, negligible if compared with the electrostatic terms. It can be generally said that the electrostatic interactions are large and long range while that of the kinetic energy is rather small and very local. We all know that HMO takes only neighboring atoms into account. The parameters $\alpha$ and $\beta$ in HMO have essentially no specified physical meanings, and, therefore, it is not unreasonable to regard $\alpha$ and $\beta$ as the kinetic energy on an atom and that between neighboring atoms.

The problem in the interpretation of the HMO–kinetic energy relationship may be the fact that kinetic energy is positive and seems to be against chemical bonding. This may be explained as follows. As already mentioned, the virial theorem holds in the molecule. Namely, the potential energy ($=E^V + E^J + E_{AB}^N$) is, theoretically, exactly double of the amount of kinetic energy ($E^T$)

with an opposite sign. Therefore, the kinetic energy with an opposite sign corresponds to the total energy ($E = -E^T$). Thus, the kinetic energy can be a measure of the total energy. The only difference between $E$ and $E^T$ is that the $\pi$ portion of $E$ does not reflect the total energy, but, somehow, that of $E^T$ does.

**Relationship between Hückel Resonance Energy and Kinetic Energy of the $\pi$ Electron.** As we have seen, the Hückel energy was found to represent $\pi$ KE. And if it is always so, it may lead one to new and fundamental interpretations to the conclusions which HMO has so far led to. The next question may be whether or not Hückel resonance energy (HRE) can be expressed in terms of $\pi$ KE. We have studied on $D_{4h}$ cyclobutadiene, benzene, $D_{8h}$ cyclooctatetraene, naphthalene, and azulene systems. Planar [10]annulene was not included since the optimized geometry is apparently out of plane.

There are some complicated problems in the solutions by ab initio theories for $D_{4h}$ cyclobutadiene and $D_{8h}$ cyclooctatetraene, i.e., those of charge-, bond-, and spin-density alternations[20] in addition to that of the triplet state. Since HMO is not energetically concerned with them, each solution is considered to be eligible for the present study. However, it is worth informing that as for $D_{4h}$ cyclobutadiene, the triplet state and single spin density wave (SDW) solutions are more stable than the singlet charge density wave (BDW) or charge density wave (CDW) solutions (the total energies are $-151.754074$, $-151.679992$, and $-151.675653$ au for the triplet, SDW, and BDW solutions, respectively). The $\pi$ kinetic energies were found to be similar ($5.34660$, $5.34604$, and $5.34624$ au for triplet, SDW, and BDW solutions). Since we have not obtained the BDW solution for $D_{8h}$ cyclooctatetraene, we took the CDW solution in this study.[21,22]

Using $\pi$ KE for the CH=CH unit, we defined the kinetic resonance energy of the $\pi$ electron (KRE) as

$$\text{KRE} = E_\pi^T \left[ \boxed{\phantom{xx}} _n \right] - 2.51224(n+1)\ \text{au} \quad (7)$$

The number of $\pi$ C–C in naphthalene or azulene is larger by one than [10]annulene. However, since we do not establish yet the $\pi$ KE contribution of the C—C unit and since the contribution is considered to be less than 25% of the C=C unit,[23] we neglected the remaining C—C contribution and simply defined the KRE for naphthalene or azulene as

$$\text{KRE} = E_\pi^T[\text{naphthalene or azulene}] - 2.51224 \times 5\ \text{au} \quad (8)$$

The relationship between KRE's and Hückel resonance energies (HRE's) is shown in Figure 2. Again we find a good correlation between HRE and KRE. This correlation gives grounds that aromaticity/antiaromaticity can be interpreted in terms of $\pi$ KE.

**Constancy of $\pi$ Kinetic Energy per Electron in Acyclic Polyenes.** So far we obtained a confidence that energetic problems of aromaticity/antiaromaticity can be based on the quantity with an apparent physical meaning, the kinetic energy of $\pi$ electron. Our interest was, then, focused on why such a kinetic energy is affected by the molecular system.

In order to compare the RE's between different systems, the resonance energy per $\pi$ electron (REPE) has been adopted.[9,24] In our previous report,[12] the kinetic energy per electron (or atom) (KEPE) was used to compare the kinetic energy in the different cyclic $H_n$ systems. Following the previous idea, we used the same technique for comparing the $\pi$ KE. Table V shows $n$ vs. KEPE for diagonal ($\sum_A E_{\pi A}^T$) and nondiagonal terms ($\sum_{A>B} E_{\pi AB}$) (eq 1) for $\pi$ electrons in the acyclic system **1**. As $n$ increases, the

**Table V.** Constancy of $\pi$ Kinetic Energy per $\pi$ Electron in Acyclic Polyenes[a]

| $n$ | $\sum E_{\pi A}^T$ | KEPE | $\sum_{a>b} E_{\pi AB}^T$ | KEPE |
|---|---|---|---|---|
| 0 | 5.042 02 | 1.260 51 | 0.325 46 | 0.081 37 |
| 1 | 7.555 28 | 1.259 21 | 0.485 68 | 0.080 95 |
| 2 | 10.067 40 | 1.258 43 | 0.645 46 | 0.080 68 |
| 3 | 12.579 40 | 1.257 94 | 0.805 22 | 0.080 52 |
| 4 | 15.091 16 | 1.257 60 | 0.964 92 | 0.080 41 |

[a]STO-3G (in terms of atomic units).

**Table VI.** Change of KEPE's in Cyclic Polyenes[a]

| | $\sum E_{\pi A}^T$ | KEPE | $\sum_{A>B} E_{\pi AB}^T$ | KEPE |
|---|---|---|---|---|
| cyclobutadiene[b] | 5.166 92 | 1.291 73 | 0.179 32 | 0.044 83 |
| benzene | 6.974 88 | 1.162 48 | 0.477 72 | 0.079 62 |
| cyclooctatetraene[c] | 9.632 20 | 1.204 03 | 0.530 88 | 0.066 36 |
| naphthalene[d] | 11.627 10 | 1.162 71 | 0.799 76 | 0.079 98 |
| azulene[d] | 11.757 61 | 1.175 61 | 0.785 18 | 0.078 52 |

[a]STO-3G (in terms of atomic units). [b]Optimized bond lengths at $D_{4h}$ symmetry: C–C, 1.4281 Å; C–H, 1.0796 Å. [c]Optimized bond lengths at $D_{8h}$ symmetry: C–C, 1.3978 Å; C–H, 1.0844 Å. [d]The optimized geometries were taken from the literature. Naphthalene: Haddon, R. C.; Raghavachari, K. *J. Chem. Phys.* **1983**, *79*, 1093. azulene: Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1982**, *104*, 3516.

KEPE's for both diagonal and nondiagonal parts gradually decrease. However, the changes are so small (0.23% (diagonal) and 1.18% (nondiagonal)), for $n$ going from 0 to 4) that they can be regarded as constants. Namely, the diagonal and nondiagonal parts of KEPE have definite values (1.258 74 (diagonal) and 0.080 79 au (nondiagonal)) in acyclic polyenes.

**Interpretation of Aromaticity in Terms of Kinetic Energy of the $\pi$ Electron.** Table VI shows the changes of KEPE's in cyclic polyenes. The KEPE changes from system to system. It is generally observed that aromatic systems have smaller values of KEPE for the diagonal term than the antiaromatic system while the KEPE values for the nondiagonal term in aromatic systems are larger than those in antiaromatic systems. If these KEPE's are compared with those in acyclic systems, it would be noticed that the KEPE values well represent the aromaticity/antiaromaticity.

A Mulliken population analysis is used to reveal the degree of localization in the STO-3G $\pi$-type localized MO's to provide a measure of aromatic character.[25] The similar analysis using nonlocalized $\pi$ MO's is shown in Table VII where cyclobutadiene, benzene, and cyclooctatetraene are recorded. The results are similar to the previous ones[25] in that in benzene, the $\pi$ electrons are abundantly and uniformly delocalized between atoms so that the $\pi$-atomic population becomes small, while in antiaromatic systems the electrons are inclined to localize on the atom and the distributions between bonding atoms are nonuniform (in cyclobutadiene) or small (in cyclooctatetraene). This can be related to the KEPE's in Table VI. The KEPE's of the diagonal term in benzene have a smaller value because the population on the atom is smaller than that in antiaromatic systems. Similarly, the large nondiagonal KEPE for benzene and naphthalene stems from the large bond populations. The results obtained here are very similar to those obtained for cyclic $H_n$ systems and lead to the same conclusion that aromatic stability is caused by releasing *the kinetic (energy) pressure* on the atom by allowing delocalization between atoms.

In summary, energy analyses of the Hartree–Fock total energies on acyclic and cyclic polyenes leaded to the following facts: (1) the energy additivity in linear polyenes holds in both $\pi$ and $\sigma$ portions of the kinetic energy, (2) the energy by HMO represents the kinetic energy of the $\pi$ electron, and (3) the Hückel resonance energy can be expressed by the kinetic resonance energy of the $\pi$ electron. Interpretations were given to them, but it remained unexplained why the $\pi$ portion of kinetic energy is proportional to the total energy with nuclear repulsion energy. The energetic

(20) (a) Ooshika, Y. *J. Phys. Soc. Jpn.* **1957**, *12*, 1249. (b) Fukutome, H. *Prog. Theor. Phys.* **1968**, *40*, 998, 1227. (d) Paldus, J.; Cizek, *J. Phys. Rev. A* **1970**, *2*, 2268. (e) Kertesz, M. *Phys. Status Solidi* B**1975**, *69*, K141. (g) Kertesz, M.; Koller, J.; Azman, A. *J. Chem. Phys.* **1977**, *67*, 1180. (h) Whangto, M.-H. *Acc. Chem. Res.* **1983**, *16*, 95.
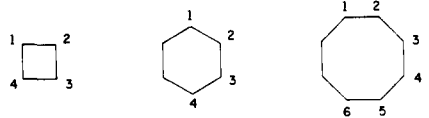
(21) Those solutions for cyclobutadiene and cyclooctatetraene are casually obtained by the GAUSSIAN 80 program.

(22) The detail of the relationship between KE and each solution will be reported in the near future.

(23) Estimated from the additivity rule in ref 9a.

(24) (a) Hess, A. B., Jr.; Schaad, L. J. *Tetrahedron Lett.* **1972**, 5113. (b) Herndon, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 2404.

(25) Haddon, R. C. *Nouv. J. Chem.* **1979**, *3*, 719.

**Table VII.** Mulliken Population Analyses of $\pi$ Electron in Cyclic Polyenes

|  | 1 | 1–2 | 1–3 | 1–4 | 1–5 | 2 | 2–4 | 2–6 |
|---|---|---|---|---|---|---|---|---|
| cyclobutadiene | 0.874 13 | 0.176 90 | −0.012 05 | −0.038 98 |  |  |  |  |
| benzene | 0.786 67 | 0.110 08 | −0.001 59 | −0.003 64 |  |  |  |  |
| cyclooctatetraene[a] | 1.127 87 | 0.094 31 | −0.005 83 | −0.000 20 | 0.000 23 | 0.501 69 | 0.002 80 | −0.000 16 |

[a] The electronic structure has the $D_{4h}$ symmetry.
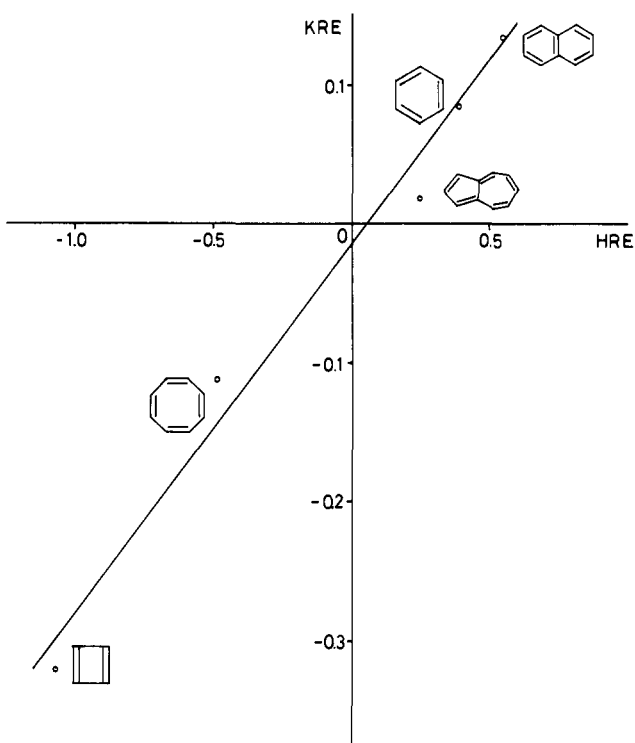


**Figure 2.** Hückel resonance energies vs. $\pi$ kinetic resonance energies. The Hückel resonance energies are taken from ref 9a.

stability (or unstability) of the aromatic (or antiaromatic) system was related to *the kinetic (energy) pressure* on the atom.

**Appendix**

A brief description of energy partitioning in ab initio Hartree–Fock theory has been given by Kollmar.[13] Since the method is considered to be widely used in the study of aromaticity and related problems, here we would like to give a more detailed description which actually has been used in the present study.

The Hamiltonian (H) of molecular system under Born–Oppenheimer approximation[26] consists of the linear operators which correspond to the kinetic energy of the electron ($T$), the attractive potential energy between nuclei and electrons ($V$), and the repulsive potential energy between electrons ($J$).

The electronic energy ($E^{el}$) is given by sandwiching the Hamiltonian with the wave function ($\Psi$) as

$$E^{el} = \langle \Psi | H | \Psi \rangle = \langle \Psi | T + V + J | \Psi \rangle \qquad (a\text{-}1)$$

Since the operators are linear, $E^T$ is obtained as

$$E^T = \langle \Psi | T | \Psi \rangle = \sum_i^n \int \psi_i^*(1)\left(-\frac{1}{2}\nabla_1^2\right)\psi_i(1)d\tau_1 =$$

$$2\sum_i^n \sum_r \sum_s \int C_r^* \phi_r^*(1)\left(-\frac{1}{2}\nabla_1^2\right)C_s\phi_s(1)d\tau_1 = \sum_r \sum_s P_{rs}T_{rs} \quad (a\text{-}2)$$

(26) Born, M.; Oppenheimer, J. R. *Ann. Phys. (Leipzig)* **1927**, *84*, 457.

where $\nabla_1^2$ is the Laplacian for arbitrary electron 1, $\psi_i$ is the $i$th MO, $n$ is the number of the occupied MO's, $\phi_r$ is the AO at shell r, $C_r$ is the MO coefficient for $\phi_r$, $P_{rs}$ is the density matrix, and $T_{rs}$ is the kinetic energy integral matrix,

$$T_{rs} = \int \phi_r^*(1)\left(-\frac{1}{2}\nabla_1^2\right)\phi_s(1)d\tau_1$$

$E^V$ is similarly given by

$$E^V = \langle \Psi | V | \Psi \rangle = 2\sum_i^n \psi_i(1)\left(-\sum_A \frac{Z_A}{r_{1A}}\right)\psi_i(1)d\tau_1 =$$

$$2\sum_i^n \sum_r \sum_s C_r^* \phi_r^*(1)\left(-\sum_A \frac{A_A}{r_{1A}}\right)C_s\phi_s(1)d\tau_1 = \sum_r \sum_s P_{rs}V_{rs} \quad (a\text{-}3)$$

In HF SCF theory, $E^J$ can be obtained via the Fock matrix (F); $E^{el}$ is expressed by eq a-4 or a-5

$$E^{el} = 2\sum_i^n F_{ii} - \sum_i^n \sum_j^n (2J_{ij} - K_{ij}) \qquad (a\text{-}4)$$

$$E^{el} = \sum_i^n (F_{ii} + H_{ii}) \qquad (a\text{-}5)$$

where $J_{ij}$ and $K_{ij}$ are the Coulomb and exchange integrals and

$$F_{ii} = \int \psi_i^*(1)F\psi_i(1)d\tau_1$$

$$H_{ii} = \int \psi_i^*(1)\left(-\frac{1}{2}\nabla_1^2 - \sum_A \frac{1}{r}_{1A}\right)\psi_i(1)d\tau_1$$

The second term of eq a-4 corresponds to $E^J$. From eq a-4 and a-5, eliminating $E^{el}$, $E^J$ is derived as

$$E^J = \sum_i^n (F_{ii} - H_{ii}) = \frac{1}{2}\sum_r \sum_s P_{rs}(F_{rs} - T_{rs} - V_{rs}) \quad (a\text{-}6)$$

In this way, the partitioned energies can be expressed at MO or AO levels. If $P_{rs}$ is divided into $P_{\pi rs}$ and $P_{\sigma rs}$ ($\pi$ and $\sigma$ parts of the density matrix, respectively),

$$\sum_r \sum_s P_{\pi rs}T_{rs}$$

can be regarded as the kinetic energy of the $\pi$ electrons. And if summation is taken as $\sum_{r \in A}\sum_{s \in B}$, the energy on atom A (diagonal) and the interaction between atoms A and B (nondiagonal) are obtained.