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What Does Hückel MO Method Calculate?-On the Relationship between HMO Energy and the Kinetic Energy of π Electrons

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The Hückel MO energies of linear polyenes (**1**—**9** in Fig. 1) were compared with each energy component of the Hartree–Fock total energy. It was concluded that the Hückel MO energy is closely proportional to the kinetic energy of the π electrons between the 2p AOs. This linear relation held in various types of these (**1**—**43**) polyenes. It was also shown that the ratio of the π kinetic energy to the total kinetic energy is almost constant. Thus, we may understand with the help of the virial theorem why the Hückel MO energy represents the total energy. We also give a physical background to the theories of aromaticity/antiaromaticity.

In 1931, E. Hückel introduced the so-called Hückel molecular orbital(HMO) theory in order to explain the abnormal stability of benzene.[1] Since then, this theory has been used in various fields of organic chemistry.[2] Today, the theory is very successful in many ways. Particularly, the studies of aromaticity have been remarkably successful.

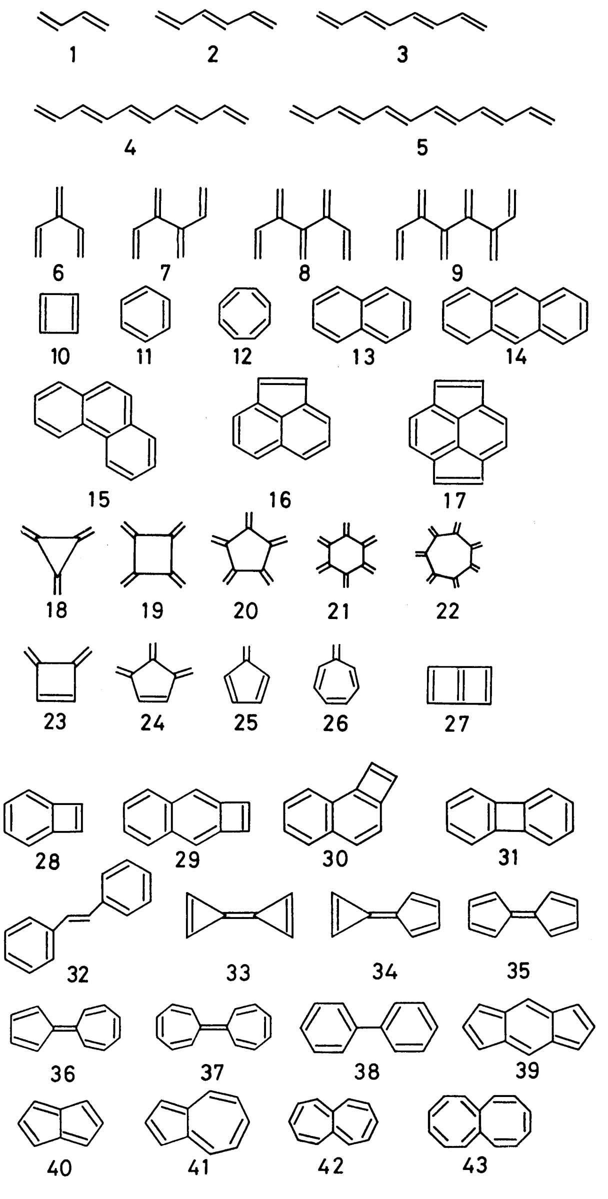

Fig. 1. Forty-three structures used to compare the π kinetic and HMO energies.

Based on the HMO theory, aromaticity or antiaromaticity in annulene has been predicted in terms of the ethylene unit,[3] graph theory,[4] and London susceptibility.[5] Results by all methods seem to be perfect. This, however, raises a problem: why is the HMO theory such a perfect method? In fact there is little in this theory which is theoretically correct: the Hamiltonian of the Hückel theory is not specified, resulting in a vagueness in the calculated results in addition to open neglect of the antisymmetrization requirement, electron-correlation, σ–π interactions, charge-redistribution effects, overlap influences, and so on. To what extend can they be justified? The first justification is that the Hückel theory works, as J. N. Murrel et al. stated.[6]

Rationalization of the HMO theory has been studied by a number of authors: rational connections of the Hückel theory with the Pariser–Parr–Pople(PPP) method in great detail by Pople,[7]McWeeny,[8]Del Re and Parr,[9] mostly during the fifties and sixties. However, studies of aromaticity using the HMO theory make one feel that beyond such a rationalization, there is something intrinsic which directly reflects the nature of conjugated π bonds. Besides, it has been pointed out that aromaticity and antiaromaticity predicted by the HMO theory reflect reality better than does that by the PPP method.[3b,10]

Hess and Schaad[11] found that the Hückel energies of linear polyenes (**1**—**5** and higher homologues) have a linear additivity in terms of the ethylene unit.[3] They, as well as Haddon and Starnes,[12] found that the total energies of **1**—**4** by STO-3G[13] or 3-21G[14] also increase linearly as the number of ethylene units increases. This means that the Hückel energy does not correspond to the energy of π electrons but, rather, to the total energy. This contradicts the idea that the theory is for π electrons.

We recently studied aromaticity using the Hartree–Fock MO theory and obtained the significant result that there is almost an exact linear relationship between the HMO energy and the kinetic energy of π electrons (π kinetic energy) of polyenes.[15] Namely, the HMO calculation is probably identical to a calculation of the kinetic energy of π electrons. If this is universally true, the physical meaning may be given in terms of the kinetic energy of π electrons. Further, the HMO results so far obtained may be reexplained based on the kinetic energy while affording new interpretations. Here, we may offer a significant suggestion as to what the HMO energy represents regarding molecular energies, while giving a reason why the HMO energy is proportional to the total energy of polyene.

Method of Calculation

In an attempt to determine what kind of energy of the π system the HMO method evaluates, we compared the HMO energy and every term of the partitioned Hartree–Fock energies. In Hartree–Fock theory[16] the total energy (E) is the sum of the electronic energy (E^{el}) and the nuclear repulsion energy (E^{N}). The E^{el} term comprises the kinetic (E^{T}) and the potential energies. The latter is further partitioned into the attactive one-electron potential (E^{V}) (i. e., interactions between electrons and nuclei) and the average of two electron energies (E^{J}):

$$E = E^{\mathrm{el}} + E^{\mathrm{N}}, \tag{1}$$

where

$$E^{\mathrm{el}} = E^{\mathrm{T}} + E^{\mathrm{V}} + E^{\mathrm{J}}. \tag{2}$$

Since the wave function (Ψ) is expressed by the Slater determinant with elements of molecular orbitals (MOs: ψ_i) expanded by a linear combination of AOs (x_r), those partitioned energies are obtained as expectation values by a general expression,

$$\begin{aligned} E^{\mathrm{X}} = <\Psi|X|\Psi> &= 2\sum_i \int \psi_i^* X \psi_i \mathrm{d}\tau_1 \\ &= 2\sum_i \sum_r \sum_s c_r^{i*} c_s^i \int x_r^* X x_s \mathrm{d}\tau_1 = \sum_r \sum_s P_{rs} X_{rs}, \end{aligned} \tag{3}$$

where c_r^i is the coefficient of x_r at the ith MO and P_{rs} is the bond order. X is the operator of the corresponding energy (E^{T}, E^{V}, or E^{J}), while X_{rs} is its element in the form of a matrix.

Since the π MOs do not mix with the σ MOs in the planar conjugated system, P_{rs} is expressed as the sum of the MOs of the σ electrons and π electrons,

$$P_{rs} = P_{rs}^{\sigma} + P_{rs}^{\pi}. \tag{4}$$

Therefore, E^{el} and its partitioned energies can also be expressed as the sum of the σ-electron (E_{σ}) and π-electron (E_{π}) energies as

$$\begin{aligned} E^{\mathrm{el}} &= 1/2\sum_r \sum_s P_{rs}(H_{rs} + F_{rs}) \\ &= 1/2\sum_r \sum_s P_{rs}^{\sigma}(H_{rs} + F_{rs}) \\ &\quad + 1/2\sum_r \sum_s P_{rs}^{\pi}(H_{rs} + F_{rs}) = E_{\sigma} + E_{\pi}, \end{aligned} \tag{5}$$

where the summations run over all atomic orbitals. The Fock matrix, F_{rs}, contains the density matrix which also consists of σ and π portions. Therefore, the E_{σ} and E_{π} energies are further partitioned into the pure σ electron energy (E_0^{σ}) and the pure π electron energy (E_0^{π}), and the interaction energy between σ and π electrons ($E_{\sigma\text{-}\pi}$ and $E_{\pi\text{-}\sigma}$) as:

$$\begin{aligned} E_{\sigma} &= 1/2\sum_r \sum_s P_{rs}^{\sigma}\{2H_{rs} + \sum_t \sum_u P_{tu}^{\sigma}[(rs/tu) - 1/2(rt/su)]\} \\ &= 1/2\sum_r \sum_s P_{rs}^{\sigma}\{\sum_t \sum_u P_{rs}^{\pi}[(rs/tu) - 1/2(rt/su)]\} \\ &= E_0^{\sigma} + E_{\sigma\text{-}\pi}. \end{aligned} \tag{6}$$

Likewise

$$E_{\pi} = E_0^{\pi} + E_{\pi\text{-}\sigma}, \tag{7}$$

Note that $E_{\sigma\text{-}\pi}$ and $E_{\pi\text{-}\sigma}$ are equal and that the interaction between σ and π electrons is caused only by electron-electron repulsion, i. e., π electrons interact with the σ electrons only through electrostatic repulsion; also, one-electron energies are given purely in a first-order approximation.

We have used the GAUSSIAN 80H program[17] to which new subroutines for energy analyses were added.

Results and Discussion

Examination of Additivity in Partitioned Hartree-Fock Molecular Energies. The total energies calculated for linear polyenes by ab initio MO methods have been shown to increase linearly as the number of ethylene (–CH=CH–) units increases.[11,12] The first problem to be examined is whether or not such a linearity holds in any term of the partitioned Hartree-Fock energies.

Figure 2-a shows the linearity/nonlinearity of the partitioned Hartree–Fock energies vs. n, the number of ethylene units, in linear polyenes. The adopted basis set was STO-3G and the geometries were optimized with respect to all internal molecular coordinates. The influences of the choice of the basis set and the geometry optimization are discussed in later sections.

As can be seen from the figures, E^{V}, E^{J}, and E^{N} are not additive, even in the Hartree-Fock electronic energy ($E^{\mathrm{el}}(=E^{\mathrm{V}}+E^{\mathrm{J}}+E^{\mathrm{T}})$). At first, we thought that the π portion of E^{el} must be energy-additive, since the energies obtained by such π molecular orbital theories as the HMO and PPP are energy-additive. This, however, was not true. Instread, a close linearity occurs regarding both total kinetic and π kinetic energies.

The additivity of the E^{T} term seems to be reasonable since the virial theorem indicates that for the station-

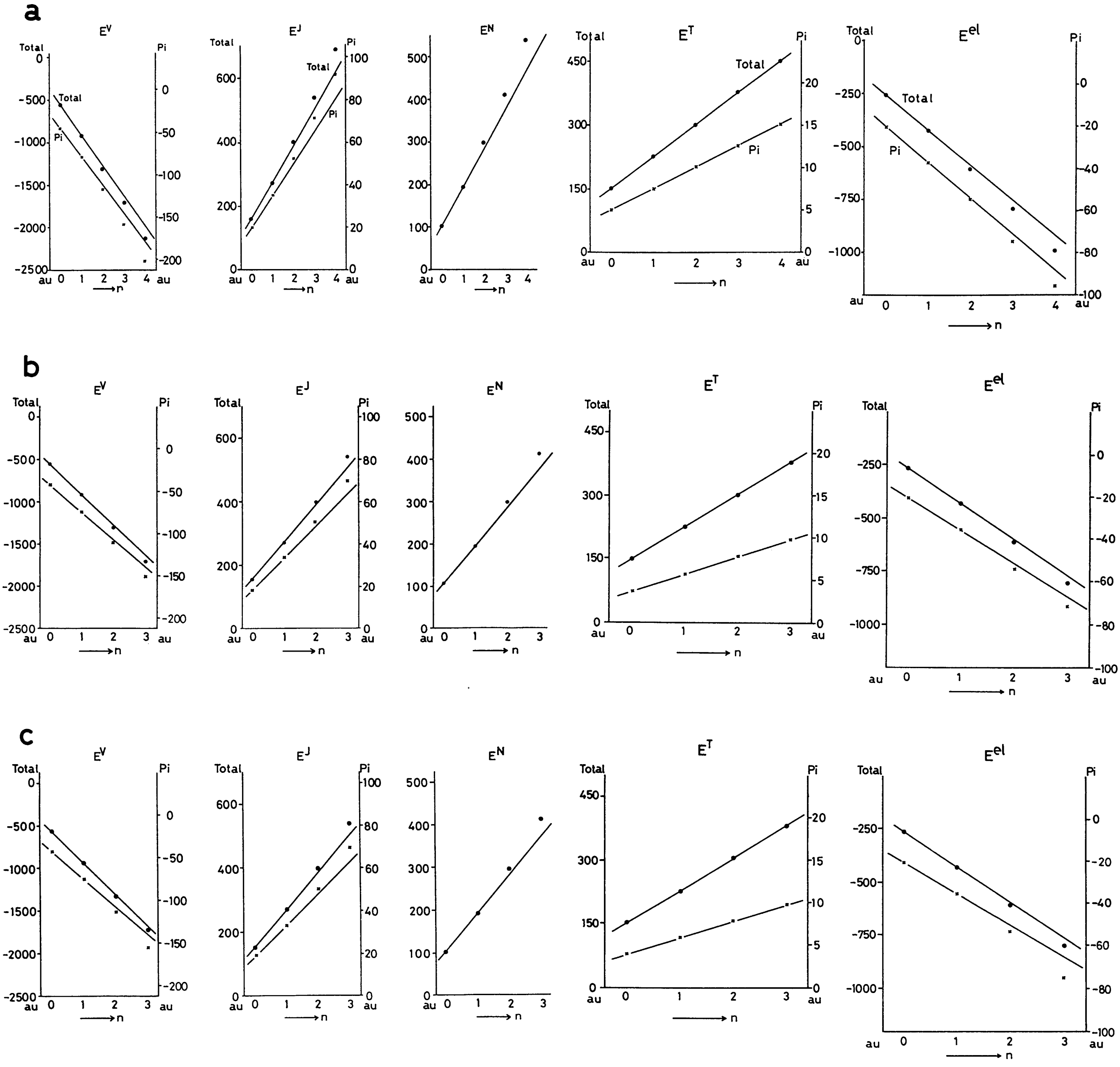

Fig. 2. Linearity/nonlinearity of the partitioned Hartree-Fock energies n vs. in linear polyenes (CH_2=CH-(CH=CH)$_n$-CH=CH_2). Scales indicated by total and pi are for those for the total and π electrons in terms of au (1 au=2625.5 kJ mol^{-1}). a: STO-3G, b: 3-21G, and c: 4-31G.

ary state the relationship

$$E = -E^{\mathrm{T}} \tag{8}$$

must hold and since the additivity of E is phenomenologically shown.[11,12] However, note that such additivity holds in the π portion of the kinetic energy.

Basis Set Dependency. We thus found that the total energy as well as the kinetic energy increases linearly with the number of ethylene units (–CH=CH–). Since the molecular energies depend largely on the adopted basis set, the influence of the adopted basis set on the linearities of the partitioned energies must be examined.

Figures 2-b and 2-c show the linearity/nonlinearity of the partitioned energies vs. the number of the ethylene units in the respective 3-21G and 4-31G basis sets. Here, the π portion of the partitioned energies is the sum of the energies of the inner and outer shells in the split 2p AOs and the interaction energies between inner and outer shells. In both cases, there is good linearity in the total and π kinetic energies. Although basis sets with polarization functions were not studied further the results by 3-21G and 4-31G led us to believe that the additivity of E^T is quite independent of the adopted basis set. Note that linearity occurs not only in the total kinetic energy, but also in the π portion of the kinetic energy.

Relationship between π Kinetic Energy and Hückel Energy in Different Types of Polyenes. Ever since the

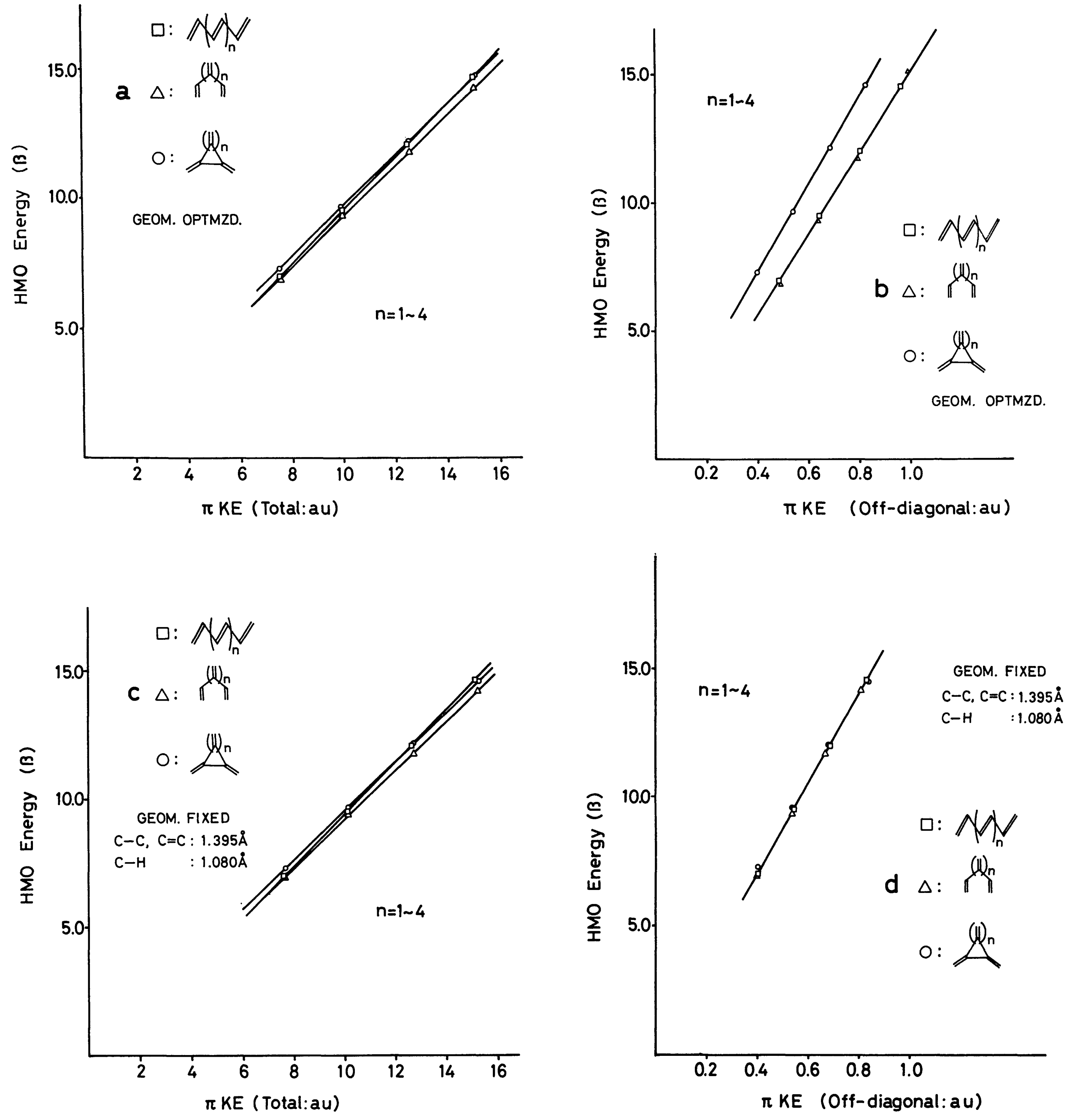

Fig. 3. Influence of geometry optimization on the linear relationship between the kinetic and HMO energies. a: The total π kinetic energies are compared with the HMO energies under complete geometry optimization. b: The π kinetic energies between the 2p AOs are compared under complete geometry optimization. c: The total π kinetic energies are compared under the fixed geometries. d: The π kinetic energies between the 2p AOs are compared under the fixed geometries.

energy additivity of the Hückel energy was established, the Hückel energy has been directly compared with the π kinetic energy in various cases. The basis set was STO-3G.

Figure 3-a shows the relationship between the HMO energy and the π kinetic energy for different types of geometry-optimized conjugated polyenes (**1—5**, **6—9**, and **18—21**). Though there is a linearity in the same series of polyenes, if considered all together the linearity is not perfect.

The Hückel energy consists of the bond energies in terms of β: as a matter of fact, the energy of the one-center term is not included. We thus examined the kinetic energy between the AOs. Figure 3-b shows the correlation of the HMO energy with the π kinetic energy of the off-diagonal part, i. e., the kinetic energy between the AOs. In this case the lines for **1—5** and **6—9** come close together, but the line for **18—21** remains apart.

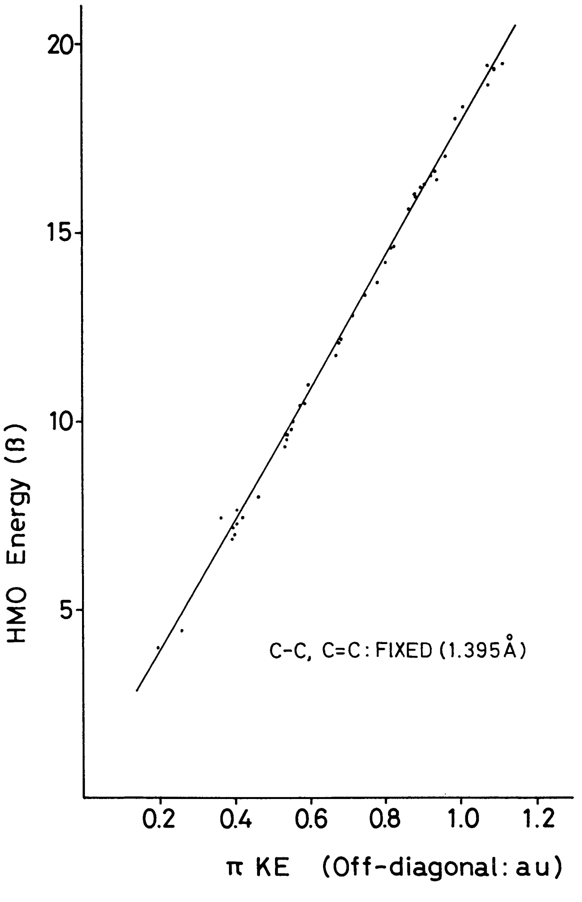

Fig. 4. The relationship between the HMO energies and the π kinetic energies between the 2p AOs in **43** conjugated hydrocarbons.

The Hückel theory does not include the effect of differences regarding the bond length. This suggests that the π kinetic energy should be compared in the fixed bond lengths. Figures 3-c and 3-d offer such comparisons, where all carbon–carbon bonds are fixed to be 1.395 Å (which equals that of benzene, i. e., the ideally conjugated bond length) with all carbon–hydrogen bonds being 1.080 Å.

If the total π kinetic energies are compared with the HMO energies, the linearity is not good. However, if only the off-diagonal part is compared, the linearity with the HMO energy seems to be quite acceptable. This confirms that the HMO energy corresponds to the π kinetic energy between the 2p atomic orbitals.

To make sure, we examined various types of conjugated hydrocarbons in which open-chain, aromatic, and antiaromatic system were included (Fig. 1). Again, all C–C bonds were fixed to be 1.395 Å and the C–H bonds 1.080 Å. As Fig. 4 shows, the linearity is farely good, showing that the HMO energy corresponds to the kinetic energy of π electrons between the 2p atomic orbitals.

Why HMO Energy is Proportional to Total Energy. As the results in the previous sections show, the HMO theory can be used to indirectly calculate the kinetic energy of π electrons. The virial theorem shows that the kinetic energy is equal to the total energy E with reverse sign (Eq. 8). Therefore, the riddle may be solved only if we can show that the total kinetic energy is proportional to the π kinetic energy.

Table 1 shows the ratio of the π-portion to the total kinetic energy (E_{π}^{T}/E^{T}) in the optimized geometries of the serial compounds **1—5**, **6—9**, and **18—21** which are used to form Fig. 3. It is understood that the ratios are almost constant (0.0332 to 0.0336), not only in one type of conjugated polyenes, but in other types. Though this ratio is changed by the method of calculation to be from 0.0256 to 0.0261 by both the 3-21G and 4-31G

Table 1. Ratio of π-Kinetic Energy to Total Kinetic Energy

n	a[a)		b[a)		c[a)	
	Ratio 1[b)	Ratio 2[c)	Ratio 1[b)	Ratio 2[c)	Ratio 1[b)	Ratio 2[c)
0	33.2	2.1				
1	33.2	2.1	33.3	2.1	33.4	2.2
2	33.3	2.1	33.3	2.1	33.4	2.2
3	33.3	2.1	33.3	2.1	33.5	2.2
4	33.3	2.1	33.4	2.1	33.6	2.1

a) a, b, and c represent linear (**1—5**), branched (**6—9**), and cyclic (**18—21**) structures in Fig. 1. b) The ratio of the total π-kinetic energy to the total kinetic energy, E_{π}^{T}/E^{T}, in 10^{-3} units. c) The ratio of the off-diagonal part of π-kinetic energy to the total kinetic energy, $E_{\pi}{}^{T}{}_{\mathrm{off}}/E^{T}$, in 10^{-3} units.

Table 2. Ratio of π-Kinetic Energy to Total Kinetic Energy

Compd	Ratio 1[a)]	Ratio 2[b)]	Compd	Ratio 1[a)]	Ratio 2[b)]
1	33.5	1.7	**23**	33.8	1.8
2	33.5	1.8	**24**	33.7	1.8
3	33.5	1.8	**25**	33.7	1.9
4	33.5	1.8	**26**	33.5	1.8
5	33.5	1.8	**27**	34.0	1.8
6	33.5	1.7	**28**	33.7	1.9
7	33.5	1.8	**29**	33.5	2.0
8	33.4	1.8	**30**	33.6	2.0
9	33.4	1.8	**31**	33.3	2.1
10	35.3	1.3	**32**	33.2	2.1
11	33.0	2.1	**33**	34.6	1.6
12	33.7	1.8	**34**	33.6	2.0
13	33.1	2.1	**35**	33.7	1.9
14	33.2	2.1	**36**	33.4	2.0
15	33.1	2.1	**37**	33.5	1.9
16	33.3	2.1	**38**	33.1	2.1
17	33.5	2.1	**39**	33.5	2.0
18	33.7	1.8	**40**	33.8	2.0
19	33.7	1.8	**41**	33.3	2.0
20	33.7	1.8	**42**	33.5	1.9
21	33.8	1.8	**43**	33.3	1.9
22	33.9	1.8			

a) $E_{\pi}{}^{T}/E^{T}$ in 10^{-3} units. b) $E_{\pi}{}^{T}{}_{\mathrm{off}}/E^{T}$ in 10^{-3} units.

methods, they are almost constant within each type of compound. Here, it may be necessary to show how geometry optimization affects this result.

Table 2 shows the ratios for the compounds used in Fig. 1. Those ratios, $E_{\pi}{}^{T}/E^{T}$, range form 0.0330 to 0.0346, showing that geometry optimization does not greatly affect the ratio. Significantly, the ratio of the off-diagonal part of the kinetic energy to the total kinetic energy is greatly changed by aromatic/antiaromatic compounds: the ratio of nonaromatic compounds is around 0.0018. However, in aromatic compounds, this ratio is shifted to a larger value (as much as 0.0021 in benzene) and in antiaromatic compounds, to a smaller value (as little as 0.0013 in cyclobutadiene) indicating that the aromaticity/antiaromaticity phenomena are caused by a delocalization of the π electrons between the 2p AOs.

Concluding Remarks

Because of the linear relationship between the HMO and the total energies, if one compares the HMO and potential energies, it is possible to obtain a similar linear relationship, due to the virial theorem, and to say that the HMO energy expresses the potential energy. However, it is an awkward way to state things: there is no common concept between them. Therefore, we focused on the kinetic energy of the π electrons. We have obtained two conclusions from energy comparisons regarding **43** polyenes of various types: the Hückel energy represents the kinetic energy of the π electrons between the 2p AOs and the ratio, the π kinetic to the total kinetic energy, is nearly constant.

The first conclusion is favorable regarding the interpretation of aromaticity, i. e., stability/instability of the $4n+2/4n$ π system is interpreted in terms of π-electron motion and/or distribution of the π MOs and this gives a physical background to the aromaticity theories.[3–5)] The reason for the resemblance between those energies is not certain. However, as we have already indicated,[15)] one possibility is that the kinetic energy between the 2p AOs rapidly decreases as the distance increases: a value more than the bonding interaction is virtually zero while that in the HMO theory is set to be zero.

The second conclusion gives a clear-cut explanation to the question why the HMO energy represents the total energy. Although the reason is not understood, the ratio of the total π kinetic energy to the total kinetic energy is constant, regardless of the type of conjugated hydrocarbon. The characteristics determined by the Hückel rule or aromaticity theories[3–5)] are brought forth only by the kinetic energy of the π electrons between the 2p AOs.

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