© 1997 The Chemical Society of Japan Bull. Chem. Soc. Jpn., **70**, 727—735 (1997)

# Analysis of Chemical Phenomena by Solving the Constrained Hartree–Fock Equation. III. Influence of Geometry Change on the Energy of π Electrons in Conjugated Hydrocarbons

**Hiroshi Ichikawa*** **and Hirotaka Kagawa**

Hoshi College of Pharmacy, Shinagawa, Tokyo 142

(Received July 1, 1996)

The total energy of a conjugated unsaturated hydrocarbon can formally be partitioned into the energy of π electrons and the frame energy. This type of partitioning has been used to study the role of π electrons; to know the relationship between the π-electronic structure and its energy, the molecular geometry has been varied. This paper examines the influences of such geometry change on the energy of π electrons from a basic point of view. It was found that there are four types of geometrical influences which disguise the relationship between the π-electronic structure and its energy. Contrary to this, the constrained Hartree–Fock method was shown to disclose the relationship between π-electronic structure and its energy clearly.

Application of the constrained Hartree–Fock method to $D_{6h}$ and $D_{3h}$ benzenes showed that in a $D_{6h}$ benzene π electrons favor the symmetrically uniform distribution independently of the bond length and the partitioning method, while in a $D_{3h}$ benzene the uniform distribution of π electrons is destroyed. Analysis of gradients of partitioned energies with respect to the bond order at a $D_{3h}$-distorted benzene indicated that π electrons favor a more uniform delocalization, but this is opposed by one- and two-electron potentials.

There are the σ–π electron and equivalent-bond (EB)[2,3] models for the expression of a multiple bond. Although both descriptions are quantum-mechanically legitimate, the concept of conjugation between adjacent multiple bonds in terms of delocalization of π electrons has been widely accepted; the interpretations of phenomena based on such a concept have been widely applied in organic chemistry. Accordingly, organic chemists have been accustomed to the idea that there are σ and π electrons in unsaturated hydrocarbons and they can be treated separately.[4—7] Since in the σ–π electron model, π electrons occupy MOs with a higher orbital energy and since they are chemically reactive, much attention has been paid on the behavior of π electrons.

The idea that π electrons are chemically reactive is liable to bring forth an idea that they are bound rather loosely and do not give much influence on the molecular geometry when compared to σ electrons. A typical example is seen in the interpretation of π electrons in benzene given by Shaik, Hiberty, and co-workers.[8—11] Their interpretation may be summarized as follows: Benzene's resistance to distortion is the result of two opposing driving forces: a strong symmetrizing driving force from the σ frame and a weak distortive driving force from the π bonding systems. Delocalization of π electrons, at a given fixed geometry, is stabilizing. Their role is to weaken the propensity of the π system to distort, enough to allow the σ driving force to win, so that a symmetrical geometry results.

Determining the role of π electrons in a conjugated system requires one to seek the relationship between the change of the π-electronic structure and its energy. To obtain an altered π-electronic structure, Shaik, Hiberty, and their co-workers disturbed the molecular geometry. An apparent difficulty is that the change of the π energy (or π-electronic energy) thus obtained includes effects from both the π electronic structure and those from the frame, i.e., the σ-electronic structure and nuclear configuration.

To find the change of π-electronic energy related to that of the π electronic structure without any geometry change, a method has been used that replaces the π MOs by others conveniently determined in other systems.[12] However, this does not meet the requirement of the variation principle in that those π MOs are not eigenfunctions of the Fock operator (an SCF Hamiltonian) of the considered electronic structure.[13] Thus, we have introduced a method that determines the total energy and its components for the predetermined electronic structure without changing the molecular geometry.[14] The mathematical expression is the constrained Hartree–Fock (HF) equation, which had been developed more than 20 years ago for different purposes.[15—17] The method has been demonstrated to work properly and to give comprehensive contributions to this kind of study.[14]

This article examines the influences of geometry change on the π-electronic energy from a mathematical point of view and discusses the questions of how the property of π electrons depends on the geometry and how the kinetic energy of π electrons behaves, using ethylene and benzene.

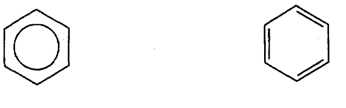
## Methods and Theoretical Consideration

**a. Adiabatic Resonance Energy vs. Vertical Resonance Energy.** The resonance energy in benzene may be given by the energy difference between structures **A** and **B** in Scheme 1. Here, the vertical resonance energy must be distinguished from the adiabatic resonance energy.[12] Although, experiments and the additivity relationship correspond to the latter resonance,[5,18,19] we only treat, here, the vertical resonance to know the role of $\pi$ electrons in the resonance. Namely, the geometry of **B** is kept the same as **A**. The reason why adiabatic resonance energy is excluded is simply because, as will be discussed, it involves the changes of nuclear configuration which affect the energies of both $\pi$ and $\sigma$ electrons.

**b. An SCF Electronic Structure.** In the SCF theory, the electronic structure of **A** is uniquely determined by solving the Hartree–Fock–Roothaan equation:[20] the electronic wave function ($\Psi^{\mathrm{SCF}}$) thus obtained is an eigenfunction of the SCF Hamiltonian of the given system. This is referred to as an SCF (or adiabatic) electronic state. The fact that $\Psi^{\mathrm{SCF}}$ is an eigenfunction of the SCF Hamiltonian of the considered system guarantees that $\Psi^{\mathrm{SCF}}$ is stationary.

The nonconjugative structure (**B**) literally means that there are no $\pi$ electrons distributed between double bonds. The wave functions always need to be one for standing waves with respect to the electronic structures. In the former study by Kollmar,[12] only the wave functions for the $\pi$ electronic structure of the considered system being altered to **B** are considered: All other electronic distributions (those of $\sigma$ electrons and inner-shell electrons) remain unchanged by the change of the distribution of $\pi$ electrons. This may be referred to as a non-SCF (or diabatic) electronic state. In a non-SCF electronic state, the electronic wave function ($\Psi^{\text{non-SCF}}$) is not an eigenfunction of *the SCF Hamiltonian of the considered electronic structure*. The difficulties of diabatic wave functions are that they cannot be uniquely defined, that they are time-dependent, and that they are unresponsive to the electrostatic forces from $\sigma$ electrons and nuclei.

The desired wave functions are those that include the effects due to the change of the distribution of $\pi$ electrons followed by a re-distribution of other electrons (SCF electronic state). Such electronic wave functions ($\Psi^{\mathrm{SCF}}$) in an SCF electronic state are eigenfunctions of the SCF Hamiltonian and that the electronic distribution associated with $\Psi^{\mathrm{SCF}}$ should be analyzed. The difference of wave functions between adiabatic and diabatic electronic states is considered to be great when it comes to the components of the total energy because, as will be mentioned, they are dependent on the first order of the scale error. Practically, a legal way to reproduce the electronic structure B may be to add to the usual Fock operator an operator that repels $\pi$ electrons from the bond region between two $\pi$ bonds.[14] The equation which includes this operator is generally called the constrained Hartree–Fock equation. The electronic wave functions ($\Psi^{\text{const-SCF}}$) thus obtained are *the eigenfunctions of the SCF Hamiltonian for the desired electronic structure*. This ensures that $\Psi^{\text{const-SCF}}$ include all interactions from nuclei and electrons and are stationary.



A: conjugated state B: isolated stated

Scheme 1. Conjugative vs. isolated electronic structures in benzene.

**c. Energy Partitioning.** A convenient method partitions $E$ into the $\pi$-energy part ($E_\pi$) and the skeletal part ($E'_\sigma$) as

$$E = E_\pi + E'_\sigma \tag{1}$$

to discuss the roles of $E_\pi$ when the $\pi$-electronic structure is perturbed. This type of partitioning has been adopted by a number of authors.[8—11,21—24] The problem involved in this method is the major concern of this report.

**d. Constrained Hartree–Fock Equation.** To investigate the relationship between the $\pi$-electronic structure and its energy, one needs a method that determines the molecular energy as a function of the electronic structure. As one method, we have introduced the constrained Hartree–Fock equation.[14] This equation was first introduced by Mukherji and Karplus in 1963 to molecular quantum mechanics.[15] The purpose was to obtain the wave function that is constrained to give the known theoretical or experimental expectation values of operators rather than the total energy. The method was generalized by Brown,[16] and was applied to the SCF theory by Björnå in the early 1970s for constraints that yield accurate expectation values for physical properties.[17]

We found that the total energy for a nonresonating electronic structure can be obtained by applying this equation, where the constraints cancel the delocalization of the $\pi$ electrons on resonating bonds.[14] The equation is

$$(F+\lambda)C = \varepsilon SC. \tag{2}$$

Here, $F$,$C$, and $S$ are matrices of Fock operator, molecular orbital (MO: $\psi$) coefficients, and overlap integrals while $\varepsilon$ is the fictitious orbital energy associated with $\psi$. The parametric matrix, $\lambda$, constrains the electron distribution to be controlled. The bond-order ($P_{rs}=2\Sigma C^i_r C^i_s$) between atomic orbitals (AOs) $r$ and $s$ is a function of $\lambda_{rs}$, an element of $\lambda$, where the $\lambda_{rs}$ value is so determined that $P_{rs}$ becomes null to cancel the delocalization between AOs $r$ and $s$. The equation also gives the total energy and its components as functions of $P_{rs}$. The detail of derivation has been described elsewhere.[14]

**e. Influence of Geometry Change on the Partitioned Energies.** The molecular geometry has been distorted to disturb the $\pi$ electronic structure in obtaining the relationship between the energies and the electronic structure of $\pi$ electrons (the geometry-distortion (GD) method).[8—11] Although the problems of this method have already been pointed out,[14,25] we discuss the same problems by examining the partitioning formulas and show that the only legal way at present to gain a solution is the constrained Hartree–Fock method.

**General Consideration Based on the Virial Relationship.** Influence of geometry change on the partitioned energies has been reported to be enormous even if that of the total energy is negligible.[14,25—27] The reason for this is given by consideration of the virial theorem.[26,27] The virial theorem is written as[28]

$$\langle T\rangle + E + \sum_{\alpha<\beta} R_{\alpha\beta}\frac{\partial E}{\partial R_{\alpha\beta}} = 0, \tag{3}$$

where $\langle T\rangle$, $E$, and $R$ are the expectation value of the kinetic energy, the total energy, and internuclear distances and where the sum runs over all internuclear distances. If the geometry of the system is optimized with respect to all nuclear centers, the third term (which is often called the virial term) turns out to be null (since $\partial E/\partial R=0$ holds concerning any of nuclear centers) to give the simple relationship, $\langle T\rangle+E=0$ or equivalently $\langle V\rangle/\langle T\rangle=-2$, where $\langle V\rangle$ is the expectation value of the potential energy. (The angle brackets indicate an expectation value.)

If the molecular geometry is disturbed, the virial term becomes nonzero, with both σ and π contributions. Morever, as the mathematical structure of the virial term suggests, *the amount of change depends on how the reaction coordinate for distortion is selected.* The relative amounts of changes of the partitioned energies to that of the total energy can be estimated by comparing the Taylor expansions of the total and partitioned energies in terms of the scale error[29] of the electronic wave function.[26] This indicates that the total energy deviates in the second-order of the scale error while those in the partitioned energies deviate in the first-order. Actual deviations of the partitioned energies were found to be up to $10^4$ times more than that of the total energy.[27,30]

**General Discussion in Terms of Force.** A more direct proof may be given by considering intramolecular forces. The total energy ($E$) is generally given as a functional,

$$E = W[C(R), \zeta(R), R], \tag{4}$$

where, $C$, $\zeta$, and $R$ represent the LCAO coefficients, the exponents of basis functions, and a set of nuclear coordinates. Under the full variational conditions, $\partial W/\partial C=0$ and $\partial W/\partial\zeta=0$, the direct differentiation of Eq. 4 gives

$$\frac{\partial E}{\partial R_{\mathrm{a}}} = \frac{\partial W}{\partial R_{\mathrm{a}}} + \sum_{r,i}\frac{\partial W}{\partial C_r^i}\frac{\partial C_r^i}{\partial R_{\mathrm{a}}} + \sum_{r}\frac{\partial W}{\partial \zeta_r}\frac{\partial \zeta_r}{\partial R_{\mathrm{a}}} = \frac{\partial W}{\partial R_{\mathrm{a}}}. \tag{5}$$

Thus, it is understood that the derivative of the total energy with respect to a nuclear coordinate ($R_{\mathrm{a}}$) is simply the force along the coordinate, *where there are no contributions from C.*

The π energy is also a functional concerning a nuclear coordinate. The derivative of π-electron energy ($E_\pi$) is given similarly as,

$$\frac{\partial E_\pi}{\partial R_{\mathrm{a}}} = \left(\frac{\partial E_\pi}{\partial R_{\mathrm{a}}}\right)_0 + \sum_{r,i}\frac{\partial E_\pi}{\partial C_r^i}\frac{\partial C_r^i}{\partial R_{\mathrm{a}}} + \sum_{r}\frac{\partial E_\pi}{\partial \zeta_r}\frac{\partial \zeta_r}{\partial R_{\mathrm{a}}}, \tag{6}$$

where $(\partial E_\pi/\partial R_{\mathrm{a}})_0$ is the derivative under the condition that the coefficients are regarded as constants. *Since Ψ is not an eigenfunction of the π-electron operator, generally both the $\partial E_\pi/\partial C$ and $\partial E_\pi/\partial\zeta$ are not null.* Therefore, the second and third terms are retained. Since the coefficients $C$ include effects of both σ and π electrons, $\partial E_\pi/\partial R_{\mathrm{a}}$ also includes effects from the σ electrons. Since energy change ($\Delta E$) is an integral of the force along the reaction coordinate, it surely contains contributions from nuclear positions and from the electrons other than π electrons.

**π Energy, π-Electronic Energy, and the Kinetic Energy of π Electrons.** Before going to the detailed discussion, we have to clarify the concepts on the energy of π electrons. The partitioned energies in Eq. 1 can further be partitioned into fundamental energies as follows.

$$E_\pi = \langle T\rangle_\pi + \langle V_{\mathrm{eN}}\rangle_\pi + \langle V_{\mathrm{ee}}\rangle_\pi + \langle V_{\mathrm{ee}}\rangle_{\pi-\sigma} \tag{7}$$

$$E'_\sigma = \langle T\rangle_\sigma + \langle V_{\mathrm{eN}}\rangle_\sigma + \langle V_{\mathrm{ee}}\rangle_\sigma + V_{\mathrm{NN}} + \langle V_{\mathrm{ee}}\rangle_{\sigma-\pi}, \tag{8}$$

where, $\langle T\rangle$, $\langle V_{\mathrm{eN}}\rangle$, $\langle V_{\mathrm{ee}}\rangle$, and $V_{\mathrm{NN}}$ are the kinetic, one-electron potential, two-electron potential, and internuclear repulsion energies while $\langle V_{\mathrm{ee}}\rangle_{\pi-\sigma}$ and $\langle V_{\mathrm{ee}}\rangle_{\sigma-\pi}$ are the electron–electron repulsion energy of π electrons that receive from σ electrons, and that of σ electrons that receive from π electrons, respectively.

Here, π-electronic energy should be distinguished from 'π energy' that is calculated by a π MO theory. π-Electronic energy is one defined by Eq. 7, which includes the potential from nuclei as $\langle V_{\mathrm{eN}}\rangle_\pi$ and shield effects of σ and inner-shell electrons as $\langle V_{\mathrm{ee}}\rangle_{\pi-\sigma}$. 'π Energy' by a π MO theory has been generally considered to include the potentials from nuclei as shielded by σ and inner-shell electrons. In this respect, 'π energy' and π-electronic energy seem to be similar. However, the most different point is that 'π energy' must have a linear-additivity nature in a series of polyenes of the same type, which is an absolute requirement because of the measure of aromaticity. As we examined,[31] the π-electronic energy does not have the property of linear additivity.

Another difficulty is that 'π energy' may be insusceptible against small displacement of nuclear positions. Such an insusceptibility may be a fact that the 'π energy' includes a part of the nuclear repulsion since $E_\pi$ and $V_{\mathrm{NN}}$ generally behave oppositely; adding a part of $V_{\mathrm{NN}}$ to $E_\pi$ reproduces the insusceptibility. However, one does not know the ratio based on a rational ground although a proposal has been presented.[22] Another proposal is that Hückel energy represents the kinetic energy of π electrons.[31] This was obtained by direct comparison; the correlation coefficient is 1.0000 among the same type of unsaturated hydrocarbons. In addition, the linear additivity and insusceptibility of small nuclear displacement hold in polyacetyles. Therefore, we strongly propose the idea that the so-called 'π energy' is a representation of the kinetic energy of π electrons. If this is accepted, the kinetic energy of electrons can be a reasonable measure of delocalization, i.e., smooth movement of electrons: The kinetic energy operator includes partial differentials of second order with respect to the position of electrons.

**Detailed Analysis of Geometry Contribution to Partitioned Energies.** Since the SCF electronic wave function

($\Psi$) is a Slater determinant of molecular orbitals (MOs: $\psi_i$) expanded in terms of a linear combination of AOs ($\chi_r$) and since the total bond order ($P_{rs}$) is the sum of π- ($P^{\pi}_{rs}$) and σ-bond orders ($P^{\sigma}_{rs}$) in a planar unsaturated hydrocarbon, those partitioned energies for π electrons are obtained as expectation values by a general expression,

$$\begin{aligned}\langle X\rangle_{\pi} &= 2\sum_{i}^{\text{occ}}\sum_{r}\sum_{s} C_r^{\pi i} C_s^{\pi i}\int \chi_r^{*} X(y)\chi_s \mathrm{d}\tau \\ &= \sum_{r}\sum_{s} P^{\pi}_{rs} X(y)_{rs},\end{aligned} \tag{9}$$

where $C_r^{\pi i}$ is the coefficient of $\chi_r$ at the $i$th π MO. $X$ is the operator of the corresponding energy ($\langle T\rangle$, $\langle V_{\mathrm{eN}}\rangle$, or $\langle V_{\mathrm{ee}}\rangle$), while $X_{rs}$ is its element in its matrix.

Thus, each partitioned energy for π electrons is given as

$$\langle T\rangle_{\pi} = \sum_{r}\sum_{s} P^{\pi}_{rs} T_{rs} = \sum_{r}\sum_{s} P^{\pi}_{rs}\int \chi_r^{*}\left(-\frac{1}{2}\nabla^2\right)\chi_s \mathrm{d}\tau, \tag{10}$$

$$\langle V_{\mathrm{eN}}\rangle_{\pi} = \sum_{r}\sum_{s} P^{\pi}_{rs} V_{rs} = \sum_{r}\sum_{s} P^{\pi}_{rs}\int \chi_r^{*}\left(\sum_{A}\frac{-Z_A}{r_{1A}}\right)\chi_s \mathrm{d}\tau, \tag{11}$$

$$\langle V_{\mathrm{ee}}\rangle_{\pi} = \frac{1}{2}\sum_{r}\sum_{s} P^{\pi}_{rs}\left\{\sum_{t}\sum_{u} P^{\pi}_{tu}\left[(rs|tu) - \frac{1}{2}(rt|su)\right]\right\}, \tag{12}$$

$$\langle V_{\mathrm{ee}}\rangle_{\pi-\sigma} = \frac{1}{2}\sum_{r}\sum_{s} P^{\pi}_{rs}\left\{\sum_{t}\sum_{u} P^{\sigma}_{tu}\left[(rs|tu) - \frac{1}{2}(rt|su)\right]\right\}, \tag{13}$$

$$V_{\mathrm{NN}} = \sum_{A>B}\frac{Z_A Z_B}{r_{AB}}, \tag{14}$$

where

$$(rs|tu) = \int\int \chi_r^{*}(1)\chi_s^{*}(1)\left(\frac{1}{r_{12}}\right)\chi_t(2)\chi_u(2)\mathrm{d}\tau_1 \mathrm{d}\tau_2. \tag{15}$$

Here, $\nabla^2$, $Z_A$, $r_{1A}$, $r_{12}$, and $r_{AB}$ are Laplacian operator, the nuclear charge of atom A, the distance between electron 1 and atom A, the distance between electrons 1 and 2, and the distance between nuclei A and B. Let us consider how those partitioned energies change when the molecular geometry is altered.

**Four Types of Geometry Influence on π Energy.** The expectation values for the kinetic energy of π electrons, one-electron potential energy, two-electron potential energy, π–σ interaction energy, and nuclear–nuclear repulsion energy are given by Eqs. 10, 11, 12, 13, and 14. The direct influence of a geometry change is seen in $\langle V_{\mathrm{eN}}\rangle$ and $V_{\mathrm{NN}}$ since both include the coordinates of all nuclei. A part of the change of $\langle V_{\mathrm{eN}}\rangle$ goes to $E_{\pi}$ when $E$ is partitioned into $E_{\pi}$ and $E'_{\sigma}$ as shown in Eq. 1. This type of influence is designated here Class I.

The kinetic-energy and two-electron potential energy operators do not include nuclear coordinates, but their matrix elements are dependent on a nuclear position through the basis functions ($\chi$) since each basis function is expanded at an atomic center. This is referred to as a Class II influence. Concerning the influence via $P_{rs}$, there are two types (Classes III and IV). The bond-order matrix, $P_{rs}$, is determined through the SCF procedure. Since the SCF is so attained that there is no contradiction of $P_{rs}$ between $n$th and $n$+1th SCF turns, $P_{rs}$'s are determined as including all interactions from nuclei (Class III) and from electrons (Class IV).

Class I, II, and III influences include the direct effects of the geometry change while Class IV effect is indirect. Namely, the change of a nuclear position affects the distribution of σ and inner-shell electrons, which affects the distribution and energies of π electrons, which again affects the distribution of σ and inner-shell electrons and so on. However, such multi-order influences cannot be treated separately as far as the SCF procedure is adopted. Therefore, the change of the π electron energy obtained by the GD method never gets rid of the influences of the change of a nuclear coordinate. Each partitioned energy includes the geometry influence, as shown in Table 1.

Then let us consider the case when the constrained Hartree–Fock equation is applied to the study of the relationship between the π-electronic structure and energy fractions. The constrained Hartree–Fock method does not involve any displacement of nuclear position. Therefore, Classes I, II, III, and IV influences are all ruled out.

## Results and Discussion

**Ethylene.** First, let us discuss how the molecular geometry is determined by π and σ electrons. Using Eq. 1, the partial derivative of the total energy with respect to a nuclear coordinate ($R$) gives

$$\frac{\partial E}{\partial R} = \frac{\partial E_{\pi}}{\partial R} + \frac{\partial E'_{\sigma}}{\partial R}. \tag{16}$$

At the optimized geometry, the following relationship holds since $\partial E/\partial R$'s are null.

$$\frac{\partial E_{\pi}}{\partial R} + \frac{\partial E'_{\sigma}}{\partial R} = 0 \tag{17}$$

Equation 17 literally means that the force from π electrons and that from the frame are balanced to give the optimized bond length $r_0$. Namely, both electron systems have the same contribution to the geometry. This argument can apply to any conjugated system and suggests that the idea of weak contribution of π electrons to the geometry is dubious. Let us examine how those derivatives behave in relation with the bond length.

Table 2 shows the changes of the π-electronic energy ($E_{\pi}$), the kinetic energy of π electrons ($\langle T\rangle_{\pi}$), and the frame energy ($E'_{\sigma}$) together with the total energy ($E$) around the optimized bond length ($r_0$). The basis set is 6-311G.[32] The calculation has been carried out on an IBM RS/6000-590 computer using

Table 1. Influence of Geometry Change on Partitioned Energies

| | GD[a)] | CHF[b)] |
|---|---|---|
| $E$ | I+II+III+IV | None |
| $E_{\pi}$ | I+II+III+IV | None |
| $E_{\sigma}{}'$ | I+II+III+IV | None |
| $\langle T_{\pi}\rangle$ | II+III+IV | None |
| $\langle V_{\mathrm{eN}}\rangle_{\pi}$ | I+II+III+IV | None |
| $\langle V_{\mathrm{ee}}\rangle_{\pi}$ | II+III+IV | None |
| $\langle V_{\mathrm{ee}}\rangle_{\pi-\sigma}$ | II+III+IV | None |

a) Geometry-distortion method. b) Constrained Hartree–Fock method.

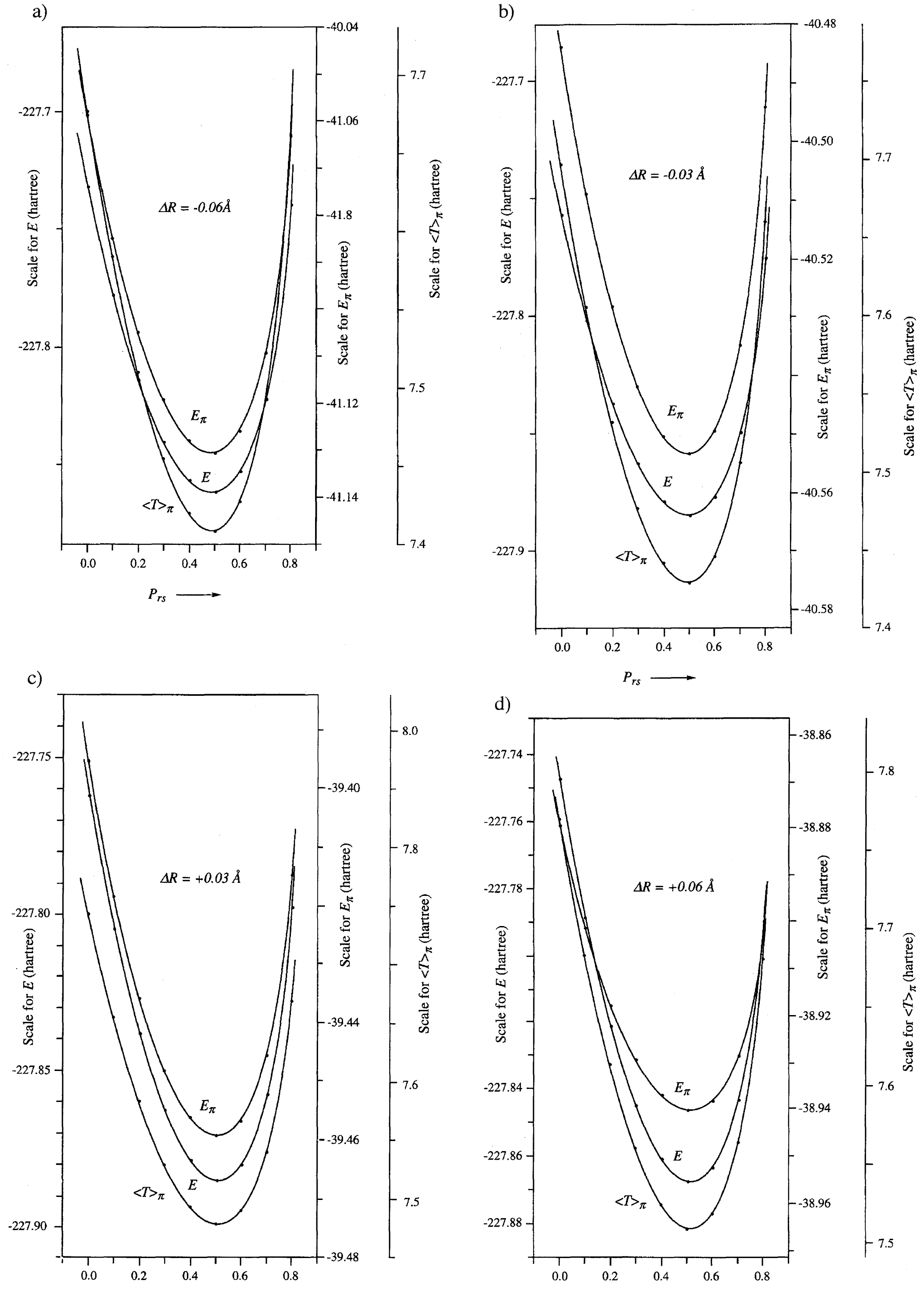
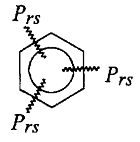


Fig. 1. Changes of $E$, $E_\pi$, and $\langle T\rangle_\pi$ as functions of $P_{rs}$'s of three every-other bonds when benzene is distorted along the $A_{1g}$ coordinate. The basis set is STO-3G. As for $\Delta R$=0 Å, see Fig. 2a.



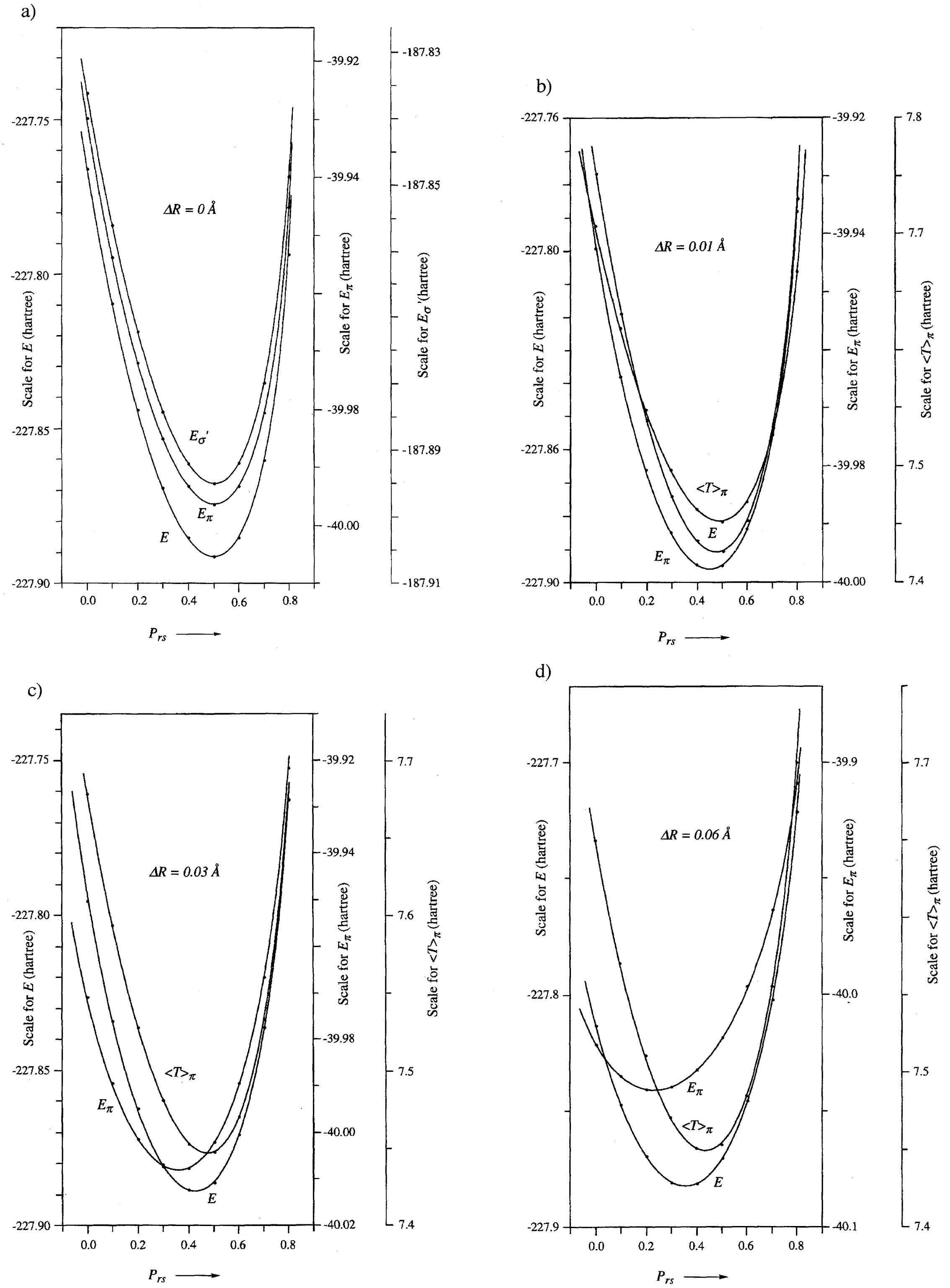


Fig. 2. Changes of $E$, $E_{\pi}$, and $\langle T\rangle_{\pi}$ as functions of $P_{rs}$'s of three every-other bonds when benzene is distorted along the $B_{2u}$ coordinate. The basis set is STO-3G.

the GAUSSIAN-90 package[33] to which we added subroutines for energy-partitioning and the constrained HF calculation.

As the bond length is increased, $E'_{\sigma}$ decreases near-linearly while $E_{\pi}$ increases near-linearly: They are balanced at $r_0$. The kinetic energy of π electrons ($\langle T\rangle_{\pi}$), on the contrary, does not have much change because this term does not have the Class I geometry influence. The partial derivatives (forces) of π-electronic energy and the σ-frame energy are, corresponding to near linearity of their energy curves, almost constant at an absolute value of ca. 2.5 hartree/Bohr. They are exactly balanced at $r_0$. Namely, the π-electron system wants to bond more closely while the σ frame opposes this and both reach the compromised bond length at $r_0$.[34]

**Benzene.** Benzene has two vibrational modes that keep the planar geometry. One is the $A_{1g}$ mode that shrinks or expands the benzene ring keeping the $D_{6h}$ symmetry, and therefore, is not a distortive coordinate concerning the localization/delocalization of π electrons (Scheme 2). The other is the $B_{2u}$ mode that involves an equal amount of stretching and shrinking of two adjacent carbon bonds at the same time and is regarded as the pure distortive coordinate. Any other coordinate concerning the geometry deformation of benzene is a combination of such fundamental modes. In the previous paper, we obtained the potential-energy surfaces of $E$, $E_\pi$, and $E'_\sigma$ concerning deformation of benzene: It was shown that there were a countless number of reaction coordinates for deformation that either lowered or increased the π energy. We examined how $E$, $E_\pi$, and $\langle T\rangle_\pi$ change by the degree of constraint on the π electron flow under deformed geometry. The deformation was imposed along the $A_{1g}$ and $B_{2u}$ coordinates.

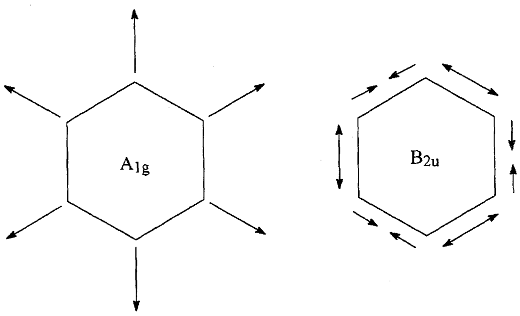
**Benzene with $D_{6h}$ Symmetry.** Figure 1 shows the energy changes as functions of bond orders of π electrons of three alternant bonds when benzene is distorted along the $A_{1g}$ coordinate. The basis set was STO-3G[35] because of the reason described in the previous paper.[36] Ordinary SCF calculation (i.e., that without constraint) gives the π bond order of 0.50446 ($P_{rs}{}^0$) at the optimized geometry. From the figure it is understood that at any distortion, all energies show the lowest values at $P_{rs}{}^0$. This simply proves that the π electrons in benzene have a propensity for the uniform distribution at any $A_{1g}$ coordinate.

The kinetic energy of π electrons ($\langle T\rangle_\pi$) has the lowest value at $P_{rs}{}^0$ in accord with the total and π energies. Comparison of the scales in the figure shows that the $\langle T\rangle_\pi$ term has the largest change and therefore is the major source for energetic behaviours of other two terms. Since the kinetic energy is a measure of delocalization, it may be deduced that the π electrons of benzene have the tendency to delocalize uniformly at the $D_{6h}$ symmetry.

**Distorted Benzene.** Figure 2 shows the case when the benzene ring is distorted along the $B_{2u}$ coordinate. A sharp contrast to the former case is that those partitioned energies behave differently: As the distortion is increased, the differences of those minimum-energy points for the partitioned energies become prominent. At $\Delta R$ being 0.06 Å, *the bond orders corresponding to the minima of the* $E$, $E_\pi$, *and* $\langle T\rangle_\pi$ *terms are 0.35537, 0.23498, and 0.43926, respectively.* Namely, each term has its own minimum.

Table 3 shows gradients of partitioned energies with respect to $P_{rs}$ when $\Delta R$ is 0.06 Å along the $B_{2u}$ coordinate and when $P_{rs}$ is 0.35537 ($P_{rs}{}^0$, the point at the total energy being minimum). That the $\mathrm{d}E/\mathrm{d}P_{rs}$ term shows the null zero at $P_{rs}{}^0$ means that the electronic structure is determined as giving a stationary value with respect to $E$ at the given geometry: This is a natural consequence due to the Hartree–Fock–Roothaan equation which is derived by the variation principle concerning orbital coefficients. Let us look at the global values.

The $\langle T\rangle$ and $\langle V_{ee}\rangle$ terms have negative gradients while



Scheme 2. Normal stretching modes in benzene.

Table 3. Gradients of Partitioned Energies with Respect to π-Bond Order When $\Delta R$ is 0.06 Å along the $B_{2u}$ Coordinate and When $P_{rs}$ is 0.35537

| E | $\langle T\rangle$ | $\langle V\rangle$ | $\langle V_{ee}\rangle$ | $V_{NN}$ |
|---|---|---|---|---|
| 0 | −493 | 721 | −228 | 0 |
| $E_\pi$ | $\langle T\rangle_\pi$ | $\langle V_{eN}\rangle_\pi$ | $\langle V_{ee}\rangle_\pi$ | |
| 204 | −498 | 770 | 128 | |
| $E'_\sigma$ | $\langle T\rangle_\sigma$ | $\langle V_{eN}\rangle_\sigma$ | $\langle V_{ee}\rangle_\sigma$ | $2\times\langle V_{ee}\rangle_{\sigma-\pi}$ |
| −204 | 5 | −49 | 36 | −392 |

Table 2. Partitioned Energies and Their Partial Derivatives at Shifted Coordinates from $r_0$ in Ethylene[a]

| $r-r_0$[b] | −0.06 | −0.03 | −0.01 | 0 | 0.01 | 0.03 | 0.06 |
|---|---|---|---|---|---|---|---|
| $\Delta E$ | 13.4[c] | 3.2[c] | 0.3[c] | −78.019444[d] | 0.3[c] | 2.9[c] | 10.9[c] |
| $\Delta E_\pi$ | −413.5 | −202.0 | −66.3 | −7.155364[d] | 65.3 | 193.0 | 377.4 |
| $\Delta E'_\sigma$ | 426.9 | 205.2 | 66.7 | −70.864081[d] | −65.0 | −190.1 | −366.5 |
| $\Delta\langle T\rangle_\pi$ | 127.3 | 60.8 | 19.7 | 1.932826[d] | −19.1 | −55.5 | −106.0 |
| $\partial E/\partial R$[e] | −0.18 | −0.08 | −0.03 | 0. | 0.02 | 0.07 | 0.13 |
| $\partial E_\pi/\partial R$[e] | 2.75 | 2.62 | 2.54 | 2.51 | 2.47 | 2.40 | 2.29 |
| $\partial E'_\sigma/\partial R$[e] | −2.92 | −2.70 | −2.57 | −2.51 | −2.44 | −2.33 | −2.16 |
| $\partial\langle T\rangle_\pi/\partial R$[e] | −0.88 | −0.81 | −0.76 | −0.74 | −0.72 | −0.67 | −0.61 |

a) The basis set is 6-311G.[32] b) Difference from $r_0$ (=1.320012 Å). c) Difference from the value at $r_0$ in kJ mol$^{-1}$. d) Actual value at $r_0$ in au. e) In au (Hartree/Bohr). The partial derivatives are obtained by numerical derivation, i.e., for example, the derivative at $R$ is given by $\frac{\partial E_X}{\partial R} = \frac{E_X(R+\Delta R, q_0 - E_X(R-\Delta R, q_0)}{2\Delta R}$ where $\Delta R$ is set at 0.001 Å and where $q_0$ represents that all other geometrical parameters are fixed.

$\langle V_{\text{eN}} \rangle$ has a positive one towards increasing $P_{rs}$. This means that the kinetic energy of electrons and the two-electron potential energy would be lowered while the one-electron potential energy would be increased by a greater delocalization of $\pi$ electrons. In other words, the amount of delocalization of $\pi$ electrons is given by the energetic balance of those energies. The behaviors of those terms may be interpreted as follows: Delocalization of electrons releases the kinetic-energy pressure[37,38] and lowers the two-electron potential energy between $\pi$ and $\sigma$ electrons. However, such a delocalization brings forth a poorer distribution of electrons around a nucleus producing a higher potential energy.

When $E$ is partitioned into $E_\pi$ and $E'_\sigma$ according to Eqs. 1, 7, and 8, their gradients are exactly balanced (simply because $\mathrm{d}E/\mathrm{d}P_{rs}$ is null). The contribution from the $\sigma$ frame looks large if one considers that the constraint is put on the $\pi$-electron flow. Look at the partitioned terms of $\sigma$ electrons. The derivatives of $\langle T \rangle_\sigma$, $\langle V_{\text{eN}} \rangle_\sigma$, and $\langle V_{\text{ee}} \rangle_\sigma$ are found to be quite small compared to those of $\pi$ electrons. The major contribution to the $E_\sigma{}'$ term comes from the $\sigma$–$\pi$ interaction ($-196\ \text{kJ mol}^{-1}\ \text{au}^{-1}$).

The $\pi$-electron terms show dominant changes. The $E_\pi$, $\langle V_{\text{eN}} \rangle_\pi$, and $\langle V_{\text{ee}} \rangle_\pi$ have positive gradients while $\langle T \rangle_\pi$ has a negative one with respect to $P_{rs}$. Since again the kinetic energy is a measure of electron delocalization, this indicates the situation that the $\pi$ electrons themselves tend to delocalize more uniformly, but the delocalization is restricted by such potentials as those from one and two electrons. Namely, the $\pi$ electrons have the propensity of delocalization but such a propensity is restricted by the circumstances. This happens at any distortion along the $B_{2u}$ coordinate. This conclusion is in sharp contrast to that given by Shaik, Hiberty, and coworkers:[8—11] According to them, the *distortive* propensity of $\pi$ electrons is weakened by the circumstance.

## Concluding Remarks

Resonance between double bonds has been considered a phenomenon of $\pi$ electron system. To study resonance by ab initio MO theories, one has to extract the energy of $\pi$ electrons from the total energy. Since the total bond order consists of the sum of those for $\pi$ and $\sigma$ electrons in an unsaturated hydrocarbon with a planar structure, it can be partitioned into the energy of $\pi$ electrons and other as Eq. 1. This type of partitioning has been used to understand the resonance in benzene. However, there is no consensus on how to define 'the $\pi$ energy'. Besides, the geometry contribution to 'the $\pi$ energy' is not taken into account. In this article, we have examined the latter problem.

Resonance may be understood by analyzing the relationship between the $\pi$-electronic structure and its energy. 'Relationship' inevitably involves changes of related terms. If one varies the geometry of the system to change the $\pi$-electronic structure, the problem is whether or not the change of the $\pi$-electronic energy thus obtained corresponds to that by the change of the $\pi$-electronic structure. Our examination shows that there are four classes of geometry influence on the $\pi$-electronic energy. Three of them are directly coupled with nuclear coordinates and disguise the very term which one needs to analyze. To avoid such geometry effect, we proposed the use of the constrained Hartree–Fock equation.

The role of the $\pi$ electrons in benzene was discussed. In $D_{6h}$ benzene, which should be distinguished from a distorted benzene, the $\pi$ electrons favor the symmetric uniform distribution independently of the C–C bond length and the partitioning method of 'the $\pi$ energy'. If benzene is distorted along the $B_{2u}$ coordinate, the uniform distribution of $\pi$ electrons is destroyed.

Analysis of gradients of partitioned energies with respect to the bond order has been carried out. If one accepts the idea that the kinetic energy of electron is a measure of delocalization, it is concluded that $\pi$ electrons themselves favor a more uniform distribution even at distorted benzene, but this is opposed by the one-electron and two-electron potentials. Namely, the $\pi$ electrons can be a driving force toward the uniform distribution in a distorted benzene. This conclusion is a sharp contrast to that given by Shaik, Hiberty, and coworkers.[8—11]

## References

1) For Part II, see Ref. 36.

2) J. C. Slater, *Phys. Rev.*, **37**, 481 (1931).

3) L. Pauling, *J. Am. Chem. Soc.*, **53**, 1367 (1931).

4) E. Hückel, *Z. Elektrochem.*, **43**, 752, 827 (1937).

5) G. W. Wheland, "Resonance in Organic Chemistry," Wiley, New York (1995).

6) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York (1961).

7) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York (1966).

8) P. C. Hiberty, S. S. Shaik, J. -M. Lefour, and G. Ohanessian, *J. Org. Chem.*, **50**, 4657 (1985).

9) S. S. Shaik, P. C. Hiberty, J. -M. Lefour, and G. Ohanessian, *J. Am. Chem. Soc.*, **109**, 363 (1987).

10) S. S. Shaik, P. C. Hiberty, G. Ohanessian, and J. -M. Lefour, *J. Phys. Chem.*, **92**, 5086 (1988).

11) P. C. Hiberty, *Top. Curr. Chem.*, **153**, 27 (1990).

12) H. Kollmar, *J. Am. Chem. Soc.*, **101**, 4832 (1979).

13) An eigenfunction ensures that the wave function is that of a standing wave for the physical state defined by the Hamiltonian (in this case, an SCF Hamiltonian).

14) H. Ichikawa and H. Kagawa, *Int. J. Quantum Chem.*, **52**, 575 (1994).

15) A. Mukherji and M. Karplus, *J. Chem. Phys.*, **38**, 44 (1963).

16) W. B. Brown, *J. Chem. Phys.*, **44**, 567 (1966).

17) a) N. Björnå, *J. Phys. B*, **4**, 424 (1971); *J. Phys. B*, **5**, 721 (1972); *J. Phys. B*, **5**, 732 (1972); b) N. Björnå, *Mol. Phys.*, **24**, 1 (1972).

18) R. S. Mulliken and R. G. Parr, *J. Chem. Phys.*, **19**, 1271 (1951).

19) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York (1969).

20) D. R. Hartree, *Proc. Cambridge Philos. Soc.*, **24**, 89 (1928); V. Fock, *Z. Phys.*, **61**, 126 (1930); C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

21) N. C. Baird, *J. Org. Chem.*, **51**, 3908 (1986).

22) K. Jug and A. M. Köster, *J. Am. Chem. Soc.*, **112**, 6772

(1990).

23) E. C. Glendening, R. Faust, A. Streitwieser, K. P. C. Vollhardt, and F. Weinhold, *J. Am. Chem. Soc.*, **115**, 10952 (1993).

24) K. Jug and M. Matuschewski, *Int. J. Quantum Chem.*, **49**, 197 (1994).

25) H. Ichikawa and H. Kagawa, *J. Phys. Chem.*, **99**, 2307 (1995).

26) L. Pedersen and K. Morokuma, *J. Chem. Phys.*, **46**, 3941 (1967).

27) D. E. Magnoli and J. R. Murdoch, *Int. J. Quantum Chem.*, **22**, 1249 (1982).

28) R. G. Parr and J. E. Brown, *J. Chem. Phys.*, **49**, 4849 (1968).

29) The scale error ($\gamma$) is the difference of the scale factor ($\eta$) from 1 ($\gamma=\eta-1$).

30) H. Ichikawa and A. Shigihara, *Bull. Chem. Soc. Jpn.*, **61**, 1837 (1988).

31) H. Ichikawa and K. Sameshima, *Bull. Chem. Soc. Jpn.*, **63**, 3248 (1990); H. Ichikawa and Y. Ebisawa, *J. Am. Chem. Soc.*, **107**, 1161 (1985).

32) R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.*, **72**, 650 (1980).

33) M. J. Frisch, M. H. Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. Defree, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol, and J. A. Pople, "GAUSSIAN 90," Gaussian, Inc., Pittsburgh (1990).

34) It should be noted that the change of π-electronic energy seems to be far greater than that of chemical experience: a displacemant of 0.06 Å from $r_0$ corresponds to the energy of the dissociation of a single bond. This is because π-electronic energy does not include the effect of nuclear displacement.

35) W. J. Hehre, R. F. Ditchfield, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **52**, 2769 (1970).

36) H. Ichikawa and H. Kagawa, *Bull. Chem. Soc. Jpn.*, **70**, 61 (1997).

37) M. J. Feinberg, K. Ruedenberg, and E. L. Mehler, "Advances in Quantum Chemistry," ed by P. Löwdin, Academic Press, New York (1970), Vol. 5, p. 27.

38) K. Ruedenberg, "Localization and Delocalization in Quantum Chemistry," ed by O. Chalvet, R. Daudel, S. Diner, and J. R. Malrieu, Reidel, Dordrecht (1975), Vol. 1, pp. 223—245.