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Yirong Mo and Sigrid D. Peyerimhoff

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Theoretical analysis of electronic delocalization

Yirong Mo^{a)} and Sigrid D. Peyerimhoff

Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstrasse 12, D 53115 Bonn, Germany

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A block-localized wave function method is introduced to evaluate the electronic delocalization effect in molecules. The wave function for the hypothetical and strictly localized structure is constructed based on the assumption that all electrons and primitive basis functions can be divided into several subgroups; each localized molecular orbital is expanded in terms of primitive orbitals belonging to only one subgroup. The molecular orbitals belonging to the same subgroup are constrained to be mutually orthogonal, while those belonging to different subgroups are free to overlap. The final block-localized wave function at the Hartree–Fock level is expressed by a Slater determinant. In this manner, the energy difference between the Hartree–Fock wave function and the block-localized wave function can be generally defined as the electronic delocalization energy. The method is applied to two cases. The first concerns the resonance stabilization in the allyl ions. We find that the vertical resonance energies for the planar cation and anion are -45.7 (or -44.7) and -46.7 (or -48.2) kcal/mol at the HF/6-31G* (or 6-31+G*) level, respectively. Their rotational barriers are decomposed in terms of conjugation, hyperconjugation, steric effect, and pyramidalization. The $n \rightarrow \sigma^*$ negative hyperconjugation in the staggered allyl anion is very strong and stabilizes the system by as much as -13 kcal/mol. The second concerns the hyperconjugation effect in propene. Our calculations suggest that the theoretical hyperconjugation energy in propene is about -5 kcal/mol, which is close to the experimental estimate (-2.7 kcal/mol) derived from the hydrogenation heats of propene and ethylene. Comparisons between the results based on the present block-localized wave function method and those based on the natural bond orbital method are presented and discussed. The examples demonstrate that the block-localized wave function method can be employed as a useful model to analyze chemical bondings and intuitive concepts. © 1998 American Institute of Physics. [S0021-9606(98)02329-0]

I. INTRODUCTION

The study of electronic delocalization in a molecule or within a system of molecules has been an active research area in chemistry not only for experimentalists but also for theoreticians. It is well established that delocalization of electrons from one part of a system into other areas can stabilize the system. This feature was intuitively characterized by Pauling¹ with the concept of resonance and was later on developed further by Wheland and others.² While the σ electronic delocalization (or hyperconjugation) was elusive at that time and was only discussed in general, the π -conjugation received numerous theoretical studies. According to Pauling's resonance theory, a π -conjugated system can be described by a set of resonance structures, and each resonance structure can be graphically represented with a Lewis structure, in which every electron is strictly localized on one atom or between two atoms. The resonance energy is the energy difference between the real system, whose wave function is composed of all possible resonance structures, and its related most stable resonance structure.

The quantitative study in this regard was pioneered by Mulliken and Parr,³ who evaluated the energy of a Kékulé

structure (namely 1,3,5-cyclohexatriene) by replacing the three delocalized π molecular orbitals (MOs) in benzene with three nonresonating ethylenelike π MOs. A similar approach was later employed by Daudey *et al.*⁴ and by Kollmar,⁵ and more recently by Glendening *et al.*⁶ Very importantly, Kollmar⁵ also considered the electronic relaxation of the σ -frame in the hypothetical localized structures and predicted that a similar treatment can be extended to study the chemical interaction between molecules. However, theoretical studies following this direction are still very sparse since in the framework of the frequently used self-consistent field (SCF) calculations all MOs are in principle extended over the entire system, i.e., delocalized.

In order to avoid the above difficulty, an experimentally determined resonance energy, which is estimated from the heats of hydrogenation of a conjugated system and its reference molecules containing nonresonating double bonds, is broadly used,^{1,2,7,8} while theoretically homodesmic⁹ and isodesmic¹⁰ reactions are designed to discuss the aromaticity or antiaromaticity in cyclic conjugated systems.^{11–13} However, in these model reactions both the steric effect and the hyperconjugation effect are inevitably involved and cannot be distinctly screened from the reaction enthalpies. Dewar's definition¹⁴ of resonance energy as the difference in heats of formation between a cyclic conjugated compound and its corresponding classical polyene is an alternative, but it also

^{a)}On leave from the Department of Chemistry, Xiamen University, Xiamen, Fujian 361005, Peoples Republic of China.

combines both π and σ effects. A more suitable refinement is to determine the aromaticity or antiaromaticity by the difference of the resonance energies, which are based on Pauling's definition, between a cyclic conjugated compound and its corresponding classical polyene.¹⁵ Thus in order to discuss the effect of electronic delocalization in the framework of conjugation and aromaticity, theoretical studies on hypothetically localized structures are highly desired.

From the theoretical viewpoints, electronic delocalization can be expressed as the interaction between some occupied fragment MOs in one part of a molecule and some unoccupied fragment MOs in another part of the molecule. By defining the natural Lewis structure constructed from filled natural localized orbitals, Weinhold *et al.*¹⁶ developed a very beautiful and general method called the natural bond orbital (NBO) method to study the inter- and intramolecular interaction. The interaction energy can be determined by deleting some antibonding orbitals from the basis set and recalculating the total energy, or it can be directly approximated by simple second-order perturbative expressions. The natural Lewis structure in the NBO method in fact corresponds to the most stable resonance structure according to Pauling's resonance theory. Schleyer *et al.*¹⁷ have studied the hyperconjugation effect in many systems using the NBO deletion procedure. Since the NBO method uses SCF wave functions for the real molecules to deduce the wave functions for the Lewis structures, the electronic structures of the Lewis structures are not relaxed. As a result, the delocalization energies computed by the NBO method may be overestimated to some extent. A more elaborate way to study the electronic delocalization effect is to relax the wave functions for the Lewis structures via SCF too.

Electronic delocalization can also be viewed as the mutual penetration of electrons belonging to different parts of a system. By restricting the physical region for every electron's movement, one can obtain a hypothetically localized molecule, which can be used as a reference for its corresponding real delocalized molecule. For several years, one of us has followed Pauling's original definition of resonance energy and used modern *ab initio* valence bond (VB) theory to study some conjugated systems.¹⁸ To get the strictly localized wave function, we defined a type of localized one-electron orbitals, or bond-distorted orbitals (BDOs),^{18c} each of which is expanded in terms of the primitive basis functions centered on two bonded atoms or only one atom (for a lone pair). Complementary, the overlap-enhanced orbitals (OEOs), which are extended to all primitive basis functions, are used as one-electron orbitals for the delocalized wave function. All BDOs or OEOs are individually optimized in the SCF steps. The computation efforts in the *ab initio* VB method prohibit us from studying systems containing more than 14 active electrons and thus it is difficult to analyze the hyperconjugation effect using this procedure, since normally all σ and π electrons are involved and the total number of active electrons is much larger than 14.

The localized MOs (LMOs)¹⁹ obtained from canonical MOs via unitary transformation are not strictly localized on bonds and possess a mixture of orthogonalization and delocalization tails. While there is no unique way to discriminate

the above two kinds of tails, only the delocalization tail makes contribution to the electronic delocalization effect. Edmiston²⁰ suggested a simple method to evaluate the delocalization energy by truncating the tails and then reorthogonalizing the MOs. However, an alternative way is to divide a system into several mutually interacting subgroups and restrict the expansion of each MO in only one subspace. This idea has been developed by several groups^{21–24} to study the intermolecular interactions based on various algorithms.

In this paper we propose a block-localized wave function (BLW) method to study the electronic delocalization within a molecule, but this procedure may also be extended to the investigation of the charge transfer between molecules.²⁵ The routine SCF wave function is used to describe the real delocalized system and its corresponding hypothetically localized reference is represented with a BLW. In the context of the resonance theory a BLW may correspond to a resonance structure, but it is more general. Like many theoretical methods in chemistry, the BLW method is a model theory intended to analyze the chemical bonding features in molecules and establish the concepts of π -conjugation and σ -hyperconjugation on more solid grounds. The present BLW method is also a generalization of our recently proposed orbital deletion procedure (ODP),^{15,26} which can only be applied to carbocations and boranes.

In Sec. II we introduce the BLW method and its algorithm, followed by two detailed applications in Sec. III. We select the allyl cation and the anion to demonstrate the utilities of the BLW method by analyzing the conjugation in planar structures and the hyperconjugation in staggered structures. A very classical example, namely the hyperconjugation in propene, is also studied with various basis sets. The discussion and the advantages of this method are presented in Sec. IV.

II. METHODOLOGY

Electronic delocalization can be viewed as the electron flow from one part of a molecule to another part of the molecule. In more technical terms, delocalization is the interaction between the occupied strictly LMOs describing one part of a molecule and the virtual strictly LMOs describing another part of the molecule. While orthogonal atomic orbitals (AOs) themselves may be truly localized,²⁷ the orthogonal LMOs resulting from a unitary transformation of the canonical MOs are generally not fully localized and possess two types of tails, namely the delocalization tail and the orthogonalization tail. Obviously, orthogonalization of nonorthogonal orbitals will not alter the molecular energy if the molecular wave function is expressed by a Slater determinant. Thus we omit both types of tails at the very beginning by imposing the restriction that each MO is expanded in a subgroup of the complete space of basis functions and allowing MOs belonging to different subgroups to overlap freely. We suppose that for a given system the entire orbital space with m primitive basis functions is partitioned into k subspaces. The i th subspace consists of $\{\chi_{i\mu}, \mu = 1, 2, \dots, m_i\}$ basis functions and is filled with n_i electrons (at present we set $n_i = \text{even}$). The total numbers of electrons (N) and primitive basis functions (m) are

$$N = \sum_{i=1}^k n_i \quad \text{and} \quad m = \sum_{i=1}^k m_i, \quad (1)$$

respectively. The MOs $\{\varphi_{ij}, j=1,2,\dots,m_i\}$ for the i th subspace are expanded in terms of $\{\chi_{i\mu}\}$,

$$\varphi_{ij} = \sum_{\mu=1}^{m_i} C_{ij\mu} \chi_{i\mu} \quad (i \in [1,k], j \in [1,m_i]). \quad (2)$$

The subsequent BLW is defined using a Slater determinant as

$$\begin{aligned} \Psi^{\text{Loc}} &= \hat{A}(\varphi_{11}^2 \varphi_{12}^2 \cdots \varphi_{1n_1/2}^2 \varphi_{21}^2 \cdots \varphi_{i1}^2 \cdots \varphi_{in_i/2}^2 \cdots \varphi_{kn_k/2}^2) \\ &= \hat{A}(\Phi_1 \Phi_2 \cdots \Phi_k), \end{aligned} \quad (3)$$

which is subject to

$$\langle \varphi_{ij} | \varphi_{iq} \rangle = \delta_{jq}, \quad (4)$$

while the MOs between different blocks are not imposed to be orthogonal.

At this point a remark about nonorthogonal orbitals may be adequate. Although mathematically orthogonal orbitals do have many advantages over nonorthogonal orbitals, as argued by Weinhold and Carpenter,²⁷ nonorthogonal orbitals are still very useful for chemical concepts since the picture of the overlap between orbitals that results in bonding or repulsion is vivid and intuitive for chemists. Due to the overwhelming advantage of orthogonal orbitals for computational aspects, most of the quantum chemistry methods are based on orthogonal orbitals. The renaissance of the VB methods during the past ten years^{18,28} shows advantages of nonorthogonal orbitals for convergence patterns. Furthermore, we can find recent publications which attempt to delete the tails of LMOs^{20,29} or NBOs³⁰ in order to revive the concept of orbitals' overlap, which is associated with the attractive (between occupied and virtual orbitals) or repulsive (between occupied orbitals like lone pairs) forces.

Based on Eqs. (1)–(4), it is apparent that the transformation matrix T from the entire basis to the occupied MOs can be written as

$$\varphi = \chi \begin{pmatrix} \mathbf{T}_1 & \mathbf{0} & \cdots & \mathbf{0} \\ \mathbf{0} & \mathbf{T}_2 & \cdots & \mathbf{0} \\ \cdots & \cdots & \cdots & \cdots \\ \mathbf{0} & \mathbf{0} & \cdots & \mathbf{T}_k \end{pmatrix} = \chi \mathbf{T}, \quad (5)$$

where \mathbf{T}_i is a $m_i \times n_i/2$ matrix and \mathbf{T} is a $m \times N/2$ matrix. It is known that a specific resonance structure is not an eigenstate of the Hamiltonian and that the resonance theory itself is a model theory which simply enables chemists to understand the relationship between molecular structures and molecular properties in a transparent and instinctive way. Accordingly, the BLW as defined in Eq. (3) is also not an eigenstate of the Hamiltonian and we can only evaluate its expectation value of energy, which can be written as²³

$$E^{\text{Loc}} = \text{Tr}[\mathbf{D}^* \mathbf{h}] + \text{Tr}[\mathbf{D}^* \mathbf{F}(\mathbf{D})], \quad (6)$$

where the density matrix \mathbf{D} is

$$\mathbf{D} = \mathbf{T}(\mathbf{T}^+ \mathbf{S} \mathbf{T})^{-1} \mathbf{T}^+, \quad (7)$$

and \mathbf{S} is the overlap matrix for the primitive basis functions.

The ensuing problem is how to optimize the BLW to make the total energy Eq. (6) be a stationary point with regard to \mathbf{T} . Here we use the Jacobi transformation to optimize the occupied MOs one by one. At first, we make an initial guess $\{\varphi_{ij}^o\}$, which may be generated from the SCF calculations for fragments or block-orthogonalized MOs after deleting the tails in LMOs.²⁰ Clearly, the final optimal MOs $\{\varphi_{ij}\}$ is simply the result of unitary transformations of $\{\varphi_{ij}^o\}$ for each subgroup; in other words, a mixture of the virtual MOs $\{\varphi_{ij}^o, j=n_i/2+1,\dots,m_i\}$ into the occupied MOs $\{\varphi_{ij}^o, j=1,\dots,n_i/2\}$. We take the optimization of an arbitrary occupied MO φ_{ij} as an example. After orthogonalizing the $N/2-1$ MOs in Eq. (3), except φ_{ij}^o , and obtaining $\{\varphi'_l, l=1,\dots,N/2-1\}$,

$$\varphi' = \varphi^{\text{ij}} \langle \varphi^{\text{ij}} | \varphi \rangle^{-1/2}, \quad (8)$$

where φ^{ij} is derived from φ by omitting φ_{ij} , we use the following projection operator \hat{P}_{ij} to make φ_{ij}^o orthogonal to $\{\varphi'_l\}$,

$$\hat{P}_{ij} = 1 - \sum_{l=1}^{N/2-1} |\varphi'_l\rangle \langle \varphi'_l|, \quad (9)$$

and obtain

$$\varphi'_{ij} = \hat{P}_{ij} \varphi_{ij}^o. \quad (10)$$

Thus, the energy expression Eq. (6) can be rewritten and the terms related to φ'_{ij} are

$$\begin{aligned} E_{ij} &= 2 \langle \varphi'_{ij} | \mathbf{h} | \varphi'_{ij} \rangle + \langle \varphi'_{ij} \varphi'_{ij} | \varphi'_{ij} \varphi'_{ij} \rangle \\ &\quad + 2 \sum_{l=1}^{N/2-1} [2 \langle \varphi'_{ij} \varphi'_{ij} | \varphi'_l \varphi'_l \rangle - \langle \varphi'_{ij} \varphi'_l | \varphi'_{ij} \varphi'_l \rangle]. \end{aligned} \quad (11)$$

Making a Jacobi rotation between φ_{ij}^o and a virtual orbital φ_{io}^o ,

$$\begin{pmatrix} \tilde{\varphi}_{ij} \\ \tilde{\varphi}_{io} \end{pmatrix} = \begin{pmatrix} \cos \theta_{ijo} & \sin \theta_{ijo} \\ -\sin \theta_{ijo} & \cos \theta_{ijo} \end{pmatrix} \begin{pmatrix} \varphi_{ij}^o \\ \varphi_{io}^o \end{pmatrix}, \quad (12)$$

and replacing φ_{ij}^o in Eq. (11) with $\tilde{\varphi}_{ij}$, we can determine θ_{ijo} using the following minimization condition,

$$\frac{\partial E_{ij}(\theta_{ijo})}{\partial \theta_{ijo}} = 0. \quad (13)$$

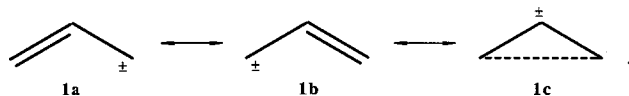
The above formula corresponds to an one-dimensional search. By successive rotation between φ_{ij}^o and all virtual MOs in the i th subspace, we obtain an optimal occupied MO φ_{ij} . While all occupied MOs can be optimized in a similar way, one iteration for the optimization of the BLW includes $\sum_{i=1}^k (m_i - n_i/2) n_i/2$ successive Jacobi rotations. When the total energy converges to a threshold (e.g., 10^{-6} a.u.), the SCF calculation finishes and the final BLW is printed out. In this work, GAUSSIAN-94 software and its internal basis sets³¹ are used to perform normal SCF calculations as well as to produce the primitive integrals which are necessary to perform our BLW calculations. It is worthwhile to emphasize that in the present BLW method, each BLW unit does not

incorporate the virtual MOs of other units. Thus electronic delocalization effects are fully deactivated. By orthogonalizing all block LMOs subject to some localization criteria, we may finally derive the orthogonal LMOs with only orthogonalization tails.

III. APPLICATIONS

A. Allyl cation and anion

The allyl cation and the allyl anion can be described by three resonance structures **1a**–**1c**, where the charge is formally centered on one of three carbon atoms,

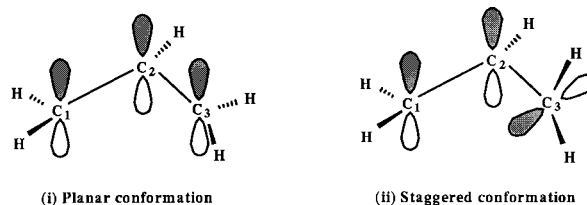


Obviously, due to the long distance between the terminal carbon atoms, **1c** is not energetically favorable compared with **1a** and **1b**, which are isoenergetic. In other words, **1a** or **1b** are the most stable resonance structures and the resonance energy in the allyl cation or anion can be derived from the difference between HF energy of the allyl cation or anion and the energy of **1a** or **1b**, according to the original definition.^{1,2}

Recently there have been some controversies^{32,33} over the importance of resonance stabilization in the allyl systems, which is essential to understanding their rotational barriers. Wiberg *et al.*³² analyzed the rotational barriers of the two ions in terms of electronic delocalization and electrostatic interaction and concluded that “whereas the cation had significant resonance stabilization, the anion had little stabilization.” In sharp contrast to this conclusion, Gobbi and Frenking³³ reinvestigated these systems using the topological analysis of the electron density distribution and the NBO partitioning scheme and claimed that the planar forms are strongly stabilized by π resonance and “the conjugation contribution to the resonance stabilization is comparable in magnitude.” To explore some quantitative justifications for the above controversy, we^{18d} used the *ab initio* VB method to study the allyl systems with the 6-31G* basis set at the level equivalent to full π -CI (configuration interaction) in MO theory and found that in the planar allyl cation and the anion their vertical resonance energies (VRE's) are -55.7 and -52.3 kcal/mol, respectively. Thus our results support Gobbi and Frenking's argument. In the previous paper,^{18d} we also proposed an energy decomposition scheme to analyze the rotational barriers in the allyl ions. However, it should be noted that in our VB calculations the σ -frames are frozen and the estimation of the hyperconjugation energies is very crude. Now, with the BLW method we can study the electronic delocalization effects and discern various energy contributions to the rotational barriers in the allyl ions in a more reasonable and detailed way than before.^{18d}

We construct the BLWs for the planar and staggered conformations, which are graphically shown below. For the staggered conformation (ii), the rotated methylene group at C_3 is perpendicular to the main plane. The trigonally bonded carbon atom C_3 is of C_s symmetry locally and we are still able to define a strictly LMO centered on C_3 , which is vacant

in the allyl cation and doubly occupied (lone pair) in the allyl anion.



In the planar conformation, there exists π -delocalization which can be characterized as a three-center–two-electron π bond for the cation and a three-center–four-electron π bond for the anion. For the resonance structure **1a**, the entire set of AOs and the electrons can be partitioned into three subgroups, of which the first is the σ frame, while the second is a two-center π bond between C_1 and C_2 and the last is the LMO (or more strictly, AO) centered on C_3 . The delocalized (HF) wave function and the BLW are

$$\Psi_p(\text{HF}) = \hat{A}(\sigma 1 b_1^2 1 a_2^{0/2})$$

and

$$\Psi_p(3\text{BLW}) = \hat{A}(\sigma \pi_{C_1 C_2}^2 n_{C_3}^{0/2}), \quad (14)$$

respectively. In the BLW, the σ -MOs are naturally orthogonal to the π -MOs, but $\pi_{C_1 C_2}$ and n_{C_3} are nonorthogonal to each other. If we keep the geometry unchanged, the energy difference between $\Psi_p(\text{HF})$ and $\Psi_p(3\text{BLW})$ is defined as the VRE¹⁸ or quantum mechanical resonance energy (QMRE) in some literatures,

$$\text{VRE} = E(\Psi_p(\text{HF})) - E(\Psi_p(3\text{BLW})). \quad (15)$$

After we rotate a methylene group around the CC bond 90° from the planar conformation (i) to the staggered conformation (ii), we can similarly construct the delocalized (HF) wave function and the BLW with three subgroups for the staggered conformation as

$$\Psi_s(\text{HF}) = \hat{A}(\sigma' 2 a''^2 10 a'^{0/2})$$

and

$$\Psi_s(3\text{BLW}) = \hat{A}(\sigma' \pi_{C_1 C_2}^2 n_{C_3}^{0/2}), \quad (16)$$

respectively. However, in the above BLW, the σ' -MOs are now nonorthogonal to $\pi_{C_1 C_2}$ and n_{C_3} (here the symbol σ' is used only for the sake of simplicity and consistency and does not represent the true symmetry), while $\pi_{C_1 C_2}$ and n_{C_3} are orthogonal to each other. Consequently, in the staggered conformation there exist two types of electronic delocalization. The first type is the hyperconjugation between the $\pi_{C_1 C_2}$ orbital and the MO of π -symmetry constructed from the staggered methylene group, which may be labeled as $\pi_{C=C} \rightarrow \pi_{C_2}^* / \pi_{C=C}^* \leftarrow \pi_{CH_2}$. To evaluate the energetic influence of the above hyperconjugation on the system, we combine the σ' and $\pi_{C_1 C_2}$ into one subgroup and construct a BLW with two subgroups,

$$\Psi'_s(2\text{BLW}) = \hat{A}(\sigma' \pi_{C_1 C_2}^2 10 a'^{0/2}), \quad (17)$$

thus this part of hyperconjugation energy (HCE) is

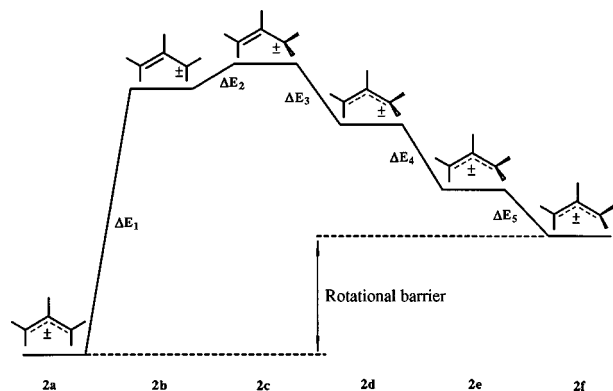


FIG. 1. Energy decomposition scheme for the rotational barriers in the allyl ions.

$$\text{HCE1} = E(\Psi_s(\text{HF})) - E(\Psi'_s(2\text{BLW})). \quad (18)$$

The second type of electronic delocalization results from the interaction between the σ -frame and the orbital centered on C_3 . This sort of interaction is normally called $\sigma \rightarrow \pi^*$ hyperconjugation in the cation and $n \rightarrow \sigma^*$ negative hyperconjugation in the anion. Again we can construct a BLW with two subgroups to evaluate the delocalization energy, namely,

$$\Psi''_s(2\text{BLW}) = \hat{A}(\sigma' 2a''^2 n_{\text{C}_3}^{0/2})$$

and

$$\text{HCE2} = E(\Psi_s(\text{HF})) - E(\Psi''_s(2\text{BLW})). \quad (19)$$

The total electronic delocalization energy is the sum of HCE1 and HCE2, which also should be equal to the energy difference between the HF wave function and the BLW with three subgroups. Our final results below manifest that this additivity rule indeed exists well.

With the above establishment, we now decompose the rotational barriers of the allyl ions into several physically understandable terms including conjugation, hyperconjugation, steric effect, and pyramidalization. The successive steps are: (1) Based on the planar geometry (C_{2v} symmetry) **2a** optimized at the HF/6-31G* level, we deactivate the π conjugation to obtain a strictly localized structure **2b** (Fig. 1). The energy variation is represented as ΔE_1 , which is the reverse of VRE; (2) Rotate the methylene group to a 90° twisted structure **2c**, which is still a strictly localized structure. The geometry of **2c** is the same as the optimized staggered structure at the HF/6-31G* level. During this step, the energy variation ΔE_2 uniquely results from the steric effect; (3) Delocalize the electrons between $\pi_{\text{C}=\text{C}}$ and π_{CH_2} , and as a consequence the electronic structure evolves from **2c** to **2d** and the lowering energy is labeled as ΔE_3 , which is equal to HCE1; (4) Delocalize the electrons among σ -frame MOs and the orbital centered on C_3 , which is empty in the allyl cation and doubly occupied in the allyl anion. The energy variation ΔE_4 between **2d** and **2e** is equal to HCE2; (5) Relax the molecular structure to **2f**, which is optimized at the HF level with the same basis set. The energy variation originates from the pyramidalization of C_3 in the rotated methylene group, which will stabilize the system by ΔE_5 . This successive de-

TABLE I. Energy contributions for the rotational barriers (RBs) in the allyl ions (kcal/mol).

	Basis set	ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE_5	RB
C_3H_5^+	HF/6-31G*	45.7	3.6	-6.8	-8.3	-0.2	34.0
	HF/6-31+G*	44.7	4.2	-6.8	-8.2	-0.1	33.8
C_3H_5^-	HF/6-31G*	46.7	3.2	-4.8	-12.9	-11.8	20.4
	HF/6-31+G*	48.2	-1.7	-5.7	-13.5	-6.0	21.2

composition scheme is pictorialized in Fig. 1 and the numerical results are listed in Table I. Since long-range functions are assumed to be important for anions, we redo the above steps using the 6-31+G* basis set and the subsequent results are also presented in Table I.

Now we are able to examine the electronic delocalization in the planar structures of the allyl ions at the *ab initio* level. Comparing the values of ΔE_1 in Table I, we can learn that both the cation and the anion have very significant resonance stabilization and the magnitudes are essentially the same. Thus our present data again support Gobbi and Frenking's³³ argument and disagree with Wiberg *et al.*'s³² statement. In our previous studies using the VB method,^{18d} the VRE's were -55.7 and -52.3 kcal/mol with the 6-31G* basis set for the allyl cation and anion, respectively, where the calculations were performed with the frozen- σ -frame approximation. Similarly, we can also adopt this approximation here to reevaluate the VRE's with the 6-31G* basis set and the results are -54.7 and -51.4 kcal/mol for the two ions, respectively, which are in excellent agreement with the VB results. These results and the comparison among them suggest two points. The first point is that the relaxation of the σ -frame is by no means negligible for ions and the localization of formal charges should remarkably affect the electron distribution inside σ -frames. The second point is that the electron correlation among the π electrons may have very limited influence on the resonance energies.

For the staggered structures, the electronic delocalization is also very impressive. We first check the interaction between $\pi_{\text{C}=\text{C}}$ and π_{CH_2} . ΔE_3 in Table I is calculated according to Eq. (18). This type of hyperconjugation in the cation is presumably stronger than that in the anion. A simple explanation is the electrostatic attraction. Since in the cation the formal positive charge on C_3 is expected to lower the energy level of the antibonding orbital $\pi_{\text{CH}_2}^*$, the movement of the electrons from $\pi_{\text{C}=\text{C}}$ to $\pi_{\text{CH}_2}^*$ will be enhanced, which correspondingly will stabilize the cation. In the anion, on the other hand, the formal negative charge on C_3 should suppress this kind of electron flow, thus the hyperconjugation will not stabilize the system as strongly as in the cation. To keep the decomposition scheme as shown in Fig. 1 consistent, we evaluate ΔE_4 with the energy difference between the BLW's with two subgroups [Eq. (17)] and with three subgroups [Eq. (16)]. If we use Eq. (19), e.g., to calculate ΔE_4 with 6-31G*, the values for the cation and the anion are -8.1 and -12.7 kcal/mol, respectively, which are very close to the data shown in Table I. Although the $\sigma \rightarrow \pi^*$ hyperconjugation in the cation was well recognized in our previous work,^{18d} there we supposed that the $n \rightarrow \sigma^*$ negative hyper-

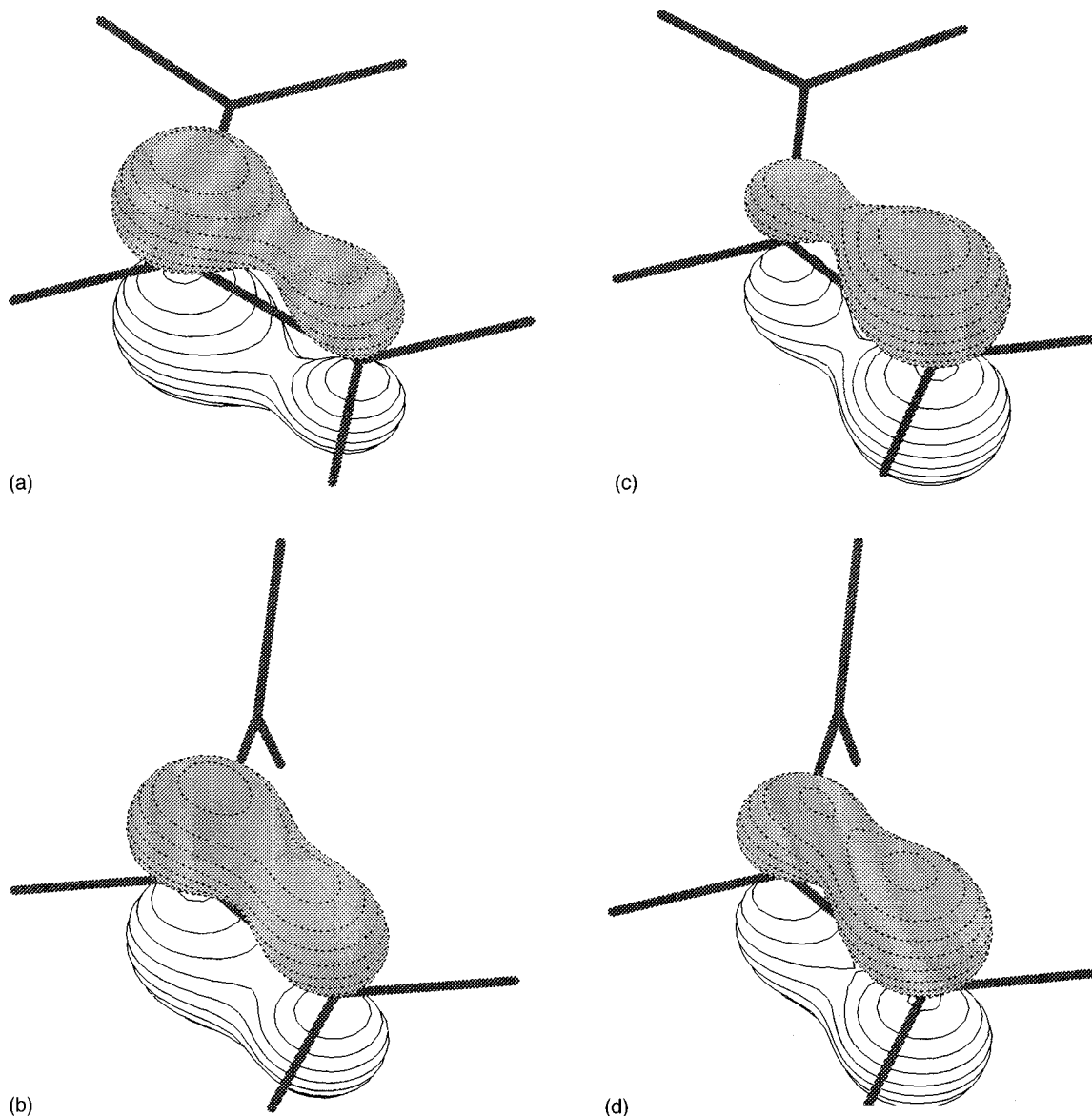


FIG. 2. The electron density maps of the π bonds in the strictly localized allyl ions. (a) In the planar cation; (b) in the staggered cation; (c) in the planar anion; (d) in the staggered anion.

conjugation in the anion was trivial due to the full occupation of the p_{π} orbital on C_3 , while in the cation, this orbital is vacant. However, our present calculations manifest that our previous belief is not entirely right. The negative hyperconjugation in the staggered allyl anion is even 50% stronger than the positive hyperconjugation in the staggered allyl cation. In the literature, there are indeed many theoretical studies on the negative hyperconjugation,^{17a,17b,34} whose rule is widely acknowledged.

The general survey of Table I indicates that there are two energy terms, namely ΔE_4 and ΔE_5 , which are different between the two ions. As we discussed previously,^{18d} the comparison between the geometries of **2e** and **2f** gives a clue. In the cation, the staggered methylene group will approximately retain a planar structure; in other words, C_3 prefers a sp^2 hybridization mode. Thus the relaxation energy will be close to zero. In contrast, in the anion, C_3 will tend to pyramidalize due to the repulsion between the lone pair and

the nearby carbon-hydrogen and carbon-carbon bonds. Thus the hybridization mode of C_3 will switch from sp^2 in the planar structure to sp^3 in the staggered structure.³⁵ The pyramidalization of the terminal carbon will stabilize the staggered allyl anion remarkably.

The strictly localized wave functions also afford us an ideal chance to see how the electrons respond to the structural changes. In Fig. 2 we depicted³⁶ the electron density maps of the LMO $\pi_{C_1C_2}$ in the planar (**2b**) and the staggered (**2c**) structures. Due to the electrostatic interactions, the π electron density in the planar cation significantly polarizes to the middle carbon C_2 , which is adjacent to the positively charged C_3 , while in the allyl anion the π electrons move away from C_2 since the adjacent atom C_3 now formally carries a negative charge. With the rotation of the methylene group, the repulsion between the π electrons and the methylene group in the cation becomes strong and the π electrons

TABLE II. VRE [Eq. (15)] in the planar $C_3H_5^+$ and HCE2 [Eq. (19)] in the staggered $C_3H_5^+$ (kcal/mol).^a

Basis set	VRE	HCE2
STO-3G	-62.7	-11.9
3-21G	-45.9	-8.2
6-31G	-45.1	-8.0
6-31G*	-45.7	-8.1
6-31+G*	-44.8	-8.0
6-311G**	-44.5	-8.4
6-311++G**	-44.3	-8.3
6-311++G(2d,2p)	-41.1	-7.2

^aThe geometries are optimized at the HF/6-31G* level.

will move from C_2 to C_1 ; however, the π population on C_2 is still a little higher than that on C_1 . This movement explains the origin of the steric effect ΔE_2 clearly. The situation in the anion is different again. Apparently in the anion the repulsion between the π electrons and the methylene group is somewhat smaller than the repulsion between the π electrons and the lone pair centered on C_3 , since the electron density moves toward C_3 with the rotation of the methylene group. This should alleviate the steric repulsion. Nevertheless, the increasing of the repulsion between the lone pair and the σ -frame in the staggered structure seems to complicate the whole picture.

Based on the data in Table I, it is seen that the energy terms for the allyl cation change very little from 6-31G* to 6-31+G*, i.e., upon addition of a long-range function. For the anion, although the final rotational barrier is insensitive to the added diffuse functions, two energy terms, ΔE_2 and ΔE_5 , do have obvious variations. The nature of both terms is the steric effect, and by adding diffuse functions, the negative charge can move further away from the nucleus of C_3 . Thus the repulsion between the lone pair and the π bond between C_1 and C_2 is increased and the strictly localized structure will prefer an eclipsed position for these two orbitals. On the other hand, the same reason reduces the stabilization resulting from the pyramidalization of C_3 so that the sum of ΔE_2 and ΔE_5 changes only a little with the addition of long-range functions.

Since our previous ODP method,^{15,26} which can be realized using GAUSSIAN-94 software with small modifications, is a special case of the BLW method, and the ΔE_1 and ΔE_4 in the allyl cation can be easily calculated using the ODP method by deleting the primitive basis functions of π symmetry on the methylene group before SCF, we performed some more calculations with various basis sets up to 6-311++G(2d,2p) to check the basis set effect on the results, which are presented in Table II.

The data in Table II suggest that the estimated delocalization energies ranging from large scale (VRE) to small scale (HCE2) are very consistent and stable with regard to the routinely used basis sets from 3-21G to 6-311++G**. Although there is the obvious possibility that a complete basis will nullify the approximation used in this work, i.e., that the basis functions can be partitioned into several subgroups, this approximation seems to still work-

TABLE III. Comparison between BLW and NBO results with 6-31G*(6-31+G*) basis set (kcal/mol).

		BLW	NBO
$C_3H_5^+$	VRE	-45.7(-44.7)	-84.1(-83.4)
	HCE1	-6.8(-6.8)	-15.6(-15.3)
	HCE2	-8.3(-8.2)	-18.1(-17.9)
$C_3H_5^-$	VRE	-46.7(-48.2)	-90.0(-81.1)
	HCE1	-4.8(-5.7)	-13.6(-14.5)
	HCE2	-12.9(-13.5)	-31.6(-26.3)

able for moderate basis sets and very useful to obtain insights into the chemical bonding mechanism.

As we stated in the pretext, the lack of electronic relaxation for the Lewis structures in the NBO method¹⁶ may overestimate the delocalization energies. To make a comparison with the BLW results, we employed the NBO procedure affiliated with GAUSSIAN-94 to evaluate the delocalization energies in the planar and staggered allyl ions. For the planar allyl cation, the NBO analysis showed that about half an electron delocalizes from the bonding orbital $\pi_{C_1C_2}$ to the antibonding orbital n_{C_3} . So we simply deleted the latter orbital and the subsequent calculation indicated that the half electron has returned into $\pi_{C_1C_2}$. The energy variation is approximately the VRE in the planar $C_3H_5^+$. On the other hand, for the planar anion, about a half electron delocalizes from n_{C_3} to $\pi_{C_1C_2}^*$. Thus the VRE in the anion roughly corresponds to the energy gain after deleting $\pi_{C_1C_2}^*$. For the staggered ions, however, we use the elements deletion procedure in the NBO program to evaluate the two types of hyperconjugation energies separately. The interaction between $\pi_{C=C}$ and π_{CH_2} (HCE1) is estimated by zeroing the four off-diagonal NBO Fock matrix elements connecting the two σ_{CH} (or σ_{CH}^*) in the rotated methylene group and $\pi_{C=C}^*$ (or $\pi_{C=C}$), while the second type of hyperconjugation (HCE2) is derived by zeroing another four off-diagonal elements connecting the four σ -bonding orbitals (or σ -antibonding orbitals) in the ethylene group and n_{C_3} for the cation (or the anion). The results from the BLW and NBO methods are collectively presented in Table III.

For both the strong and the weak interactions, the NBO values are larger than the BLW values. However, it should be noted that it is difficult to judge which set of data is more reliable since there is no direct experimental proofs. In this context it is helpful to resort to the isodesmic reactions for a rough estimate. We calculated the enthalpies of the following isodesmic reactions:



To keep the bonding pattern and environment for every atom as similar as possible on both sides of the above reactions, CH_3^- is forced to be planar. The enthalpies are believed to result in the main from the delocalization energies in the allyl ions. We performed calculations at the HF, MP2(Full), and MP4(SDTQ) levels with all geometries optimized at the HF level with the 6-31G* basis set. Results are given in

TABLE IV. Enthalpies of the isodesmic reactions at various levels with 6-31G* basis set (kcal/mol).^a

Level	For $C_3H_5^+$	For $C_3H_5^-$
HF	-54.1	-44.6
MP2(Full)	-60.1	-48.7
MP4(SDTQ)	-59.8	-48.0

^aThe geometries are optimized at the HF/6-31G* level.

Table IV. The resonance energies estimated with the BLW method are closer to the enthalpies of the above isodesmic reactions than the energies derived from the NBO method. However, it is clear that the enthalpies need not be perfectly comparable to the resonance energies in the allyl ions since not only the structural variations in the isodesmic reactions may make small contributions to the enthalpies, but also there is some electronic delocalization in propene, which is a very typical example to introduce the concept of hyperconjugation.

B. Propene

Qualitatively it is understood that the hyperconjugation effect in propene results from the interaction between the methyl group and the antibonding orbital $\pi_{C=C}^*$ of the double bond and results in the shortening and the strengthening of the single bond connecting the methyl group and the double bond, which consequently stabilize the system. On the other hand, experimental data show that the double bond length in propene (1.342 Å)³⁷ is only very slightly longer than the pure double bond length in ethylene (1.3372 Å),³⁸ which implies that the hyperconjugation effect in propene may be very weak. This claim can be rationalized by the previous analysis of 1,3-butadiene,^{18(e)} where the double bond lengths in the delocalized and localized structures are 1.347 and 1.342 Å, respectively, while the resonance energy is only -7.9 kcal/mol. Experimentally, like the estimate of the conjugation effect in conjugated systems, the hyperconjugation effect in propene is estimated based on the hydrogenation heats of propene and ethylene,

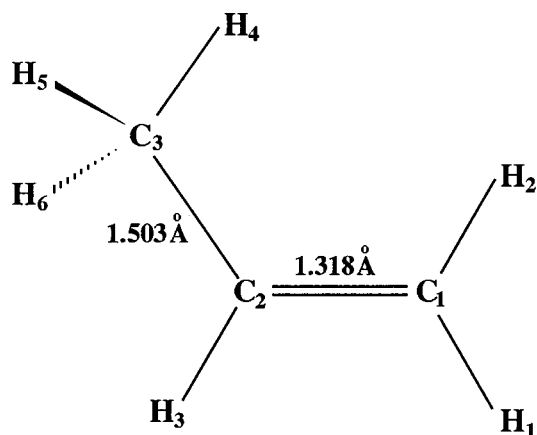
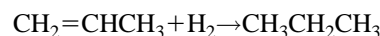


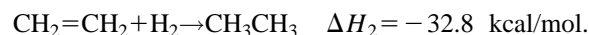
FIG. 3. Geometry of the ground state of propene optimized at the HF/6-31G* level.

TABLE V. Energies of the delocalized and the localized propene^a with different basis sets (a.u.).

Basis set	E_{HF}	E_{BLW}
STO-6G	-116.790 59	-116.784 18
6-31G	-117.028 22	-117.020 94
6-31G*	-117.071 47	-117.063 54
6-31+G*	-117.075 42	-117.066 76
6-311G**	-117.103 41	-117.094 20

^aThe geometry is optimized at the HF/6-31* level.

$$\Delta H_1 = -30.1 \text{ kcal/mol,}$$



Due to the hyperconjugative stabilization in propene, its hydrogenation heat (ΔH_1) is higher than the hydrogenation heat of a pure double bond, which can be well represented by ethylene (ΔH_2). The difference between ΔH_2 and ΔH_1 is -2.7 kcal/mol, which is normally regarded as the experimental HCE in propene. Theoretical studies on the hyperconjugation effect in propene are very scarce.²⁹

Here we apply the BLW method to the most stable conformation of propene (C_s symmetry) as shown in Fig. 3.

The geometry optimized at the HF/6-31G* is in very good agreement with the experimental data³⁶ (e.g., the single and double carbon-carbon bond lengths are 1.508 and 1.342 Å, respectively). The lengths of the two out-of-plane carbon-hydrogen bonds (1.087 Å) in the methyl group are very close to the length of the in-plane carbon-hydrogen bond (1.084 Å), which makes no contribution to the hyperconjugation effect due to the constraint of symmetry. The large angle $\angle C_1C_2C_3 = 125.3^\circ$ with regard to the remaining three $\angle HCC$ angles in the ethylene group originates mainly from the steric effect. From the viewpoint of fragment analysis the methyl group can be regarded as a heteroatom that has a lone pair parallel to the π bond between C_1 and C_2 . Thus the treatment of propene is similar to the case of the planar allyl anion. The HF wave function and the BLW for propene can be constructed as

$$\Psi(HF) = \hat{A}(\sigma' 1 a''^2 2 a''^2)$$

and

$$\Psi(BLW) = \hat{A}(\sigma' \pi_{C=C}^2 \pi_{CH_3}^2). \quad (20)$$

TABLE VI. Vertical hyperconjugation energies in propene^a based on the BLW and NBO methods (kcal/mol).

Basis set	BLW	NBO (scheme 1)	NOB (scheme 2)
STO-6G	-4.0	-13.4	-12.2
6-31G	-4.6	-15.5	-14.4
6-31G*	-5.0	-14.8	-13.7
6-31+G*	-5.4	-14.6	-13.6
6-311G**	-5.8	-16.0	-15.5

^aThe geometry is optimized at the HF/6-31* level.

The energy difference between $\Psi(\text{HF})$ and $\Psi(\text{BLW})$ reflects the vicinal interaction between the π double bond and the adjacent methyl group; in other words, it is the HCE of the methyl group in propene. With the geometry optimized at the HF/6-31G* level, we performed HF and BLW calculations by employing basis sets of different size. The total energies are listed in Table V, while Table VI presents the vertical HCE in propene based on the BLW method. Also, in Table VI we list the NBO results for comparisons.

In the NBO method there are two possible schemes to evaluate the HCE in propene. One (scheme 1) is to delete the three antibonding orbitals, namely $\pi_{\text{C}=\text{C}}^*$ and two σ_{CH}^* corresponding to the $\text{C}_3\text{--H}_5$ and $\text{C}_3\text{--H}_6$ bonds in the methyl group as shown in Fig. 3. The other (scheme 2) is to zero the four off-diagonal NBO Fock matrix elements between the $\pi_{\text{C}=\text{C}}$ (or $\pi_{\text{C}=\text{C}}^*$) and the two σ_{CH}^* (or the two σ_{CH}) in the methyl group. Both schemes can generate very consistent results, as listed in Table VI. The magnitude of the HCE based on the BLW method becomes slightly large with increasing basis set, and similar fluctuation is observed using the NBO method. The difference between the NBO data and the BLW data is very obvious, however. All NBO results are much larger than the BLW results, as already found in the allyl ions. The BLW study yields a value for the HCE which is much closer to the experimental estimate and agrees very well with previous calculations²⁹ based on Edmiston's approach²⁰ (−4.1, −4.7, and −5.1 kcal/mol with the STO-6G, 6-31G, and 6-31G* basis sets). This agreement suggests that the electronic delocalization energy corresponding to the energetic variation by simply deleting the tails of the LMOs, initially proposed by Edmiston,²⁰ may be reliable for the systems with small electronic delocalization effects. The HCE in propene resulting from the BLW method does not have to be exactly the same as the experimental value based on the hydrogenation heats, since small structural differences between propene (propane) and ethylene (ethane) are expected; the energy changes due to these structural differences should be very small, however, as discussed before.²⁹

To illustrate the polarization of the double bond, we depicted in Fig. 4 the electron density map of the block LMO $\pi_{\text{C}=\text{C}}$. Owing to the repulsion between the double bond and the methyl group, the distribution of the electron density around C_1 and C_2 will not be equal as in ethylene, and the π electrons polarize from C_2 to C_1 . Thus the π electron population on the terminal carbon atom is somewhat larger than that on the carbon atom adjacent to the methyl group.

In order to study the quantitative relationship between molecular structures and electronic delocalization effect, we estimated the optimal carbon–carbon bond lengths by varying the related bond lengths with single point calculations while keeping all the other structural parameters fixed at the optimized values from the HF/6-31G* level. Our calculations show that if there were no hyperconjugative interaction in propene, the double and single carbon–carbon bond lengths would be 1.316 and 1.530 Å. These trends have been well recognized and understood for a long time. While the hyperconjugation will very trivially lengthen the double bond (from 1.316 to 1.318 Å), it will shorten the single carbon–carbon bond very significantly from 1.530 to 1.503

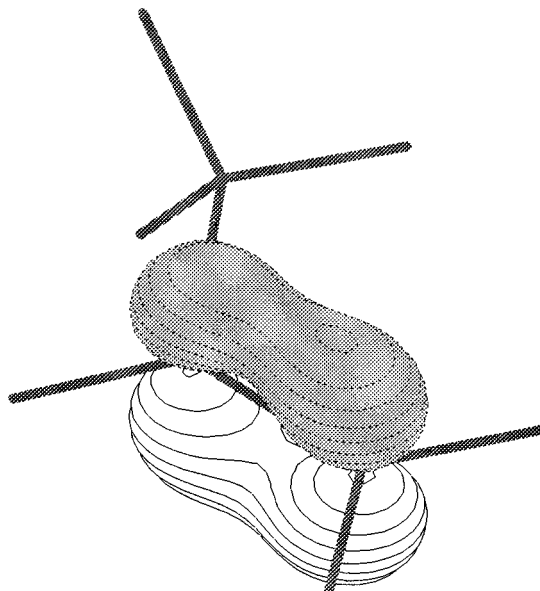


FIG. 4. The electron density map of the π bond in the strictly localized propene.

Å. In fact, the single bond ($\text{Csp}^2\text{--Csp}^3$) length in the optimized strictly localized propene is very close to the single $\text{Csp}^3\text{--Csp}^3$ bond length in ethane (1.527 Å optimized at the HF/6-31G* level) and longer than we have predicted by averaging the optimal $\text{Csp}^2\text{--Csp}^2$ single bond length (1.508 Å) and the $\text{Csp}^3\text{--Csp}^3$ bond length.^{18(e)} For the optimal carbon–carbon bond lengths of the fully localized propene (1.316 and 1.530 Å), the BLW energies are listed in Table VII. Generally, the energy difference between a delocalized structure and its corresponding localized structure whose geometries are optimized individually is defined as the theoretical delocalization energy, to differentiate it from the vertical delocalization energy, which is the energy difference if the geometries for the delocalized and the localized structures are kept the same.¹⁸ Although in the present case we only optimized the carbon–carbon bond lengths, we believe that the remaining structural parameters have little influence on the molecular energy. From Tables VI and VII we observe that the difference between the theoretical HCE and the vertical HCE in propene is about −0.3 kcal/mol, which reflects the relief of the repulsive force between the double bond and the methyl group.

TABLE VII. Total energies of the optimal localized propene^a and the theoretical hyperconjugation energies (THCE's) with different basis sets.

Basis set	E_{BLW} (a.u.)	THCE (kcal/mol)
STO-6G	−116.784 93	−3.6
6-31G	−117.021 27	−4.4
6-31G*	−117.064 01	−4.7
6-31+G*	−117.067 24	−5.1
6-311G**	−117.094 75	−5.4

^aThe carbon–carbon bond lengths are optimized at the BLW/6-31G* level.

IV. DISCUSSIONS

In this paper we introduced the BLW method. The central idea of this method is to partition the basis functions and electrons into several subgroups, then expand every LMO in terms of the basis functions from only one subgroup. These subgroups are by no means noninteracting; in fact, they interact with one another via electrostatic and Pauli exchange effects. Similar to a HF wave function, we use one Slater determinant, which employs the LMOs as the one-electron basis, to describe the hypothetical localized structure. In the BLW, the LMOs belonging to the same subgroup are subject to orthogonality while no such constraint is imposed in the LMOs belonging to different subgroups. All block LMOs can be reorthogonalized to obtain a set of new orthogonal LMOs subject to some localization criteria.¹⁹ The final orthogonal LMOs are expected to contain only orthogonalization tails and no delocalization tails. Thus the comparison between the BLW and the HF wave function will allow the analyzing of the electronic delocalization within molecules and possible charge-transfer effect between molecules. As in other partition schemes, there is an element of arbitrariness, since it is not possible to decide *a priori* to which subgroup certain basis functions belong if basis functions are centered off the nuclei (e.g., bond functions), or if the basis set become complete. In these cases, we believe that the prenatural AOs (pre-NAOs), as introduced and constructed as the first step in the NBO method by Weinhold *et al.*,¹⁶ are the best starting point for orbital partition. The present orbital partition scheme should be applicable for all standard basis sets, which are generally optimized for each atom separately.

We demonstrated the utilities of the BLW method with two applications. In the first case, we confirmed the equal importance of electronic delocalization in the allyl cation and the anion. Furthermore, a very detailed energy decomposition scheme for the rotational barriers is available now and the results support the high stabilization due to the negative hyperconjugation in the staggered conformation of the anion. The strong $n \rightarrow \sigma^*$ negative hyperconjugation plus the pyramidalization of the carbon atom in the rotated methylene group make the rotational barrier in the anion lower than in the cation. Such kind of analysis is very valuable to justify at the *ab initio* level the parameterization in the molecular mechanics methods, where the force field is basically composed of bonded terms and nonbonded terms.³⁹ While the nonbonded terms deal with the electronic delocalization directly, few works have ever been done to unambiguously prove the legitimization of these terms at the *ab initio* level. The second application concerns the hyperconjugation effect in propene, which is much weaker than the conjugation effect in the allyl ions. Since the hyperconjugation in propene is related to the interaction between the double bond and the adjacent methyl group, we partition the space of π orbitals into two subgroups. One subgroup is used to describe the pure double bond and the other is employed to describe the π -symmetric orbital in the methyl group. The BLW calculations showed that the theoretical value for the HCE in propene is about -5 kcal/mol, which is reasonably close to the experimentally estimated value -2.7 kcal/mol. Further calculations demonstrated that the single carbon-carbon bond

length is sensitive to the hyperconjugation effect as well as to steric effects.

The study has not yet incorporated the effect of electron correlation. A transparent and initial way to study the charge-transfer effects at the correlated level would be to perform singly excited CI calculations with the BLW as reference wave function. Generally, we may classify the excited configurations into two classes. The first class concerns only the electronic excitation inside one subgroup, while the second class includes the excitation between two subgroups. Obviously, one could further classify the second class into more subclasses, and each subclass refers to the excitation from one specific subgroup to another specific subgroup. This kind of treatment is a natural extension of Mulliken's concept regarding charge-transfer complexes.⁴⁰ Work in this regard will be reported later.

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