



# Rotational barriers in alkanes

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Rotational barriers in alkanes play a fundamental role in the stereochemistry and dynamics of alkanes and others such as proteins. Yet, the proper understanding of their origin which is central to chemical theory remains controversial. Currently, there are two major competing models to interpret the barriers, one is the steric repulsion model and the other is hyperconjugation model. No consensus has been reached. It is thus important to critically examine the quantum mechanical approaches producing conflicting data which lead to these models, as various approximations must be introduced to derive either the steric or hyperconjugative interaction energies in these approaches. The hyperconjugation model is largely based on the popular natural bond orbital (NBO) analysis which can estimate individual interactions between occupied bond orbitals and vicinal unoccupied antibond orbitals. But the concern is that these localized bond orbitals are projected out from a delocalized wavefunction and thus nonoptimal. Alternatively, recent studies with other methods notably the *ab initio* valence bond theory where localized orbitals are self-consistently optimized reinstate the conventional steric repulsion model, although the NBO method correctly predicts that there is stronger hyperconjugative interaction in staggered structures than in eclipsed structures. After all, it is the steric effect rather than the hyperconjugation effect that plays a dominating role in rotational barriers in alkanes. © 2011 John Wiley & Sons, Ltd. *WIREs Comput Mol Sci* 2011 1 164–171 DOI: 10.1002/wcms.22

## INTRODUCTION

Saturated alkanes exhibit low barriers (3–10 kcal/mol) to rotations about single C–C bonds with preference for *trans*-gauche conformers. For the example of ethane, the staggered conformer is more stable than the eclipsed form by 2.9 kcal/mol with a slight shortening of the C–C bond.<sup>1–4</sup> For butane, however, based on the relative positions of two terminal methyl groups, there are two different staggered conformers with respect to the central C–C bond, one is the anticonformer and the other is the gauche conformer, in addition to two different eclipsed conformers with either H/CH<sub>3</sub> or CH<sub>3</sub>/CH<sub>3</sub> eclipsed. Because both staggered conformers are minima at the energy profile, the continuing rotation around the central C–C bond starting from the anticonformer experiences two successive barriers of 3.3 and 5.1 kcal/mol, respectively.<sup>5</sup> Due to low rotational barriers, minima corresponding to various

equilibrium configurations of an alkane molecule can transform to each other at extremely high rates at ambient condition.<sup>6</sup> But, it has also been well recognized that rotations around C–C bonds in alkanes have important consequences in molecular structure and dynamics.

Among linear or cyclic alkanes, both ethane and butane are textbook prototypes for the introduction of steric hindrance in organic chemistry, but the contributing effects to conformational isomerism remain controversial as there is no rigid and generally accepted approach to measure the effects either experimentally or computationally.<sup>7</sup> The understanding of rotational barriers in alkanes is central to conformational chemistry and the proper mathematical description of the torsional potential is fundamental to the development of force fields to obtain an accurate representation of three-dimensional structures of molecules.<sup>8,9</sup> It has been shown that changes to the torsional potentials can severely affect the accuracy of forces fields,<sup>9–11</sup> which have been playing a critical role in computer simulations of protein and DNA molecules as well as inorganic, organic (notably polymer), and even nanomaterials. Of particular relevance to the torsional potential includes the reproduction and prediction of phase behavior of chemicals such as alkanes.<sup>12</sup> At the molecular mechanical level, the

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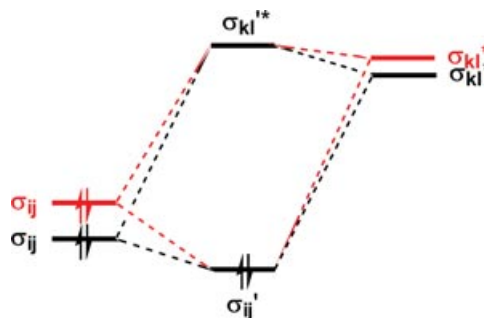
potential function is usually expanded in a Fourier series in the torsional angle  $\varphi$  as

$$V(\varphi) = \frac{1}{2} \sum_n V_n (1 - \cos n\varphi) \quad (1)$$

Quantum mechanically, however, as rotations does not involve any bond making or breaking, the corresponding barriers can be derived fairly accurately even at quite low levels, largely due to the comparability of the electron correlation effect on isomers of the same molecule.<sup>13,14</sup> Although both experiments and theories can produce comparable values for rotational barriers, fundamental insights into the nature of torsional barriers can only be gleaned with a number of necessary approximations. As such, controversies linger for this seemingly simple but enormously significant problem and various explanations have been proposed to elucidate the origin of rotational barriers, based on different approximations introduced in the process of treatment. In this sense, the reliability of an explanation solely relies on the approximations leading to this explanation. Here we briefly review the evolution of the understanding of the rotational barriers in alkanes by focusing on the typical examples of ethane and butane.

## ETHANE

The hindered internal rotation about the C–C bond in ethane was arguably first (see, the historical review in Ref 3) discovered in the thermodynamic measurements by Kemp and Pitzer in 1936,<sup>1,2</sup> who showed that only when an internal rotation barrier of about 3 kcal/mol is taken into account, one could obtain thermodynamic quantities in agreement with experiment.<sup>3</sup> Later experimental and theoretical studies further confirmed the staggered not the eclipsed structure as the lower energy one,<sup>15–25</sup> and a revised experimental value of  $2.90 \pm 0.03$  kcal/mol were proposed.<sup>26</sup> In the early days of theoretical chemistry, many insights were gained based on Lewis's valence theory, where molecules are composed of chemical bonds sharing two electrons between two atoms. It was consequently envisioned that the ethane rotation barrier results from the repulsive Pauli exchange interactions between electrons in the two methyl groups, or more specifically, among the C–H bonds.<sup>27</sup> This intuitive, steric repulsion theory fits to our simple stick–ball model for molecules very well, and was quantitatively confirmed by Sover et al.'s analyses by means of bond-orbital model in the 1960s,<sup>22</sup> and still remains a popular and illuminating explanation in organic chemistry textbooks.



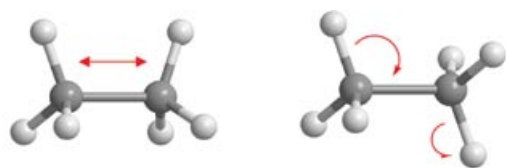
**FIGURE 1** | Illustration of the hyperconjugation effect. The red lines refer to nonoptimal bond orbitals.

In terms of quantum theory, steric repulsion is often assumed as a combination of Pauli exchange and electrostatic interactions between two objects. But when the interacting parts belong to the same molecular system, it becomes extremely tricky how to convincingly evaluate the steric interaction, as the definition of parts *per se* is open to questions. Nevertheless, various energy decompositions based on the quantum mechanics, albeit more or less arbitrary, have been proposed to explore the factors governing the staggered conformation of ethane.<sup>13,21,25,28</sup> For instance, Allen decomposed the total energy into the attractive contribution (the nuclear–electron attractive potential energy  $V_{ne}$ ) and repulsive contribution (the electron kinetic energy  $T$  plus the electron–electron  $V_{ee}$  and nuclear–nuclear  $V_{nn}$  repulsive energy) and concluded that the repulsion controls the rotational barrier in ethane.<sup>13,21</sup> Within the Density Functional Theory (DFT) framework, recently Liu hypothesized that the total energy density functional can be partitioned into the steric, electrostatic, and quantum effects and showed that both steric and electrostatic effects are comparable and repulsive in the conformational change from the staggered to the eclipsed ethane.<sup>28</sup>

Alternatively, the possible role of hyperconjugation effect in the ethane rotation barrier has been widely speculated ever since the introduction of the hyperconjugation concept by Mulliken in 1939.<sup>23,29–31</sup> Hyperconjugation corresponds to the interaction between an occupied bond orbital  $\sigma_{ij}$  and a vicinal unoccupied antibond orbital  $\sigma_{kl}^*$ , which results in an occupied delocalized orbital  $\sigma'_{ij}$  ( $\lambda \ll 1$ )

$$\sigma'_{ij} = \sigma_{ij} + \lambda \sigma_{kl}^* \quad (2)$$

and the stabilization of the system, as shown in Figure 1. The critical issue here is how to derive the optimal localized orbitals  $\sigma_{ij}$  and  $\sigma_{kl}^*$ , which are used as references for the estimation of the hyperconjugative stabilization energy.



(a) Repulsion model (b) Hyperconjugation model

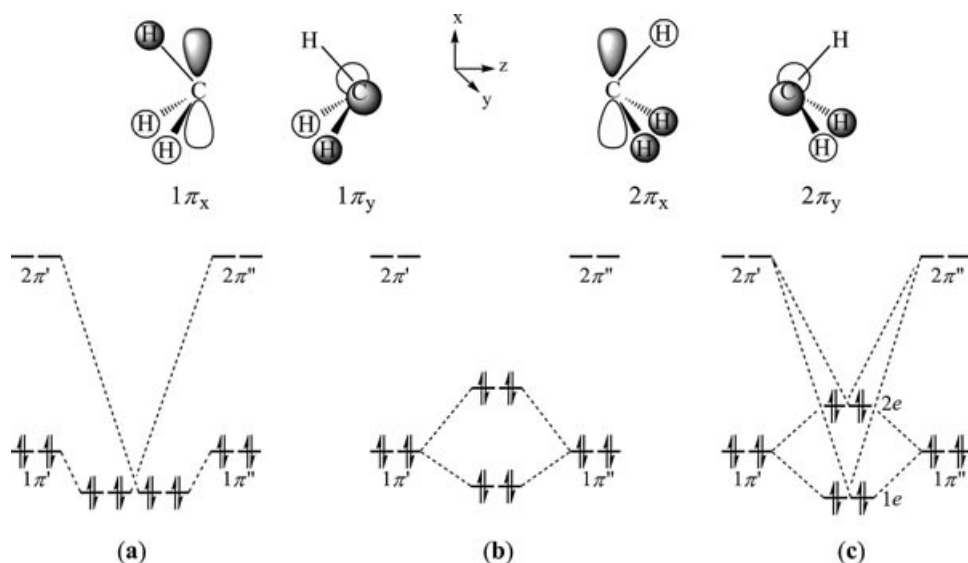
**FIGURE 2** | Major competing explanations for the ethane rotation barrier.

Brunck and Weinhold first approximated the molecular orbitals (MOs) in terms of linear combination of bond orbitals at the semi-empirical level and proposed that the shortening of the central C–C bond involving vicinal hyperconjugative interaction between the  $\sigma_{\text{CH}}$  occupied orbitals in one methyl group and the  $\sigma_{\text{CH}}^*$  antibonding orbitals in the other methyl group stabilizes the staggered conformation and thus is the dominant force responsible for the rotational barrier in ethane.<sup>24</sup> Later, Weinhold et al. further developed the natural bond orbital (NBO) approach at the *ab initio* level that verified their initial semi-empirical results.<sup>32,33</sup> Bader et al. offered an alternative explanation, in terms of the polarization of charge density in the central carbon–carbon bond as a result of variations in symmetry from  $S_3$  in staggered to  $C_3$  in eclipsed structures.<sup>25</sup> Although other explanations have been proposed, essentially there are two major competing models to interpret the origin of the ethane rotation barrier,<sup>34–36</sup> one is the steric repulsion model where in general the steric interaction is a sum of the Pauli exchange and electrostatic interaction (including the dispersion energy), and the other is hyperconjugation model, as illustrated in Figure 2. Recently, this debate was rekindled by Goodman and coworkers.<sup>37–40</sup> On the basis of the NBO method, they carried out a ‘flexing’ analysis in terms of energies associated with structural, steric, exchange, and hyperconjugative interactions during a methyl rotation. By removing the  $\sigma_{\text{CH}}-\sigma_{\text{CH}}^*$  hyperconjugative interaction, they claimed that steric repulsion favors the eclipsed conformation, thus repulsive forces have no effect on the preference for a staggered conformation.<sup>40</sup> This finding is in accord with previous studies by Weinhold and coworkers,<sup>33,41</sup> who similarly employed the NBO analysis and found that Pauli exchange energy destabilizes the eclipsed structure less than the staggered structure of ethane. In fact, the qualitative bonding picture presented by the NBO method is rather convincing and attractive, as a C–H bond orbital  $\sigma_{\text{CH}}$  has a better overlap with another  $\sigma_{\text{CH}}^*$  antibonding orbital at the staggered posi-

tion than at the eclipsed position.<sup>42</sup> But the question is how this qualitative picture can be appropriately translated to quantitative data.

Goodman et al.s’ claim that steric repulsion favors the eclipsed structure inspired more studies.<sup>43–45</sup> Bickelhaupt and Baerends first evaluated the Pauli and electrostatic interactions explicitly using a wavefunction composed of fragmental MOs of methyl groups and showed that although hyperconjugation does favor the staggered ethane conformer, Pauli exchange repulsions are the dominant force responsible for the rotational barrier in ethane.<sup>43</sup> As *ab initio* valence bond (VB) theory can uniquely define an electron-localized state with the Heitler–London–Slater–Pauling (HLSP) function, we explicitly computed the hyperconjugation energy in ethane using *ab initio* VB theory and demonstrated that, in accord with Bickelhaupt and Baerends’s findings, although the hyperconjugation effect indeed favors the staggered conformation, its contribution to the barrier is only secondary.<sup>44</sup> We note that in the VB calculations, the wavefunction (i.e., all orbitals) for the electron-localized state was self-consistently optimized. In contrast, the NBO approach is a post-SCF analysis where the localized bond orbitals are projected out from the electron delocalized state without further optimization. Nonoptimal orbitals which lie at higher energy levels than optimal orbitals could result in the severe overestimation of hyperconjugation energies, as illustrated in Figure 1 with red lines.

A reasonable and maybe ultimate solution to the nature of the ethane rotation barrier within the MO theory, however, was laid out by Mulliken himself when he proposed the hyperconjugation concept in 1939, though he also cautioned that ‘hyperconjugation in ethane should have little or no direct effect in restricting free rotation’ since it is ‘only of second order’.<sup>29</sup> For either staggered structure ( $D_{3d}$  symmetry) or eclipsed structure ( $D_{3h}$  symmetry), hyperconjugation in ethane involves eight electrons which occupy the degenerate *e*-symmetric orbitals, as the rest electrons occupy the fully symmetric orbitals and thus are unaffected by the rotation. In the absence of any hyperconjugation, each set of *e* orbitals with four electrons is localized on one  $\text{CH}_3$  group. As Figure 3 shows, hyperconjugative interaction involves charge transfer from occupied group-localized orbitals to vicinal unoccupied group-localized orbitals (i.e.,  $1\pi' \rightarrow 2\pi''$  and  $1\pi'' \rightarrow 2\pi'$ ), which consequently stabilizes the system, whereas steric effect reflects the interaction between neighboring occupied orbitals ( $1\pi'$  and  $1\pi''$ ), which generally comprises the classical electrostatic term and the quantum mechanical Pauli exchange repulsion.



**FIGURE 3** | The *e*-symmetric group-localized orbitals of methyl groups in ethane.  $1\pi_x$  and  $1\pi_y$  are degenerate and occupied, whereas the degenerate  $2\pi_x$  and  $2\pi_y$  are unoccupied. Orbital interactions in ethane: (a) hyperconjugative interaction, (b) steric interaction, and (c) overall interactions.

Recently, we realized the Mulliken proposal using our developed block-localized wavefunction (BLW) method which combines the advantages of VB and MO theories and can be regarded as the simplest variant of the VB theory.<sup>46–50</sup> At first, we defined a wavefunction in the absence of hyperconjugative interactions as<sup>51</sup>

$$\Phi_L = \hat{A}(1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 1\pi'^4 1\pi''^4) \quad (3)$$

where  $1\pi'$  and  $2\pi''$  are group-localized orbitals confined to only one of the two methyl groups, respectively, as Mulliken initially suggested. Afterwards, we allow the hyperconjugation between two methyl groups and subsequently the wavefunction evolves to the familiar Hartree–Fock (HF) wavefunction

$$\Psi = \hat{A}(1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 1e^4 2e^4) \quad (4)$$

where the two pairs of degenerate molecular orbitals,  $1e$  and  $2e$ , are delocalized over the entire system or more specifically, combinations of  $1\pi'$ ,  $1\pi''$ ,  $2\pi'$ , and  $1\pi''$ . It should be pointed out that in our BLW computations,  $\Phi_L$  are optimized variationally like  $\Psi$ . At last, the energy difference between the delocalized and localized states reflects the hyperconjugative stabilization

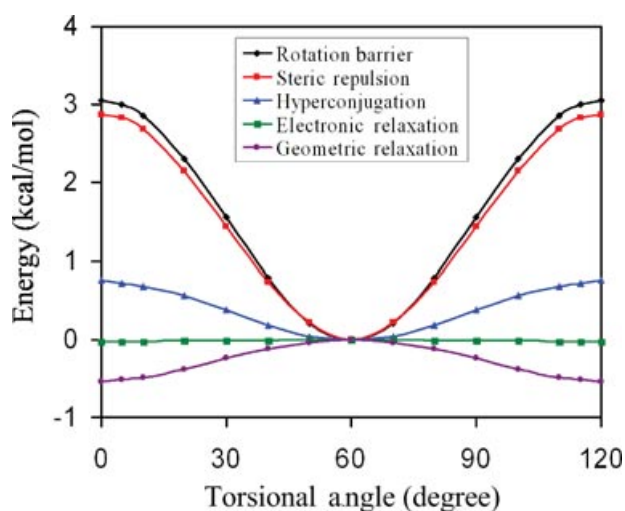
$$E_{bc} = E(\Psi) - E(\Phi_L) \quad (5)$$

Computations once again showed that the hyperconjugation effect does favor the staggered struc-

ture over the eclipsed structure, but it contributes only about 0.8 kcal/mol to the rotational barrier. Significantly, the steric effect was independently estimated by using frozen group-localized orbitals in the process of rigid rotations. Starting from the staggered structure, we froze the orbitals and all structural parameters except the torsional angle, and derived the one-dimensional energy profile for the rigid rotation. The energy change to the eclipsed structure amounts to 2.8 kcal/mol. Similarly, if we started from the eclipsed structure and froze the group-localized orbitals, rigid rotations toward the staggered structure reduce the molecular energy by 2.6 kcal/mol. The difference between 2.8 and 2.6 kcal/mol is due to the longer C–C bond distance in the eclipsed structure than in the staggered structure. The sum of hyperconjugation and steric effects (3.4–3.6 kcal/mol) is slightly offset by the geometric relaxation due to the lengthening of the C–C bond. Figure 4 shows the decomposition of the barrier in terms of steric repulsion, hyperconjugation, electronic, and geometric relaxations along the rotation. This picture concurred that the conventional steric repulsion is the dominant factor for the rotational barrier in ethane.

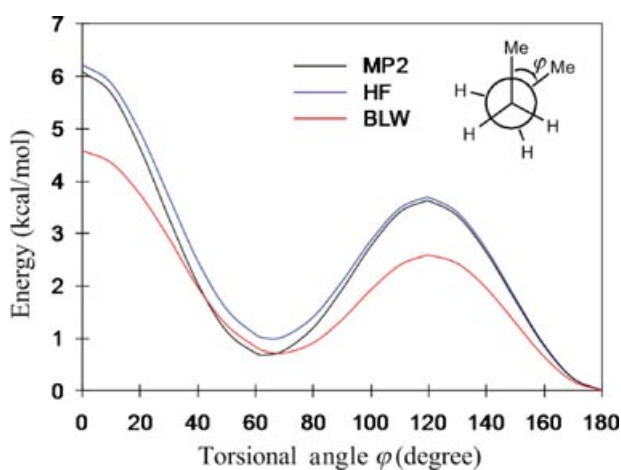
## BUTANE

Rotational barriers are highly sensitive to the local chemical structure of focused C–C bonds, as best exemplified by butane. In the matter of fact, the rotation



**FIGURE 4** | Rotation barrier along with the steric repulsion, hyperconjugation, electronic relaxation, and geometric relaxation energy changes with respect to the torsional angle.

about the central C–C bond of butane is of general interest as it is a prototype for studying longer alkane chains. In general, the preference of stable conformers as well as the rotational barriers is influenced by a few factors, including interactions among substituted groups, bond lengths, and the lone pairs on heteroatoms. Compared with ethane, butane exhibits remarkably different rotational energy profile about the central C–C bond due to the two substituted methyl groups. Simple computations with the basis set of 6–31G(d) at the Second-order Møller-Plesset Perturbation Theory (MP2) and HF levels result in consistent barriers as shown in Figure 5. Starting from the anticonformer ( $\varphi = 180^\circ$ ), the approaching of the two methyl groups is accompanied by two nonequivalent barriers, which are 3.6 or 3.7 and 5.3 or 5.4 kcal/mol at the MP2 or HF level. These data are only slightly higher than the very accurate G2 results 3.3 and 5.2 kcal/mol,<sup>5</sup> indicating the insensitivity of rotational barriers in alkanes to the theoretical level used in calculations. It should be noted that all theoretical studies have resulted in a much higher energy difference between the syn ( $\varphi = 0^\circ$ ) and anticonformers than the experimental estimate (3.78 kcal/mol<sup>52</sup>). Unlike other 1,2-disubstituted ethanes with polar groups, the gauche conformer ( $\varphi \approx 60^\circ$ ) of butane is slightly destabilized by less than 1 kcal/mol compared with the anticonformer. Similar to the ethane case, however, the governing factors ruling the conformational isomerism of butane are controversial.<sup>7,53,54</sup> Intuitively, the much larger size of methyl group than hydrogen atom invokes the steric repulsion model,



**FIGURE 5** | Rotational potential energy profiles for butane around the central C–C bond with the MP2, HF, and block-localized wavefunction methods.

as the barrier gets high with the approaching of the two terminal methyl groups. But the NBO analysis showed that the stabilization energy of the anticonformer with respect to the gauche structure comes from the hyperconjugation effect.<sup>53</sup> In other words, if there were no hyperconjugation effect, the gauche and anticonformers of butane would be nearly isoenergetic.

Most recently, Cormanich and Freitas calculated the potential energy surfaces for the relaxed and rigid (with bond distances and angles frozen) rotations, and concluded that the steric repulsion between methyl groups is the important effect defining the relative conformational energies.<sup>7</sup> Peculiarly, although they demonstrated that the anticonformer would be more stable than the gauche conformer when the hyperconjugation effect was turned off based on the NBO deletion calculations, their results showed that the energy difference between the gauche and anti-structures would increase from 0.9 kcal/mol when the hyperconjugation is considered to 10.7 kcal/mol when the vicinal antiperiplanar hyperconjugation is turned off by deleting the six related antibond orbitals. In other words, the NBO hyperconjugation energies are very high, so is the steric repulsion.

Using the BLW method,<sup>46–50</sup> we can define a wavefunction for the electron-localized Lewis structure as<sup>55</sup>

$$\Phi_L = \hat{A} \left\{ \prod_{i=1}^4 K_C^2(i) \prod_{j=1}^{10} \sigma_{\text{CH}}^2(j) \prod_{k=1}^3 \sigma_{\text{CC}}^2(k) \right\} \quad (6)$$

where  $K$  refers to a carbon core orbital and  $\sigma_{\text{CH}}$  denotes a doubly occupied CH bond orbital which

is expanded with the basis functions of only the bonding C and H atoms. Similarly,  $\sigma_{CC}$  corresponds to a CC bond orbital. Apparently, due to the expansion constraint, all these bond orbitals are nonorthogonal. Unlike Eq. (5), the difference between  $\Phi_L$  and the HF wavefunction  $\Psi$  involves not only the hyperconjugative interactions, but mostly the geminal interactions among the CH bonds sharing common apex carbon atoms.<sup>56</sup> The hyperconjugative and geminal interactions occur simultaneously, but generally the latter is much stronger and conserved among different conformers, as proved in the ethane case.

Figure 5 shows the energy profile of  $\Phi_L$  at the MP2/6-31G(d) geometries optimized along the torsional angle. The comparison between the HF and BLW curves indicated that the antistructure is more stable than the gauche structure by a similar amount of energy. This is in sharp contrast to the NBO results<sup>7</sup> and suggests that in both structures the hyperconjugative interactions are of comparable strengths. Interestingly, the rotational barriers reduce to 2.6 and 3.8 kcal/mol, respectively. For comparison, at the same theoretical level, the HF barriers are 3.7 and 5.2 kcal/mol. The discrepancies highlight the contribution from the hyperconjugation effect, i.e., there are stronger hyperconjugative interactions in staggered structures than eclipsed structures. However, the steric effect still plays a dominant role in the barriers. We note that recently Liu et al. quantified the steric effect within the DFT theory and showed that an eclipsed conformer has a larger steric energy than a staggered conformer,<sup>54</sup> and this is in accord with the BLW analysis but different from the NBO finding that the eclipsed conformer of *n*-butane possesses smaller steric repulsion than the staggered conformer. In essence, conclusion from Figure 5 is the same as that from Figure 4, i.e., the steric effect dominates the

rotational barriers in butane, whereas the hyperconjugation effect plays a secondary role and contributes about 30% to the barriers.

## CONCLUSION

The rotational barriers in alkanes, although low can be overcome easily at room temperature, play a fundamental role in stereochemistry and the dynamics of alkanes in both the gas and liquid phases. Although its understanding seems simple with the conventional steric repulsion model, the proposal and development of various quantum mechanical approaches constantly challenges our intellectual intuitions. It is thus important that before bracing any new interpretation, we should critically examine the approximations implied in these approaches and computations. Currently, the controversy over the origin of rotational barriers in alkanes seems still unsettled, and both the hyperconjugation explanation and steric repulsion explanation have supporters. But we note that essentially all supporting data for the hyperconjugation model come from the NBO method, where the wavefunction for the Lewis structure is transformed from the wavefunction for the delocalized state without further optimization. Theoretically, VB theory is more suitable for the evaluation of the hyperconjugation energy as it defines the Lewis structure with HLSP function which can be optimized self-consistently. Both *ab initio* VB and its variant, the BLW method, have demonstrated that staggered structures exhibit stronger hyperconjugative interactions than eclipsed structures, in accord with the beautiful qualitative pictures painted by the NBO method. However, numerically the magnitude of these hyperconjugative interactions is far from enough to interpret the barriers. The conventional steric interaction is still dominantly responsible for the barriers in alkanes.

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