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A Localized Atomic Orbital Description of the Rotational Barrier in Ethane

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The rotational barrier in ethane is analyzed in terms of localized atomic orbitals (LAOs). It is discerned that the barrier can be ascribed to energies representative of vicinal interactions between C—H bonds. It is found that exchange energies are of special importance. Variations in the vicinal interaction energies can ultimately be traced to charge flows into and out of various vicinal LAO distributions upon rotation, and the impetus for these charge flows is easily rationalized based on simple physical considerations.

I. INTRODUCTION

Barriers to internal rotation about single bonds were first postulated in 1936[1]. Since then perhaps hundreds of publications have concerned themselves with this phenomenon, particularly as regards ethane and ethane-like systems. In spite of these efforts, the factors responsible for the barriers are still disputed. The elusive nature of the barriers apparently has a two-fold origin. First, the *total* answer to what is obviously a complex, many-faceted problem is not likely to be divulged within the framework of the approximate quantum mechanical methods available. This is a dilemma over which most of us have no control and the best one may hope for is that the principal salient features of the barriers are represented adequately by the computational appliances at one's disposal. Even after making such an assumption we are still faced with the second problem, that being the isolation, elucidation and interpretation of these principal constituents of the barriers. This is nontrivial. In ethane, for instance, the barrier to internal rotation is the difference in total energy between the staggered and eclipsed conformers. This difference is miniscule in comparison to the energies of the conformers themselves. To further complicate matters, the total *ab initio* energy of either comformer is comprised of contributions from tens of thousands of integrals, densities, *etc.* The problem of interpretation involves *grouping* these contributions in such a way that only a small number of the grouped terms are of any consequence with respect to the barrier. These few collective terms are then assumed to be primarily responsible for the barrier. Given the monument of this chore it is hardly surprising that no entirely suitable results have been forthcoming.

No attempt will be made to comprehensively review the literature on rotational barriers; the interested reader is referred to review articles cited in Ref. 9. While valence bond (VB) and perturbation techniques[2] have been used with some success, we here restrict ourselves to a consideration of molecular orbital (MO) methods because of their widespread usage, understandability and success.

We may arbitrarily divide previous MO rotational barrier studies into three categories:

(1) valence basis techniques, all of which neglect, at least partly, differential overlap. Included are CNDO, INDO and others.

(2) minimal basis *ab initio* studies.

(3) large-scale MO calculations including refinements such as extended basis sets, polarization functions and configuration interaction or some other method of accounting for electron correlation.

Among these, the most useful for many conformational studies are the INDO and minimal basis *ab initio* schemes. The reasons for this are as follows. First, valence basis methods cruder than INDO are quantitatively untrustworthy although, surprisingly, they are often qualitatively correct[3]. On the other hand, large-scale MO methods are commonly both quantitatively and qualitatively correct. Indeed, in particularly troublesome molecules such as H_2O_2[4] it is necessary to employ a number of refinements in order to accurately reproduce the barrier. Unfortunately, large-scale MO computations are difficult to interpret in a simple manner. Furthermore it has been shown that the rotational barriers in ethane and many ethane-like systems are relatively insensitive to such refinements as extended basis sets, configuration interaction, *etc.*[5] In these instances minimal basis *ab initio* calculations are to be preferred both from the conceptual and computational viewpoints. The foregoing shows that frequently the INDO and minimal basis *ab initio* methods provide the most reliable and understandable results for the least computational effort.

While there are a number of interpretations of rotational barriers in ethane and ethane-like systems which are based on the aforementioned *ab initio* and INDO methodologies, the following are particularly noteworthy as regards the present work.

Lowe[6] examined the ethane barrier, determining which of the *ab initio* canonical MOs (CMOs) varied most under rotation. The most energetically influential CMOs were found to be the degenerate pair representing »pseudo π bonding« (the $1E_u$ and $1E'$ pairs for staggered and eclipsed ethane, respectively) and the degenerate pair representing »pseudo π antibonding« (the $1E_g$ and $1E''$ pairs for staggered and eclipsed ethane, respectively). According to Lowe, the barrier reflects the fact that nuclear repulsion energies (using standard geometry) and the pseudo π antibonding CMOs prefer the staggered conformation to a greater extent than the pseudo π bonding CMOs prefer the eclipsed orientation. There are several problems with this approach. First, the forms of the CMOs change with molecular symmetry so any conclusions drawn for a small class of molecules of similar symmetry are not likely to be readily transferable to a wide range of species. Additionally, CMOs are delocalized; yet, it seems natural to discuss rotational barriers in terms of *localized* interactions (*eg*: bond-bond and bond-lone pair interactions, *etc.*) rather than in terms of alterations in delocalized entities upon rotation. The localized description has the additional advantage that the results are expected to be transferable to a wider variety of barriers than are the results of a delocalized model.

From the above discussion, it is not surprising that a localized MO (LMO) analysis of the ethane barrier has been carried out.[7] The authors used the INDO form of the LMO equations of Edmiston and Ruedenberg[8] and the results are quite interesting. The interpretation rests upon destabilizing interference effects in the coplanar vicinal tails of the C—H bond LMOs upon rotation from the staggered to eclipsed conformation. That is, a C—H bond LMO is localized principally in the region surrounding the C—H bond axis. Yet, small delocalized tails exist elsewhere, including near the coplanar vicinal hydrogen. The tail and the localized portion may evidence constructive interference, which is stabilizing, or destructive interference, which is destabilizing. For ethane it was found that a C—H bond LMO experiences constructive interference from its coplanar vicinal tail in the staggered conformation and net destructive interference in the eclipsed conformation. It was furthermore discerned that these interference effects were sufficient to account for most of the *calculated* barrier. These results are entirely viable but are still quite different from the outcome one might have hoped for. One of the most attractive features of LMOs is that they partition MOs into localized entities (core, bond and lone pair LMOs) and this, in turn, would seem to provide a mechanism whereby barriers could be studied in terms of interorbital (*eg*: bond-bond) interactions, as this is a popular, easily understood model. Instead, the LMO analysis yielded an interpretation based not upon interactions *between* LMOs but one which relied upon the concept of *self-destruction* of an LMO upon rotation. While this is by no means invalid it is likewise not entirely desirable: the sophisticated and rather elusive concept of interference energies has not made this a popular mode of attack for barrier problems.

The author feels that what is needed is a simple method of partitioning that will result in a small, manageable number of terms which, by their variations upon rotation, will produce a suitable interpretation within the framework of classical or pseudo-classical thought. The interpretation would ideally include notions such as bonded and nonbonded (interorbital) interactions between localized entities (bonds, lone pairs), charge transfer, *etc*. Recently a study of the barriers in ethane and many ethane-like systems was published by Brunck and Weinhold[9] which conforms fairly well to most of these specifications. Bond orbitals (BOs) were formed. BOs may be of three types: bond BO (σ), antibond BO (σ^*) and lone pair BO (n). In spite of their VB-like appearance, BOs are used to construct CMOs within the INDO scheme. While the authors examined numerous ethane-like barriers, we shall consider only the ethane result here. Since ethane evidences no lone pairs, only σ and σ^* BOs are present. Hence there are three types of interorbital interactions possible: bond-bond ($\sigma\sigma$), bond-antibond ($\sigma\sigma^*$) and antibond-antibond ($\sigma^*\sigma^*$). Of these, the ethane barrier shows only a small dependence on the $\sigma\sigma$ and $\sigma^*\sigma^*$ interactions. Instead the barrier may be considered to be primarily due to the vicinal $\sigma\sigma^*$ interactions. Overlap considerations alone are sufficient to illustrate the trans-$\sigma\sigma^*$ interaction (present in staggered ethane) is more stabilizing than the cis-$\sigma\sigma^*$ contribution (present in eclipsed ethane). The other vicinal $\sigma\sigma^*$ interactions are less important than their cis and trans counterparts and are ignored in the analysis. This represents perhaps the most satisfying and enlightening study yet published on ethane and ethane-like barriers. Yet, the study suffers in one regard. Even though BOs are constructed for use within the CMO framework, the concept of $\sigma\sigma^*$ interactions is an awkward one within the confines of MO theory.

The question arises regarding the possibility of formulating a Brunck-Weinhold type of interpretation without invoking the concept of antibonding orbitals. That is, we wish to preserve the interpretation of the barrier in terms of vicinal C—H interactions. However, it is preferred that these be of the bond-bond variety rather than the bond-antibond variety, as this latter interaction is something of an anomaly in MO theory. One rather obvious way to achieve the desired result would seem to be replacement of BOs with localized atomic orbitals (LAOs)[10].

LAOs are typically formed on atoms in closed-shell molecules treated within the single-determinant *ab initio* framework wherein each CMO is originally expanded in terms of a minimal basis of orthonormal Slater-type orbitals (STOs). LAOs partition naturally into sets of core, lone pair and bonding orbitals. Their orientations, populations and compositions provide a Lewis structure-like view of hybridization and bonding. Like BOs, LAOs are truly localized and so would not be expected to give rise, in any obvious fashion, to an interference interpretation of barriers like that found in the LMO analysis. Unlike BOs, however, LAOs evidence no antibonding functions and so the barrier interpretation would not rest upon the concept of $\sigma\sigma^*$ interactions. LAOs do, however, have the potential to account for rotational barriers in terms of useful concepts such as bond-bond and bond-lone pair interactions. As we show in subsequent sections, LAOs do in fact account for the rotational barrier in ethane in terms of interactions between vicinal C—H bonds.

II. THE CALCULATIONS

Figure 1 shows the coordinate system employed and the positions and labels of all atoms in the two conformations relative to this coordinate system. GAUSSIAN 70[11] was used to carry out four electronic structure calculations:

STG/STD staggered ethane using standard geometry[12]
ECL/STD eclipsed ethane using standard geometry
STG/OPT staggered ethane using optimized geometry[13]
ECL/OPT eclipsed ethane using optimized geometry

In each instance the CMOs were initially expanded in terms of a minimal basis of STOs which are labeled as follows:

C_mk	1*s* STO on the *mth* ($m = 1, 2$) carbon atom
C_ms	2*s* STO on the *mth* C atom, made orthogonal to the C_mk orbital
C_mx, C_my, C_mz	$2p_x$, $2p_y$ and $2p_z$ STOs, respectively, on the *mth* C atom.
H_mk	1*s* STO on the *mth* ($m = 1, 2, \ldots, 6$) hydrogen atom

Once CMOs were known in terms of the minimal STO basis, LAOs were formed by performing an orthogonal, intra-atomic transformation of the STOs on each carbon. If n_A represents the number of STOs on atom A then the matrix relating the STOs to the LAOs on A will be $n_A \times n_A$ and will therefore require n_A^2 constraints for its complete specification. Of these, $^1/_2 n_A (n_A + 1)$ are fixed by the orthogonality requirement. The remaining $^1/_2 n_A (n_A - 1)$ constraints are determined by requiring that the sum of LAO »self-MO-label exchanges« be a maximum[10a]. We shall have more to say about »MO-label exchange« momentarily.

In all four calculations the LAOs obtained are of the following varieties:

iC_m	core LAO on the *mth* C atom
bσC_m (C_n)	σ bond LAO on the *mth* C atom and polarized toward the *nth* C atom
btjC_m (H_n) ($j = 1, 2, 3$)	three trigonally equivalent σ bond LAOs, each on the *mth* C atom and each polarized toward one of the three bonded H_n atoms.

Since each H has only one STO it follows that the LAO on each H is the same as the STO. The basic spatial patterns of the LAOs are shown in Figure 1 for

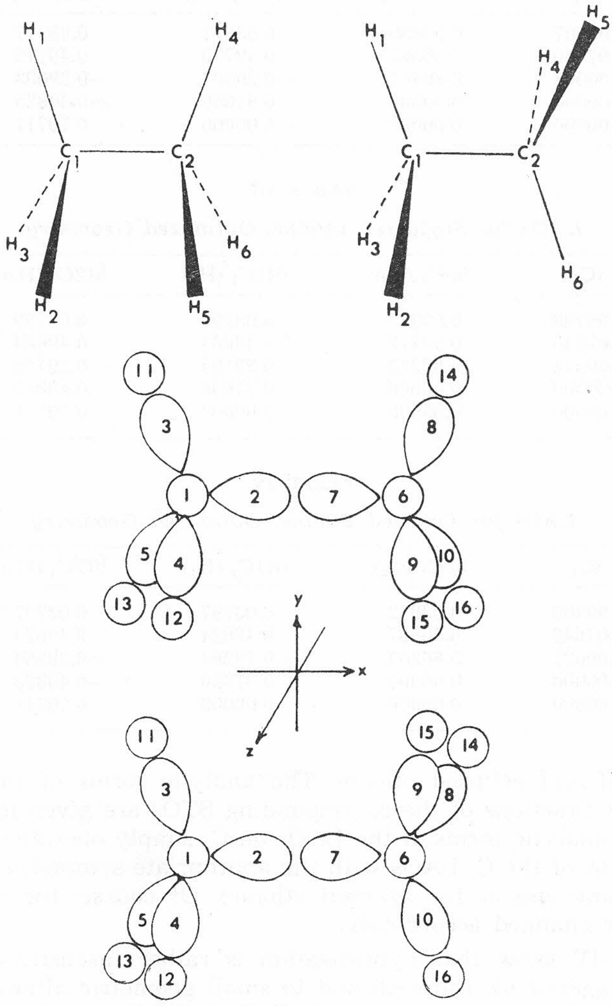

Figure 1. Coordinate system, atom arrangements and labeling and LAO labeling schemes for staggered and eclipsed ethanes.

TABLE I

LAOs for Staggered Ethane, Standard Geometry

	iC_1	$b\sigma C_1$ (C_2)	$bt1C_1$ (H_1)	$bt2C_1$ (H_2)	$bt3C_1$ (H_3)
C_1k	0.99707	0.03847	0.03818	0.03818	0.03818
C_1s	—0.07651	0.50078	0.49778	0.49778	0.49778
C_1x	—0.00005	0.86472	—0.28998	—0.28998	—0.28998
C_1y	0.00000	0.00000	0.81650	—0.40825	—0.40825
C_1z	0.00000	0.00000	0.00000	0.70711	—0.70711

TABLE II

LAOs for Eclipsed Ethane, Standard Geometry

	iC_1	$b\sigma C_1$ (C_2)	$bt1C_1$ (H_1)	$bt2C_1$ (H_2)	$bt3C_1$ (H_3)
C_1k	0.99707	0.03850	0.03817	0.03817	0.03817
C_1s	—0.07650	0.50087	0.49775	0.49775	0.49775
C_1x	—0.00008	0.86467	—0.29003	—0.29003	—0.29003
C_1y	0.00000	0.00000	0.81650	—0.40825	—0.40825
C_1z	0.00000	0.00000	0.00000	0.70711	—0.70711

TABLE III

LAOs for Staggered Ethane, Optimized Geometry

	iC_1	$b\sigma C_1$ (C_2)	$bt1C_1$ (H_1)	$bt2C_1$ (H_2)	$bt3C_1$ (H_3)
C_1k	0.99708	0.03873	0.03799	0.03799	0.03799
C_1s	—0.07636	0.50419	0.49664	0.49664	0.49664
C_1x	—0.00014	0.86273	—0.29195	—0.29195	—0.29195
C_1y	0.00000	0.00000	0.81650	—0.40825	—0.40825
C_1z	0.00000	0.00000	0.00000	0.70711	—0.70711

TABLE IV

LAOs for Eclipsed Ethane, Optimized Geometry

	iC_1	$b\sigma C_1$ (C_2)	$bt1C_1$ (H_1)	$bt2C_1$ (H_2)	$bt3C_1$ (H_3)
C_1k	0.99708	0.03892	0.03797	0.03797	0.03797
C_1s	—0.07642	0.50537	0.49624	0.49624	0.49624
C_1x	—0.00021	0.86203	—0.29264	—0.29264	—0.29264
C_1y	0.00000	0.00000	0.81650	—0.40825	—0.40825
C_1z	0.00000	0.00000	0.00000	0.70711	—0.70711

both staggered and eclipsed ethane. The analytic forms of the four sets of LAOs on C_1 as functions of the corresponding STOs are given in Tables I—IV. To obtain the analytic forms of the LAOs on C_2 simply operate on the C_1x, C_1y and C_1z portions of the C_1 LAOs with the appropriate symmetry operator (i for staggered ethane and σ_h for eclipsed ethane). Of course, the C and H atom labels must be changed accordingly.

Tables I—IV show that hybridization is rather insensitive both to conformation (staggered *vs.* eclipsed) and to small geometric alterations (STD *vs.* OPT). These results are to be expected. In Ref. 10d it was shown that hybridization depends primarily on two parameters, the saturation fraction (S) and the bonding fraction (B). In all four cases under consideration, carbon evidences identical values for both S and B. Therefore hybridization is expected to be relatively constant.

In the ensuing it will be convenient to assign numerical labels to all LAOs in addition to the descriptive labels ordinarily employed. For example, iC_1 may be labeled »1«, $b\sigma C_1 (C_2)$ may be labeled »2«, *etc.* The total labeling scheme adopted is shown in Figure 1 for both conformations.

III. DEFINITIONS, CONVENTIONS AND METHODS

Let $(\mathrm{Aa})^{(q)}$ represent the *ath* LAO on atom A as a function of the coordinates of the *qth* electron. Similarly, $(\mathrm{Bb})^{(q)}$ represents the *bth* LAO on atom B, *etc.* Each occupied CMO, $\psi_\mu^{(q)}$, $\psi_\nu^{(q)}, \ldots$, is expanded in terms of a minimal basis of LAOs. For example,

$$\psi_\mu^{(q)} = \Sigma_{\mathrm{Aa}}\, C_{\mathrm{Aa},\mu}\, (\mathrm{Aa})^{(q)} \tag{1}$$

where $\Sigma_{\mathrm{Aa}} = \Sigma_{\mathrm{A}}\, \Sigma_{\mathrm{a\ on\ A}}$ and where the $C_{\mathrm{Aa},\mu}$ are the coefficients relating the μth occupied CMO and the Aa*th* LAO; the coefficients are determined by an SCF calculation[14]. The LAOs form charge distributions (CDs) either with themselves (orbital distributions of the form $(\mathrm{Aa^*Aa})^{(q)}$) or with one another (overlap distributions of the form $(\mathrm{Aa^*Bb})^{(q)}$). It is to be understood that the complex conjugate sign is retained only as a useful book-keeping index; all LAOs are real. Associated with LAO CDs are various energy quantities. These have been largely discussed in Ref. 10a as well as elsewhere[12]. Only the more important aspects will be reviewed here.

The core Hamiltonian matrix elements, $H(\mathrm{Aa}\,|\,\mathrm{Bb})$, are defined as

$$H(\mathrm{Aa}\,|\,\mathrm{Bb}) = [(\mathrm{Aa}^*)^{(1)}\,|\,-1/2\,\{\nabla^{(1)}\}^2 - \Sigma_{\mathrm{C}}\, Z_{\mathrm{C}}/r_{1\mathrm{C}}\,|\,(\mathrm{Bb})^{(1)}] \tag{2}$$

where $\{\nabla^{(1)}\}^2$ is the Laplacian operator, Z_{C} is the atomic number of atom C, $r_{1\mathrm{C}}$ is the distance between electron 1 and the nucleus of atom C, and the brackets signify integration over the displayed electron coordinates. An element, $p(\mathrm{Aa}\,|\,\mathrm{Bb})$, of the first order density matrix is defined as

$$p(\mathrm{Aa}\,|\,\mathrm{Bb}) = 2\, \Sigma_\mu\, C^*_{\mathrm{Aa},\mu}\, C_{\mathrm{Bb},\mu} \tag{3}$$

where the sum in this and all subsequent equations runs only over occupied MOs, μ. Given the above, it becomes possible to interpret the term

$$C(\mathrm{Aa}\,|\,\mathrm{Bb}) = 1/2\, p(\mathrm{Aa}\,|\,\mathrm{Bb})\, H(\mathrm{Aa}\,|\,\mathrm{Bb}) \tag{4}$$

as a simple fraction ($^1/_2$ if Aa = Bb $^1/_4$ if Aa ≠ Bb) of the total kinetic and nuclear attraction energy experienced by charge in the LAO CD $(\mathrm{Aa^*Bb})^{(1)}$.

Electron interactions at the LAO level require examination of several terms. Let us begin by defining the basic two-electron LAO repulsion integral as

$$g(\mathrm{AaEe}\,|\,\mathrm{BbFf}) = [(\mathrm{Aa^*Bb})^{(1)}\,|\,r_{12}^{-1}\,|\,(\mathrm{Ee^*Ff})^{(2)}] \tag{5}$$

where r_{12} is the distance between electrons 1 and 2. Coulombic repulsion at the AO level is described by elements of the form

$$\begin{aligned} 2\,J(\mathrm{Aa}\,|\,\mathrm{Bb}) &= 2\, \Sigma_{\mu,\nu}\, \Sigma_{\mathrm{Ee,Ff}}\, C^*_{\mathrm{Aa},\mu}\, C^*_{\mathrm{Ee},\nu}\, C_{\mathrm{Bb},\mu}\, C_{\mathrm{Ff},\nu}\, [(\mathrm{Aa^*Bb})^{(1)}\,|\,r_{12}^{-1}\,|\,(\mathrm{Ee^*Ff})^{(2)}] = \\ &= (1/2)\, p(\mathrm{Aa}\,|\,\mathrm{Bb})\, \Sigma_{\mathrm{Ee,Ff}}\, p(\mathrm{Ee}\,|\,\mathrm{Ff})\, g(\mathrm{AaEe}\,|\,\mathrm{BbFf}) \end{aligned} \tag{6}$$

$2J\,(\mathrm{Aa} \mid \mathrm{Bb})$ can be interpreted as representing a simple fraction ($^1/_2$ if $\mathrm{Aa} = \mathrm{Bb}$, $^1/_4$ if $\mathrm{Aa} \neq \mathrm{Bb}$) of the total Coulombic repulsion between charge in the LAO CD $(\mathrm{Aa^*Bb})^{(1)}$ and charge in all the other LAO CDs, $(\mathrm{Ee^*Ff})^{(2)}$, in the molecule.

It was shown in Ref. 10a that the description of exchange energy at the AO level may be with respect to either of the two elements $K\,(\mathrm{Aa} \mid \mathrm{Bb})$ or $L\,(\mathrm{Aa} \mid \mathrm{Bb})$:

$$K\,(\mathrm{Aa} \mid \mathrm{Bb}) = \Sigma_{\mu,\nu}\, \Sigma_{\mathrm{Ee,Ff}}\, C^*_{\mathrm{Aa},\mu}\, C^*_{\mathrm{Ee},\nu}\, C_{\mathrm{Bb},\mu}\, C_{\mathrm{Ff},\nu}\, [(\mathrm{Aa^*Ff})^{(1)} \mid r_{12}^{-1} \mid (\mathrm{Ee^*Bb})^{(2)}] =$$
$$= 1/4\, p\,(\mathrm{Aa} \mid \mathrm{Bb})\, \Sigma_{\mathrm{Ee,Ff}}\, p\,(\mathrm{Ee} \mid \mathrm{Ff})\, g\,(\mathrm{AaEe} \mid \mathrm{FfBb}) \tag{7}$$

$$L\,(\mathrm{Aa} \mid \mathrm{Bb}) = \Sigma_{\mu,\nu}\, \Sigma_{\mathrm{Ee,Ff}}\, C^*_{\mathrm{Aa},\mu}\, C^*_{\mathrm{Ee},\nu}\, C_{\mathrm{Bb},\nu}\, C_{\mathrm{Ff},\mu}\, [(\mathrm{Aa^*Bb})^{(1)} \mid r_{12}^{-1} \mid (\mathrm{Ee^*Ff})^{(2)}] =$$
$$= 1/4\, \Sigma_{\mathrm{Ee,Ff}}\, p\,(\mathrm{Aa} \mid \mathrm{Ff})\, p\,(\mathrm{Ee} \mid \mathrm{Bb})\, g\,(\mathrm{AaEe} \mid \mathrm{BbFf}) \tag{8}$$

$K\,(\mathrm{Aa} \mid \mathrm{Bb})$ is called an electron-label exchange element since it can be formed from the corresponding Coulomb term, $J\,(\mathrm{Aa} \mid \mathrm{Bb})$, by interchange of the electron labels for $(\mathrm{Bb})^{(1)}$ and $(\mathrm{Ff})^{(2)}$. $L\,(\mathrm{Aa} \mid \mathrm{Bb})$ is called an MO-label exchange element because it can be formed from the corresponding Coulomb term by interchange of the MO labels for $C_{\mathrm{Bb},\mu}$ and $C_{\mathrm{Ff},\nu}$.

Because of this duality of exchange description at the AO level it is possible to describe total electronic interactions in two different fashions:

$$I\,(\mathrm{Aa} \mid \mathrm{Bb}) = 2\,J\,(\mathrm{Aa} \mid \mathrm{Bb}) - L\,(\mathrm{Aa} \mid \mathrm{Bb}) \tag{9}$$

$$I'\,(\mathrm{Aa} \mid \mathrm{Bb}) = 2\,J\,(\mathrm{Aa} \mid \mathrm{Bb}) - K\,(\mathrm{Aa} \mid \mathrm{Bb}) \tag{10}$$

Since $\Sigma_{\mathrm{Aa,Bb}}\ L\,(\mathrm{Aa} \mid \mathrm{Bb}) = \Sigma_{\mathrm{Aa,Bb}}\ K\,(\mathrm{Aa} \mid \mathrm{Bb})$ it follows that $\Sigma_{\mathrm{Aa,Bb}}\ I\,(\mathrm{Aa} \mid \mathrm{Bb}) = \Sigma_{\mathrm{Aa,\,Bb}}\ I'\,(\mathrm{Aa} \mid \mathrm{Bb})$. In this *overall* sense Eqs. (9) and (10) are equally satisfactory. However, LAOs themselves are defined by requiring the intra-atomic sum of LAO self-MO-label exchanges be a maximum on each atom:

$$\Sigma_{\mathrm{a\ on\ A}}\, L\,(\mathrm{Aa} \mid \mathrm{Aa}) \rightarrow \text{maximum in the LAO basis for all atoms, A} \tag{11}$$

Because of this it is natural for us to employ $I\,(\mathrm{Aa} \mid \mathrm{Bb})$ as a measure of electron interaction rather than $I'\,(\mathrm{Aa} \mid \mathrm{Bb})$. The interpretation of $I\,(\mathrm{Aa} \mid \mathrm{Bb})$ is that it represents a simple fraction ($^1/_2$ if $\mathrm{Aa} = \mathrm{Bb}$, $^1/_4$ if $\mathrm{Aa} \neq \mathrm{Bb}$) of the total electron interaction energy between charge in the LAO CD $(\mathrm{Aa^*Bb})^{(1)}$ and charge in all the other LAO Cds, $(\mathrm{Ee^*Ff})^{(2)}$, in the molecule.

The preceding analyses suggest definition of the quantity

$$e\,(\mathrm{Aa} \mid \mathrm{Bb}) = C\,(\mathrm{Aa} \mid \mathrm{Bb}) + I\,(\mathrm{Aa} \mid \mathrm{Bb}) \tag{12}$$

Obviously, $e\,(\mathrm{Aa} \mid \mathrm{Bb})$ can be taken to represent a simple fraction ($^1/_2$ if $\mathrm{Aa} = \mathrm{Bb}$, $^1/_4$ if $\mathrm{Aa} \neq \mathrm{Bb}$) of the total electronic energy associated with charge in the LAO CD $(\mathrm{Aa^*Bb})^{(1)}$ when it is allowed to interact with all other components of the molecule. Essentially, $e\,(\mathrm{Aa} \mid \mathrm{Aa})$ is the AO analog of one-electron CMO orbital energies; however, $e\,(\mathrm{Aa} \mid \mathrm{Bb})$ $(\mathrm{Aa} \neq \mathrm{Bb})$ has no CMO analog.

If $S\,(\mathrm{Aa} \mid \mathrm{Bb})$ is the overlap integral, $[(\mathrm{Aa^*Bb})^{(1)}]$, then the Mulliken charge, $q\,(\mathrm{Aa} \mid \mathrm{Bb})$, is defined as

$$q\,(\mathrm{Aa} \mid \mathrm{Bb}) = p\,(\mathrm{Aa} \mid \mathrm{Bb})\, S\,(\mathrm{Aa} \mid \mathrm{Bb}) \tag{13}$$

Mulliken charges are quite important for our analysis since any variations in the aforementioned energy quantities upon rotation might be expected to be accompanied by (or in fact be induced by) concurrent charge flow within the molecule.

To summarize, we have a group of quantities which are of interest to us. These may be referred to collectively as terms of the form $X\,(\mathrm{Aa} \mid \mathrm{Bb})$, where $X = q, C, 2J, L, I$ or e. If one examines the definitions of the $X\,(\mathrm{Aa} \mid \mathrm{Bb})$ it will be apparent that all are fourth rank tensors, each being second rank in coefficients and second rank in LAOs. Thus, by treating only the general elements $X\,(\mathrm{Aa} \mid \mathrm{Bb})$ we may deduce results which are simultaneously applicable to $X = q, C, 2J, L, I$ and e.

Because $X\,(\mathrm{Aa} \mid \mathrm{Bb}) = X\,(\mathrm{Bb} \mid \mathrm{Aa})$ in every instance, it follows that

$$X = \Sigma_{\mathrm{Aa,Bb}}\, X\,(\mathrm{Aa} \mid \mathrm{Bb}) = \Sigma_{\mathrm{Aa}}\, X\,(\mathrm{Aa} \mid \mathrm{Aa}) + 2\,\Sigma_{\mathrm{Aa<Bb}}\, X\,(\mathrm{Aa} \mid \mathrm{Bb}) \tag{14}$$

where $\Sigma_{\mathrm{Aa<Bb}} = \Sigma_{\mathrm{Aa}}\, \Sigma_{\mathrm{Bb>Aa}}$. For example, $q = \Sigma_{\mathrm{Aa}}\, q\,(\mathrm{Aa} \mid \mathrm{Aa}) + 2\,\Sigma_{\mathrm{Aa<Bb}}\, q\,(\mathrm{Aa} \mid \mathrm{Bb})$ represents the total charge in the molecule. Similarly, $e = \Sigma_{\mathrm{Aa}}\, e\,(\mathrm{Aa} \mid \mathrm{Aa}) + 2\,\Sigma_{\mathrm{Aa<Bb}}\, e\,(\mathrm{Aa} \mid \mathrm{Bb})$ represents $1/2$ the total electronic energy of the LAO CDs in the molecule when *each* LAO CD is allowed to interact with all other components of the molecule; the factor of $1/2$ follows from our previous interpretations of the $e\,(\mathrm{Aa} \mid \mathrm{Aa})$ and $e\,(\mathrm{Aa} \mid \mathrm{Bb})$ $(\mathrm{Aa} \neq \mathrm{Bb})$ elements.

Given our desired interpretation of the ethane rotational barrier it is obvious that we should be more concerned with how much of property X is associated with a *bond,* for example, than the amount of X associated with a *bond LAO*. For instance, $X\,(2 \mid 2)$ (see Figure 1 for labeling scheme) gives the amount of X associated with the orbital CD formed by the $b\sigma\mathrm{C}_1\,(\mathrm{C}_2)$ LAO. We would prefer, though, to know the amount of X attributable to the entire C—C bond, $B\,(\mathrm{CC}')$. Since $B\,(\mathrm{CC}')$ is principally the result of interactions between the $b\sigma\mathrm{C}_1\,(\mathrm{C}_2)$ and $b\sigma\mathrm{C}_2\,(\mathrm{C}_1)$ LAOs, we propose that the amount of X associated with $B\,(\mathrm{CC}')$ is that portion of Eq. (14) given by $X\,(2 \mid 2) + X\,(7 \mid 7) + 2\,X\,(2 \mid 7) = 2\,[X\,(2 \mid 2) + X\,(2 \mid 7)]$. The equality follows from the fact that $X\,(2 \mid 2) = X\,(7 \mid 7)$ for symmetry reasons. Further, the above equation would be valid for both the staggered and eclipsed conformers although, of course, $X\,(2 \mid 2)$ will be different in the two instances, as will be $X\,(2 \mid 7)$. The quantity $2\,[X\,(2 \mid 2) + X\,(2 \mid 7)]$ might best be referred to as a condensed element, $X_{\mathrm{C}}\,[B\,(\mathrm{CC}') \mid B\,(\mathrm{CC}')]$, which gives directly the amount of X associated with the C—C bond in ethane.

Consider a second example. Suppose we wish to know what portion of X is attributable to interaction between two C—H bonds belonging to the same methyl group. These might be called the $B\,(\mathrm{CH})$ and $B\,(\mathrm{CH}')$ bonds, the prime being used to indicate that $H \neq H'$. Figure 1 will show that there are six such interactions: $B\,(\mathrm{C_1H_1}) — B\,(\mathrm{C_1H_2})$, $B\,(\mathrm{C_1H_1}) — B\,(\mathrm{C_1H_3})$, $B\,(\mathrm{C_1H_2}) — B\,(\mathrm{C_1H_3})$, $B\,(\mathrm{C_2H_4}) — B\,(\mathrm{C_2H_5})$, $B\,(\mathrm{C_2H_4}) — B\,(\mathrm{C_2H_6})$ and $B\,(\mathrm{C_2H_5}) — B\,(\mathrm{C_2H_6})$. The same six interactions are present in both conformations. In a particular conformation all six interactions are equivalent so that the total amount of X due to all $B\,(\mathrm{CH}) — B\,(\mathrm{CH}')$ interactions is six times the amount due to any one of them. From Figure 1 and Eq. (14) this total is seen to be $12\,[X\,(3 \mid 4) + X\,(3 \mid 12) + X\,(4 \mid 11) + X\,(11 \mid 12)] = 12\,[X\,(3 \mid 4) + 2\,X\,(3 \mid 12) + X\,(11 \mid 12)]$, where the equality follows from symmetry requirements. The foregoing sum can be referred to as $X_{\mathrm{C}}\,[\mathrm{B}\,(\mathrm{CH}) \mid B\,(\mathrm{CH}')]$, a condensed term representing the total portion of X resulting from interaction of two C—H bonds on the same methyl group.

In ethane it is possible to identify three functional groups of interest to us: I (C), the core orbital on a C atom; B (CC′), the C—C bond functional; and B (CH), a C—H bond functional. These three units interact among themselves and by grouping the LAO terms $X\,(\mathrm{Aa} \mid \mathrm{Bb})$ in certain obvious ways it is possible to account for how much of X is associated with a particular variety of interaction. As above, this is equivalent to defining a set of condensed elements, $X_C\,[M \mid N]$, where M and N are chosen from the set $\{I\,(\mathrm{C}), B\,(\mathrm{CC'}), B\,(\mathrm{CH})\}$ and are furthermore chosen so as to represent unique interactions. The $X_C\,[M \mid N]$ have the property that

$$X = \Sigma_{M \leq N}\, X_C\,[\mathrm{M} \mid \mathrm{N}] \tag{15}$$

where $\Sigma_{M \leq N} = \Sigma_M\, \Sigma_{M \geq N}$. Table V summarizes the possible unique values of M and N for ethane together with the forms of the $X_C\,[M \mid N]$ elements as

TABLE V

Analytic Forms of the $X_C\,[M \mid N]$ as Functions of the $X\,(Aa \mid Bb)$ for Staggered and Eclipsed Ethanes. Only $M \leq N$ are Shown, as Demanded by Eq. (15)

M	N	$X_C\,[M \mid N]$
I (C)	I (C)	$2X\,(1 \mid 1)$
I (C)	I (C′)	$2X\,(1 \mid 6)$
I (C)	B (CC′)	$4\,[X\,(1 \mid 2) + X\,(1 \mid 7)]$
I (C)	B (CH)	$12\,[X\,(1 \mid 3) + X\,(1 \mid 11)]$
I (C)	B (C′H)	$12\,[X\,(1 \mid 8) + X\,(1 \mid 14)]$
B (CC′)	B (CC′)	$2\,[X\,(2 \mid 2) + X\,(2 \mid 7)]$
B (CC′)	B (CH)	$12\,[X\,(2 \mid 3) + X\,(2 \mid 11) + X\,(3 \mid 7) + X\,(7 \mid 11)]$
B (CH)	B (CH)	$6\,[X\,(3 \mid 3) + 2X\,(3 \mid 11) + X\,(11 \mid 11)]$
B (CH)	B (CH′)	$12\,[X\,(3 \mid 4) + 2X\,(3 \mid 12) + X\,(11 \mid 12)]$
B (CH)	$B\,(\mathrm{C'H'})_c^{*}$	$6\,[X\,(3 \mid 8) + 2X\,(3 \mid 14) + X\,(11 \mid 14)]$
B (CH)	$B\,(\mathrm{C'H'})_g^{**}$	$12\,[X\,(3 \mid 9) + 2X\,(3 \mid 15) + X\,(11 \mid 15)]$
B (CH)	$B\,(\mathrm{C'H'})_\gamma^{*}$	$12\,[X\,(3 \mid 9) + 2X\,(3 \mid 15) + X\,(11 \mid 15)]$
B (CH)	$B\,(\mathrm{C'H'})_t^{**}$	$6\,[X\,(3 \mid 10) + 2X\,(3 \mid 16) + X\,(11 \mid 16)]$

* Occurs only in eclipsed ethane.

** Occurs only in staggered ethane.

functions of the $X\,(\mathrm{Aa} \mid \mathrm{Bb})$. These are all obtained in the same fashion employed in the previous two examples. Further use of the table is illustrated as follows. The entry for $X_C\,[B\,(\mathrm{CC'}) \mid B\,(\mathrm{CC'})]$ gives the total amount of X deriving from LAOs which are principally responsible for formation of the C—C bond while the $X_C\,[B\,(\mathrm{CH}) \mid B\,(\mathrm{CH})]$ entry would yield the total amount of X associated with *all* C—H bonds (or, more precisely, the amount of X associated with the

LAOs which are primarily responsible for formation of the C—H bonds). Further, the $X_C\,[B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'}]_c$ term gives the portion of property X associated with the interaction of all C—H bonds which are in different methyl groups ($\mathrm{C} \neq \mathrm{C'}$ and $\mathrm{H} \neq \mathrm{H'}$) and which are oriented *cis* to one another (dihedral angle = 0°). Obviously this arrangement is possible only in eclipsed ethane. Similarly, $X_C\,[B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]_g$ is the amount of X deriving from interaction of C—H bonds in different methyl groups and which are *gauche* to one another (dihedral angle = 60°). This, of course, may occur only in the staggered form. Other vicinal C—H interactions are also categorized in terms of Ito's[15] scheme: $X_C\,[B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]_\gamma$ represents vicinal interactions of C—H bonds which are γ to one another (dihedral angle = 120°) while $X_C\,[B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]_t$ represents the *trans* vicinal interaction (dihedral angle = 180°). Note that any $X_C\,[M \mid N]$ is exactly the same function of the $X\,(Aa \mid Bb)$ for both conformations unless otherwise noted in the table. Henceforth, all properties X ($X = q$, C, $2J$, L, I, or e) will be reported in terms of the condensed elements, $X_C\,[M \mid N]$, rather than with respect to the LAO quantities, $X\,(\mathrm{Aa} \mid \mathrm{Bb})$. This allows direct reporting of a small number of results in a maximally meaningful fashion.

To conclude the requisite definitions, the total electronic energy, E_e, is given by

$$E_e = 2e - I \tag{16}$$

where e and I are defined by Eq. (15). Note that since e effectively counts all electron interactions twice it is necessary to subtract off one set of these as $-I$. This is completely analogous to E_e as a function of one-electron MO orbital energies. The nuclear repulsion energy, N, is given by

$$N = \Sigma_{\mathrm{A}<\mathrm{B}}\, Z_\mathrm{A} Z_\mathrm{A} / r_\mathrm{AB} \tag{17}$$

where r_AB is the distance between the nuclei of atoms A and B. The total energy, E_t, of the molecule is expressed as

$$E_t = E_e + N = 2e - I + N. \tag{18}$$

Finally, we consider rotation to proceed from the eclipsed to the staggered form so the rotational barrier, ΔE_t, is given by

$$\Delta E_t = E_t(\text{staggered}) - E_t(\text{eclipsed}) = 2\,\Delta e - \Delta I + \Delta N \tag{19}$$

Because the staggered conformation is the more stable this gives $\Delta E_t < 0$, in contrast to many authors who report the barrier as $-\Delta E_t > 0$.

IV. RESULTS

The difference, of course, between the STD and OPT calculations is that the former assumes that the only geometric alteration occuring upon rotation is a change in the dihedral angle between vicinal C—H bonds. The OPT computation allows for variation of other geometric parameters, since the total energy of each conformer is minimized with respect to geometry. The primary geometric alterations which OPT provides for are a 0.0010 nm decrease in the C—C bond length in staggered ethane (0.1538 nm) *versus* that in eclipsed ethane (0.1548 nm) and a decrease in the HCC bond angle from 111.1° in the eclipsed form to 110.7° in the staggered form. Naturally this means there is a corresponding increase in the HCH angles in going from the eclipsed to the staggered arrangement. The STD computation holds the C—C bond length constant at 0.154 nm and all bond angles are taken to be 109.5°. It is to be hoped that any barrier interpretation is invariant in its fundamental premises under the small geometric discrepancies which differentiate the STD and OPT calculations.

We adopt the following conventions. When an energy quantity has the same sign as ΔE_t we shall say that this term »favors« or »follows« the barrier, while a quantity having sign opposite that of ΔE_t shall be said to »oppose« the barrier. Table VI lists the macro-constituents of the STD and OPT barriers, as described by Eq. (19). Both STD and OPT computations show barriers comparable to the experimental value of — 12.25 kJ/mol,[16] and it is seen that both calculations predict the staggered conformer to be the most stable. Both STD and OPT show $2\Delta e$ components which follow the barrier, indicating that $2\Delta e$ consistently prefers the staggered conformation. The $2\Delta e$ values seem not to be very sensitive to the small geometric differences existing between the STD and OPT arrangements. This is to be contrasted with the $-\Delta I$ and ΔN components which appear surprisingly sensitive in this regard. The STD calculation shows a $-\Delta I$ component which opposes the barrier while the $-\Delta I$ portion of OPT follows the barrier. Conversely, ΔN favors the barrier in STD but opposes it in the OPT instance. The geometric sensitivity of $-\Delta I$ and ΔN, first noted by Stevens[17] and Epstein and Lipscomb[18], implies the *fundamental interpretation* of $-\Delta I$ and ΔN changes in response to relatively tiny geometric alterations.

TABLE VI

The Macro-Constituents of the STD and OPT Barriers

Calculation	$2\Delta e$ a. u.	$-\Delta I$ a. u.	ΔN a. u.	ΔE_t a. u.	ΔE_t kJ mol^{-1}
STD	—0.020722	0.022856	—0.007428	—0.005294	—13.90
OPT	—0.025584	—0.115438	0.136446	—0.004576	—12.01

Since we desire that our interpretation of the barrier be the same for STD and OPT geometries, this appears to be a rather frustrating result. However, a bit of further consideration allows a satisfactory resolution of this problem. Since ΔE_t is similar for both STD and OPT, as is $2\Delta e$, and since $2\Delta e - \Delta I + \Delta N = \Delta E_t$, it must follow that the *combined* term, $(-\Delta I + \Delta N)$ is approximately the same for both STD and OPT even though the individual components, $-\Delta I$ and ΔN, fluctuate widely. This is indeed true: $(-\Delta I + \Delta N)$ equals 0.015428 for STD and 0.021008 for OPT. Thus, both STD and OPT show values of $(-\Delta I + \Delta N)$ which consistently oppose the barrier to a slightly less extent than the corresponding values of $2\Delta e$ favor the barrier. We conclude that $2\Delta e$ is the primary driving force responsible for the barrier and that $2\Delta e$ is opposed by the driving force $(-\Delta I + \Delta N)$.

Since $2\Delta e$ and the combined term $(-\Delta I + \Delta N)$ always act to oppose one another it seems natural to express the latter in terms of the former, which has been seen to be the predominant influence on ΔE_t. That is, we find a k such that

$$(-\Delta I + \Delta N) = 2k\Delta e. \tag{20}$$

For STD, $k = -0.74452$ while for OPT, $k = -0.82114$. Using these values, we substitute Eq. (20) into Eq. (19) to obtain

$$\text{STD:} \qquad \Delta E_t = 0.51096 \, \Delta e \tag{21}$$

$$\text{OPT:} \qquad \Delta E_t = 0.35772 \, \Delta e. \tag{21'}$$

Eqs. (21) and (21′) are useful in that they provide an expression for ΔE_t in terms of only Δe, which we have already noted to be the principal driving force behind the barrier. Eqs. (21) and (21′) are conceptually similar to assumptions employed in the Brunck-Weinhold method. In the INDO calculations, $-\Delta I + \Delta N \approx 0$ so $\Delta E_t \approx 2 \Delta e$. Thus, by studying the variation of Δe upon rotation, the authors were hopeful of elucidating those factors primarily responsible for the barrier. Eqs. (21) and (21′) represent a similar point of departure in that they explicitly recognize Δe as the basic source of the barrier. The fact that the proportionality constant between ΔE_t and Δe is no longer equal to 2 (as it is in the INDO work) is simply a reflection of the fact that $-\Delta I$ and ΔN no longer cancel one another, even approximately, in the *ab initio* results. This discrepancy between the two calculations is due almost exclusively to differences in the $-\Delta I$ elements owing to the partial neglect of differential overlap in the INDO calculation. In the *ab initio* instance, then, we simply treat $(-\Delta I + \Delta N)$ as an additive nonzero constant whereas in the INDO case $(-\Delta I + \Delta N)$ is taken as an additive constant equal to zero. The components of Δe are now examined so as to simplify Eqs. (21) and (21′) even further.

It is expected that the largest contributions to e will come from the condensed »self-energies«, $e_C[M \mid M]$, since self-energies tend to be consistently more substantial than interaction energies, $e_C[M \mid N]$ $(M \neq N)$. Table VII, which lists the $e_C[M \mid N]$ components for the four computations considered here, supports this. In all instances the $e_C[M \mid M]$ terms are negative and are of substantial magnitude and therefore represent the primary stabilizing com-

TABLE VII

$e_C[M \mid N]$ $(M \leq N)$ *for STG/STD, ECL/STD, STG/OPT and ECL/OPT Ethanes*

M	N	$e_C[M \mid N]$/a. u.			
		STG/STD	ECL/STD	STG/OPT	ECL/OPT
I(C)	I(C)	—21.885065	—21.881357	—21.888938	—21.884746
I(C)	I(C′)	0.000153	0.000151	0.000156	0.000150
I(C)	B(CC′)	—0.011817	—0.011785	—0.010980	—0.013641
I(C)	B(CH)	0.022591	0.022611	0.024668	0.025106
I(C)	B(C′H)	—0.002155	—0.002202	—0.002095	—0.002040
B(CC′)	B(CC′)	—0.661708	—0.661276	—0.662548	—0.654763
B(CC′)	B(CH)	—0.018007	—0.017410	—0.024255	—0.029575
B(CH)	B(CH)	—3.894865	—3.898587	—3.909709	—3.911136
B(CH)	B(CH′)	0.036536	0.037514	0.048379	0.052930
B(CH)	$B(\mathrm{C'H'})_c$	—	0.051692	—	0.045467
B(CH)	$B(\mathrm{C'H'})_g$	0.038492	—	0.036237	—
B(CH)	$B(\mathrm{C'H'})_\gamma$	—	—0.015908	—	—0.015023
B(CH)	$B(\mathrm{C'H'})_t$	—0.011054	—	—0.011000	—

ponents of e. The interaction energies, $e_C [M | N]$ $(M \neq N)$ are uniformly small in magnitude and may be either stabilizing or destabilizing.

It follows from Eq. (15) that

$$\Delta e = \Sigma_{M \leq N} \Delta e_C [M | N] \qquad (22)$$

where $\Delta e_C [M | N] = e_C [M | N]$(staggered) — $e_C [M | N]$(eclipsed). All $\Delta e_C [M | N]$ are well-defined except those corresponding to the vicinal interactions of the C—H bonds. These interactions may be treated in one of two ultimately equivalent fashions:

(1) Pair the cis and gauche interactions together and the gamma and trans interactions together to form two terms:

$$\Delta e_C [B\,(\mathrm{CH}) | B\,(\mathrm{C'H'})]_{c \to g} = e_C [B\,(\mathrm{CH}) | B\,(\mathrm{C'H'})]_g - e_C [B\,(\mathrm{CH}) | B\,(\mathrm{C'H'})]_c \qquad (23)$$

$$\Delta e_C [B\,(\mathrm{CH}) | B\,(\mathrm{C'H'})]_{\gamma \to t} = e_C [B\,(\mathrm{CH}) | B\,(\mathrm{C'H'})]_t - e_C [B\,(\mathrm{CH}) | B\,(\mathrm{C'H'})]_\gamma \qquad (24)$$

Conceptually this corresponds to rotating eclipsed ethane by 60° to yield the staggered form. Hence the cis interaction becomes a gauche interaction (and the Δe_C is described by Eq. (23)) while the gamma interaction becomes a trans interaction (with Δe_C described by Eq. (24)).

(2) Pair the cis and trans interactions together and the gamma and gauche interactions together to form two elements:

$$\Delta e_C [B\,(\mathrm{CH}) | B\,(\mathrm{C'H'})]_{c \to t} = e_C [B\,(\mathrm{CH}) | B\,(\mathrm{C'H'})]_t - e_C [B\,(\mathrm{CH}) | B\,(\mathrm{C'H'})]_c \qquad (25)$$

$$\Delta e_C [B\,(\mathrm{CH}) | B\,(\mathrm{C'H'})]_{\gamma \to g} = e_C [B\,(\mathrm{CH}) | B\,(\mathrm{C'H'})]_g - e_C [B\,(\mathrm{CH}) | B\,(\mathrm{C'H'})]_\gamma \qquad (26)$$

Conceptually it is perhaps easiest to imagine this partitioning as corresponding to rotation of eclipsed ethane by 180° to yield the staggered form. Thus the cis interaction becomes a trans interaction (with Δe_C given by Eq. (25)) and the gamma interaction becomes a gauche interaction (with Δe_C given by Eq. (26)).

As far as book-keeping is concerned, either approach is equally satisfactory. However there are several compelling reasons for choosing the latter method. First, the LMO analysis of England and Gordon ascribed the barrier to interference between a C—H bond LMO and its own tail near the coplanar vicinal hydrogen. Such interactions are cis in eclipsed ethane and trans in staggered ethane. The interferences between a C—H bond LMO and its tail near non-coplanar (gauche or gamma) vicinal hydrogens show net opposition to the barrier and are therefore of less importance than the cis and trans terms. In the same way, Brunck and Weinhold ascribed the barrier to a destabilizing cis-$\sigma\sigma^*$ interaction in eclipsed ethane which becomes a stabilizing trans-$\sigma\sigma^*$ interaction in stagerred ethane. The gauche and gamma $\sigma\sigma^*$ interactions are of substantially less importance. Both the aforementioned analyses suggest the partitioning given in Eqs. (25) and (26). Indeed, analysis of the present data using both the proposed methods also shows the second partitioning to be the more useful. Values of $\Delta e_C [M | N]$ are tabulated in Table VIII using Eqs. (25) and (26) to compute the vicinal contributions.

While the bulk of e derives from the $e_C [M | M]$ elements, it obviously does not follow that the $\Delta e_C [M | M]$ terms will be the major contributors to Δe. In fact the reverse might be supposed: since the self-energies, $e_C [M | M]$, are the primary stabilizing influences acting upon e and since both conformers have nearly identical total energies then it is reasonable to suspect that the

TABLE VIII

$\Delta\, e_C\, [M \mid N]$ $(M \leq N)$ for STD and OPT Ethanes

M	N	$\Delta\, e_{\mathrm{C}}$ [M | N]/a. u.	
		STD	OPT
I (C)	I (C)	—0.003708	—0.004192
I (C)	I (C′)	0.000002	0.000006
I (C)	B (CC′)	—0.000032	0.002661
I (C)	B (CH)	—0.000020	—0.000438
I (C)	B (C′H)	0.000047	—0.000055
B (CC′)	B (CC′)	—0.000432	—0.007785
B (CC′)	B (CH)	—0.000597	0.005320
B (CH)	B (CH)	0.003722	0.001427
B (CH)	B (CH′)	—0.000978	—0.004551
B (CH)	$B\,(\mathrm{C'H'})_{\mathrm{c}\to\mathrm{t}}$	—0.062746	—0.056467
B (CH)	$B\,(\mathrm{C'H'})_{\gamma\to\mathrm{g}}$	0.054400	0.051260

self-energy terms, $e_{\mathrm{C}}\, [M \mid M]$, change very little upon rotation. Table VIII shows this to be true. In all instances the $\Delta\, e_{\mathrm{C}}\, [M \mid M]$ values are small, which is to say that the energies of core orbitals and bonds are only very slightly altered upon rotation. Likewise, most of the interaction energies are affected negligibly by rotation, the $\Delta\, e_{\mathrm{C}}\, [M \mid N]$ $(M \neq N)$ being predominantly miniscule. The only exceptions to this are the vicinal C—H interactions, which make the most substantial contributions to $\Delta\, e$. Table VIII indicates that, for both STD and OPT, the cis ⟶ trans interactions (represented by $\Delta\, e_{\mathrm{C}}\, [B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]_{\mathrm{c}\to\mathrm{t}}$) are quite stabilizing, meaning that the trans (staggered) orientation is preferred. In contrast, both STD and OPT show the gamma ⟶ gauche interactions (represented by $\Delta\, e_{\mathrm{C}}\, [B\,(\mathrm{CH}) \mid (\mathrm{C'H'})]_{\gamma\to\mathrm{g}}$) to be destabilizing, indicating that the gamma (eclipsed) arrangement is favored. Note that, for both STD and OPT, the destabilizing gamma ⟶ gauche vicinal interactions are smaller in magnitude than the stabilizing cis ⟶ trans terms so the net preference is for the staggered conformation.

Because the major contributions to $\Delta\, e$ arise from the vicinal C—H interactions it is convenient to express $\Delta\, e$ as being proportional to the total vicinal interaction. To do so we find the value of k' such that

$$\Delta\, e = k' \{\Delta\, e_{\mathrm{C}}\, [B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]_{\mathrm{c}\to\mathrm{t}} + \Delta\, e_{\mathrm{C}}\, [B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]_{\gamma\to\mathrm{g}}\}. \tag{27}$$

For STD, $k' = 1.2414$, while for OPT, $k' = 2.4567$. These, together with a substitution of Eq. (27) into Eqs. (21) and (21′) yield

$$\text{STD:} \quad \Delta\, E_{\mathrm{t}} = 0.63431\, \{\Delta\, e_{\mathrm{C}}\, [B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]_{\mathrm{c}\to\mathrm{t}} + \Delta\, e_{\mathrm{C}}\, [B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]_{\gamma\to\mathrm{g}}\} \tag{28}$$

$$\text{OPT:} \quad \Delta\, E_{\mathrm{t}} = 0.87881\, \{\Delta\, e_{\mathrm{C}}\, [B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]_{\mathrm{c}\to\mathrm{t}} + \Delta\, e_{\mathrm{C}}\, [B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]_{\gamma\to\mathrm{g}}\} \tag{28′}$$

Just as $\Delta\, e$ is the principal driving force behind $\Delta\, E_{\mathrm{t}}$, it is observed that the primary factors affecting $\Delta\, e$ are the vicinal cis ⟶ trans and gamma ⟶ gauche interactions. Eqs. (28) and (28′) simply seek to express these observations.

From Eqs. (9) and (12) and the discussion in Sec. III we see that

$$\Delta\, e_{\mathrm{C}}\, [M \mid N] = \Delta\, C_{\mathrm{C}}\, [M \mid N] + 2\, \Delta\, J_{\mathrm{C}}\, [M \mid N] - \Delta\, L_{\mathrm{C}}\, [M \mid N]. \tag{29}$$

Since Eqs. (28) and (28′) relate ΔE_t to $\Delta e_C[B(CH) \mid B(C'H')]_{c\to t}$ and $\Delta e_C[B(CH) \mid B(C'H')]_{\gamma\to g}$, it is useful to examine the components of these terms as given by Eq. (29). Table IX lists these quantities and the following features are evident. The core and exchange terms, $\Delta C_C[B(CH) \mid B(C'H')]$ and $-\Delta L_C[B(CH) \mid B(C'H')]$, are of the same sign as the corresponding $\Delta e_C[B(CH) \mid B(C'H')]$ elements. That is, all these terms are stabilizing for the cis → trans interactions while all are destabilizing for the gamma → gauche interactions. These results are true for both STD and OPT. The Coulomb terms follow just the reverse trends: for both STD and OPT, the cis → trans Coulomb term is destabilizing while the gamma → gauche element is stabilizing.

TABLE IX

Changes in the Condensed Core, Coulomb and Exchange Elements Associated with the cis → trans and the gamma → gauche Vicinal Distributions

Geometry	M	N	$\Delta C_C[M \mid N]$ a. u.	$2\Delta J_C[M \mid N]$ a. u.	$-\Delta L_C[M \mid N]$ a. u.
STD	B (CH)	$B(C'H')_{c\to t}$	—0.476415	0.444134	—0.030466
	B (CH)	$B(C'H')_{\gamma\to g}$	0.404481	—0.374641	0.024560
OPT	B (CH)	$B(C'H')_{c\to t}$	—0.425791	0.396352	—0.027028
	B (CH)	$B(C'H')_{\gamma\to g}$	0.382833	—0.354611	0.023039

Inspection of Table IX will show that, for both types of vicinal interactions,

$$\Delta C_C[B(CH) \mid B(C'H')] + 2\Delta J_C[B(CH) \mid B(C'H')] \approx -\Delta L_C[B(CH) \mid B(C'H')] \quad (30)$$

It must therefore follow that, for both types of interactions,

$$\Delta e_C[B(CH) \mid B(C'H')] \approx -2\Delta L_C[B(CH) \mid B(C'H')]. \quad (31)$$

This equation may be seen to be approximately valid by comparing the relevant entries of Tables VIII and IX. This suggests we find the proportionality constant, k'', such that

$$\Delta e_C[B(CH) \mid B(C'H')]_{c\to t} + \Delta e_C[B(CH) \mid B(C'H')]_{\gamma\to g}$$
$$= k''\{-\Delta L_C[B(CH) \mid B(C'H')]_{c\to t} - \Delta L_C[B(CH) \mid B(C'H')]_{\gamma\to g}\}. \quad (32)$$

STD has $k'' = 1.413$ and OPT shows $k'' = 1.305$. Substituting Eq. (32) into Eqs. (28) and (28′), we arrive at

STD: $\Delta E_t = 0.8963\{-\Delta L_C[B(CH) \mid B(C'H')]_{c\to t} - \Delta L_C[B(CH) \mid B(C'H')]_{\gamma\to g}\}$ (33)

OPT: $\Delta E_t = 1.147\{-\Delta L_C[B(CH) \mid B(C'H')]_{c\to t} - \Delta L_C[B(CH) \mid B(C'H')]_{\gamma\to g}\}$ (33′)

Examination of Eqs. (33) and (33′) reveals that the coefficients for both STD and OPT are approximately equal to 1. Thus, to a good estimation, the rotational barrier in ethane may be given by

$$\Delta E_t \approx -\Delta L_C[B(CH) \mid B(C'H')]_{c\to t} - \Delta L_C[B(CH) \mid B(C'H')]_{\gamma\to g}. \quad (34)$$

Note that Eq. (34) applies to both STD and OPT geometries, which is quite fortunate given the oscillating behaviour of terms such as $-\Delta I$ and ΔN as geometry is altered from STD to OPT. For STD, Eq. (34) overestimates the calculated barrier by about 12% while, for OPT, Eq. (34) underestimates the calculated barrier by about 13%. These deviations are satisfactory in comparison to other barrier analyses. For example, the England-Gordon interference interpretation overestimates the INDO barrier by 1% for STD and by 9% for OPT. However, the INDO barriers, themselves, are in error by 25% (STD) and 23% (OPT) whereas the *ab initio* barriers are in error by only 13% (STD) and 2% (OPT). We are therefore able to describe, to within about 12—13%, the *ab initio* barrier in ethane as deriving from vicinal C—H exchange interactions. The trans exchange interactions in staggered ethane are more stabilizing than the cis exchange interactions in eclipsed ethane so that $-\Delta L_C [B(CH) \mid B(C'H')]_{c \to t}$ is the principal stabilizing component of ΔE_t. This is counterbalanced, somewhat, by the fact that the gauche exchange interactions in staggered ethane are less stabilizing than the gamma interactions in eclipsed ethane so that $-\Delta L_C [B(CH) \mid B(C'H')]_{\gamma \to g}$ represents the primary destabilizing component of ΔE_t. Because the cis → trans contribution is greater in magnitude than the gamma → gauche term, the staggered conformer is favored, overall.

One may wonder why it is reasonable to ascribe the barrier to vicinal terms such as those we have examined. One way to rationalize this result is by examining the condensed Mulliken charges, $q_C [M \mid N]$, as defined by Eq. (13) and Table V. Values of the $q_C [M \mid N]$ are given in Table X and the corresponding $\Delta q_C [M \mid N]$ elements are presented in Table XI. The following features are noted.

TABLE X

Condensed Mulliken Charges, $q_C [M \mid N]$ ($M \leq N$), for STG/STD, ECL/STD, STG/OPT and ECL/OPT Ethanes

M	*N*	$q_C [M \mid N]$			
		STG/STD	ECL/STD	STG/OPT	ECL/OPT
I (C)	I (C)	4.013608	4.013618	4.013945	4.013789
I (C)	I (C′)	—0.000016	—0.000016	—0.000017	—0.000016
I (C)	B (CC′)	—0.003841	—0.003843	—0.003940	—0.003704
I (C)	B (CH)	—0.016226	—0.016250	—0.016519	—0.016527
I (C)	B (C′H)	—0.000114	—0.000116	—0.000104	—0.000107
B (CC′)	B (CC′)	2.182612	2.182772	2.174021	2.169800
B (CC′)	B (CH)	—0.345886	—0.346376	—0.331295	—0.321894
B (CH)	B (CH)	12.682119	12.704730	12.695398	12.712019
B (CH)	B (CH′)	—0.435705	—0.436876	—0.459944	—0.468622
B (CH)	B (C′H′)$_c$	—	—0.121008	—	—0.106835
B (CH)	B (C′H′)$_g$	—0.080670	—	—0.076236	—
B (CH)	B (C′H′)$_\gamma$	—	0.023420	—	0.022282
B (CH)	B (C′H′)$_t$	0.004184	—	0.004750	—

TABLE XI

$\Delta q_{\mathrm{C}}\,[M \mid N]\;(M \leq N)$ *for STD and OPT Ethanes*

M	N	$\Delta q_{\mathrm{C}}\,[M \mid N]$ STD	$\Delta q_{\mathrm{C}}\,[M \mid N]$ OPT
I (C)	I (C)	—0.000010	0.000156
I (C)	I (C′)	0.000000	—0.000001
I (C)	B (CC′)	0.000002	—0.000236
I (C)	B (CH)	0.000024	0.000008
I (C)	B (C′H)	0.000002	0.000003
B (CC′)	B (CC′)	—0.000160	0.004221
B (CC′)	B (CH)	0.000490	—0.009401
B (CH)	B (CH)	—0.022611	—0.016621
B (CH)	B (CH′)	0.001171	0.008678
B (CH)	$B\,(\mathrm{C'H'})_{\mathrm{c}\to\mathrm{t}}$	0.125192	0.111585
B (CH)	$B\,(\mathrm{C'H'})_{\gamma\to\mathrm{g}}$	—0.104090	—0.098518

(1) One would expect that the effective potential experienced by electrons in either the core or the C—C bond functionals is very similar in both the staggered and eclipsed conformations. Thus, there, is little impetus for charge to flow into or out of distributions involving these groups when rotation occurs. This is verified by Table XI which shows that all the $\Delta q_{\mathrm{C}}\,[M \mid N]$ terms are practically negligible when either M or N is equal to I (C) or B (CC′). Whenever a distribution experiences negligible charge flow during rotation, we anticipate the corresponding energy term, $\Delta e_{\mathrm{C}}\,[M \mid N]$, to be small. This is easily verified by examination of Table VIII. Precisely the same arguments suggest that there is to be expected only slight charge flow associated with the distributions between two C—H functionals on the same methyl group. Table XI verifies this and, again, we find that $\Delta e_{\mathrm{C}}\,[B\,(\mathrm{CH}) \mid B\,(\mathrm{CH'})]$ is small, as expected.

(2) In contrast to the above, one would anticipate more substantial charge flow to occur both for a C—H bond functional and for the vicinal distributions between these groups. Simple electron repulsion considerations would suggest that charge should be excluded from the cis vicinal overlap distributions to a greater extent than from gauche overlap distributions. Overlap considerations alone (see Eq. (13)) predict the magnitudes of charges in the cis and gauche distributions to be larger than the magnitudes of changes in the gamma and trans distributions. Table X verifies these trends. In light of the above, it is reasonable that there is net charge transfer from C—H bond functionals to the vicinal overlap distributions between C—H groups as eclipsed ethane is rotated into the staggered form. That is, in eclipsed ethane charge is expelled from the cis distribution and into the C—H bond. However, in staggered ethane, where the strong cis interaction is replaced by the less objectionable gauche interaction, some of this charge leaves the C—H bond and enters the vicinal overlap distributions. This is verified in Table XI where it is seen that $\Delta q_{\mathrm{C}}\,[B\,(\mathrm{CH}) \mid B\,(\mathrm{CH})]$ is negative. It is also clear that $\Delta q_{\mathrm{C}}\,[B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]_{c\to\mathrm{t}}$ should be positive since the cis component is so negative while the trans con-

tribution is small in magnitude. The same rationale predicts $\Delta q_C [B(CH) | B(C'H')]_{\gamma \to g}$ to be negative. It is interesting to note that, for both STD and OPT,

$$\Delta q_C [B(CH) | B(CH)] + \Delta q_C [B(CH) | B(C'H')]_{\gamma \to g} \approx - \Delta q_C [B(CH) | B(C'H')]_{c \to t} \quad (35)$$

This is consistent with the discussion in (1) above: since the three terms in Eq. (35) are the only substantial $\Delta q_C [M | N]$ elements, it must follow that all the charge leaving the C—H bond group and the gamma → gauche distributions must enter the cis → trans distributions.

(3) It might be supposed that when a substantial amount of charge leaves a distribution then the distribution will be destabilized. Conversely, transfer of charge of a substantial amount to a distribution might be presumed to be stabilizing. Table VIII shows this to be true for the three distributions discussed above. This analysis might seem to suggest that the terms $\Delta e_C [B(CH) | B(CH)]$, $\Delta e_C [B(CH) | B(C'H')]_{c \to t}$ and $\Delta e_C [B(CH) | B(C'H')]_{\gamma \to g}$ would be the most influential components of Δe and therefore of ΔE_t. The flaw in this reasoning is easy to understand. While Table XI shows $\Delta q_C [B(CH) | B(CH)]$ to be the third largest of the $\Delta q_C [M | N]$ elements, Table X reveals that the individual $q_C [B(CH) | B(CH)]$ terms are all quite large. In fact, all calculations show there to be roughly 12.7 electrons associated with C—H bond groups; naturally, this amounts to about 2.1 electrons associated with each C—H bond group. In contrast, $\Delta q_C [B(CH) | B(CH)]$ is roughly — 0.02 electron for *all six C—H bonds treated collectively*. While this is substantial in contrast to most of the other $\Delta q_C [M | N]$ elements, it is almost a negligible fraction of the total charge residing in the C—H bond groups. Thus, while $\Delta e_C [B(CH) | B(CH)]$ is in fact destabilizing, the magnitude of the term is quite small. In contrast, all the $q_C [B(CH) | B(C'H')]$ terms are small in magnitude so the small charge flowing into or out of these distributions makes a large percent difference in the total amount of resident charge. This causes the $\Delta e_C [B(CH) | B(C'H')]_{c \to t}$ and $\Delta e_C [B(CH) | B(C'H')]_{\gamma \to g}$ terms to be substantial in magnitude. The fact that the cis → trans term is more stabilizing than the gamma → gauche term is destabilizing can be rationalized based on the fact that more charge enters the cis → trans distributions than leaves the gamma → gauche distributions (see Eq. (35)).

V. CONCLUSION

To summarize, we have shown why it is reasonable to examine ΔE_t with respect to its Δe components (see discussion at the outset of Sec. IV). Simple considerations reveal why the only substantial $\Delta q_C [M | N]$ elements correspond to a building-up of charge in the cis → trans distributions at the expense of charge in the C—H bond groups and the gamma → gauche distributions. Finally, we have shown why $\Delta e_C [B(CH) | B(CH)]$ is relatively unimportant even though $\Delta q_C [B(CH) | B(CH)]$ is of some importance. We are therefore left with the fact that the only charge flows which result in concurrently important contributions to Δe are those involving the cis → trans and gamma → gauche vicinal distributions. Because more charge enters the cis → trans distributions than leaves the gamma → gauche distributions, $\Delta e_C [B(CH) | B(C'H')]_{c \to t}$ becomes the factor which principally controls the barrier. It is attenuated to some extent by $\Delta e_C [B(CH) | B(C'H')]_{\gamma \to g}$ but the net effect is still a preference for the staggered form. The above provides an explanation of (and justification for) Eqs. (27), (28) and (28′). Further, it is hoped that the same sort of analysis can be used to understand the rotational barriers in other systems. Presently, LAO studies of the barriers in CH_3OH, CH_3NH_2, N_2H_4, $CH_2F—NH_2$, CH_3CH_2F and $CH_2F—CH_2F$ are underway to test this hypothesis.

The existence of Eq. (34) is more difficult to understand. Our analysis of the $\Delta\, q_C\, [M \mid N]$ elements is sufficient to explain the signs and relative magnitudes of the $-\Delta\, L_C\, [B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]_{c\to t}$ and $-\Delta\, L_C\, [B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]_{\gamma\to g}$ terms. However, the existence of Eq. (30) is something of a mystery. To the author's knowledge, there is no rigorous theoretical reason why the approximation evident in Eq. (30) should be broadly applicable. The possibility exists that the result is a numerical fluke for ethane, in which event future analyses would have to be carried out only with respect to the $\Delta\, q_C\, [M \mid N]$ and the $\Delta\, e_C\, [M \mid N]$ elements, the variations of which do appear to be explicable. However, the possibility also exists that other ethane-like barriers can ultimately be represented with respect to vicinal exchange interactions. This is one of the more fundamental questions to be answered by the studies currently being carried out.

It is felt that the understandability of the present approach is comparable to that inherent in the Brunck-Weinhold analysis. Yet, the present explanation of the barrier in terms of vicinal $\Delta\, q_C\, [B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]$, $\Delta\, e_C\, [B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]$ and $-\Delta\, L_C\, [B\,(\mathrm{CH}) \mid B\,(\mathrm{C'H'})]$ terms is more conceptually consistent with the basic formalism of MO theory than is the Brunck-Weinhold interpretation, which employs the concept of vicinal $\sigma\sigma^*$ interactions. It can only be hoped that the present scheme is eventually as broadly successful in its predictive powers as the Brunck-Weinhold approach. This, of course, has yet to be shown and is the subject of the studies currently underway.

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FOOTNOTES AND REFERENCES

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SAŽETAK

Opis rotacijskih barijera etana s pomoću lokaliziranih atomskih orbitala

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Analizirana je barijera unutrašnje rotacije etana s pomoću lokaliziranih atomskih orbitala (LAO). Rezultati analize pokazuju da se pojava barijere može pripisati vicinalnim interakcijama C—H veza. Pri tome su posebno važne interakcije izmjene. Promjene vicinalnih interakcija za vrijeme rotacije mogu se objasniti migracijom elektronskog naboja. Dano je jednostavno fizikalno objašnjenje te migracije.