Rotational Barrier in Ethane (2)

Rebuttal to the Bickelhaupt–Baerends Case for Steric Repulsion Causing the Staggered Conformation of Ethane**

*Frank Weinhold**

Introduction

In the preceding article, Bickelhaupt and Baerends [1] present arguments and numerical calculations in support of the concept (still all too pervasive[2] in organic chemistry textbooks) that torsional barriers in ethane-like molecules are primarily a result of steric repulsions. This concept is usually rationalized[3] in terms of the qualitative molecular orbital (MO) diagram for "four-electron (4e) destabilizing interactions," as shown in Figure 1. This diagram originates[4] in a simple observation concerning diagonalization of a 2×2 matrix $\underline{\underline{\mathbf{H}}}$ [Eq. (1)] in a nonorthogonal basis set ϕ_a, ϕ_b with

$$\underline{\underline{\mathbf{H}}} = \begin{pmatrix} \epsilon_a & h_{ab} \\ h_{ab} & \epsilon_b \end{pmatrix} \xrightarrow{\text{diagonalize}} \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \qquad (1)$$

overlap $S_{ab} = \langle \phi_a | \phi_b \rangle$ where $\varepsilon_a = \langle \phi_a | \mathscr{H} | \phi_a \rangle$, $\varepsilon_b = \langle \phi_b | \mathscr{H} | \phi_b >$, and $h_{ab} = < \phi_a | \mathscr{H} | \phi_b >$ for the relevant orbital Hamiltonian (e.g., Fock or Kohn–Sham operator), and E_1, E_2 are

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[*] Prof. Dr. F. Weinhold
Theoretical Chemistry Institute and
Department of Chemistry
University of Wisconsin
Madison, WI 53706 (USA)
Fax: (+1) 208–262–9918
E-mail: weinhold@chem.wisc.edu

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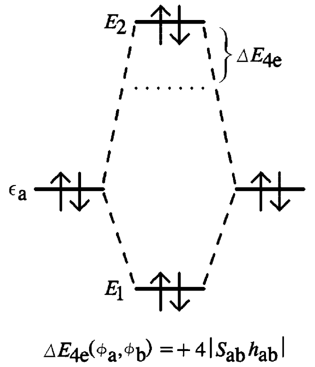

Figure 1. Four-electron destabilizing interaction (see Supporting Information Section A.1), expressed in terms of nonorthogonal "unperturbed" orbitals ϕ_a, ϕ_b (for which there is no imaginable Hermitian perturbation theory).

the final eigenvalues. It is found (see Supporting Information Section A.1 for algebraic details) that the sum of final eigenvalues $E_1 + E_2$ is raised ("destabilized") relative to the initial diagonal elements $\varepsilon_a + \varepsilon_b$, which leads to net destabilization [Eq. 2] when the MOs are fully occupied by four

$$\Delta E_{4e} = +4|S_{ab}\,h_{ab}| \tag{2}$$

electrons, as schematically depicted in the "perturbative splitting diagram" of Figure 1. (Equation (2) gives the leading-order result for $h_{ab} \neq 0$, but significantly, a net "destabilization effect" is obtained whether the interaction element h_{ab} is zero or non-zero!)

For the ethane barrier problem, ϕ_a, ϕ_b are identified as filled C–H bond orbitals ($\phi_a = \sigma_{C-H}$, $\phi_b = \sigma_{C'-H'}$) on opposite ends of the torsional C–C axis, and the four electrons occupying these orbitals are considered to experience stronger "destabilizations" as they rotate into the eclipsed (*cis*-like) alignments where S_{ab} is strongest. Because the same model applies with equal aptness to the repulsive interactions of two closed-shell helium atoms (generally attributed to "steric repulsions"), it is inferred[3] that the ethane torsional barrier may similarly be assigned a steric origin.

It is no accident that the Bickelhaupt–Baerends (BB) analysis leads to a similar conclusion. Their method,[5] as implemented in the ADF package,[6] was expressly developed to be a bridge between modern density function theory (DFT) calculations and the qualitative MO concepts outlined in ref. [3] (as cited also by Bickelhaupt and Baerends[5]). For this purpose they developed a modification of Kitaura–Morokuma (KM)-type self consistant field (SCF)–MO analysis[7] (following related work of Ziegler and Rauk[8]) which may be identified as the "BB–KM method." The philosophical, mathematical, and numerical basis of the BB–KM method is outlined with admirable clarity and thoroughness in Ref. [5], and we shall quote this reference as the definitive exposition of the technical details underlying the BB case.

Critique of BB–KM Analysis

Bickelhaupt and Baerends characterize their method as "widely used and simple," "well-established and straightforward," and so forth. This characterization is far from accurate. The original KM method (and related nonorthogonal energy decomposition schemes) were severely criticized from the Natural Bond Orbital (NBO) perspective[9] as well as on grounds of basis-related numerical instabilities.[10] Natural Energy Decomposition Analysis (NEDA)[11] has emerged as a clear alternative, with strengthened interpretive foundations, better convergence to asymptotic classical quantities, and improved agreement with empirical chemical concepts (such as the uniqueness of hydrogen-bonding and the traditional σ-bonding/π-backbonding picture of transition-metal coordination). Recent experimental and theoretical evidence strongly suggests the erroneous physical picture that is presented by older KM-type analyses with regard to the important effects of intermolecular charge transfer and cooperative resonance-type phenomena in hydrogen-bonding interactions.[12] We need not reiterate here the specific criticisms of KM analysis,[9] but we emphasize that they apply with equal force to the BB–KM reformulation.

The BB–KM extension actually goes far beyond the original KM formulation by attempting a similar nonorthogonal decomposition in the short-range region of covalent bonding where the overlap-related interpretational ambiguities increase dramatically. As outlined by Bickelhaupt and Baerends in Equations (1) and (2) of the preceding communication, ref. [1] and detailed in ref. [5], the BB–KM method employs Slater determinants Ψ^A, Ψ^B of isolated fragments (e.g., two CH_3 radicals) to construct an "unperturbed" product function $\Psi^0 = \eta \det|\Psi^A\Psi^B|$ and energy ΔE^0 for overlapping fragments brought up to the final bonding geometry. Ziegler and Rauk[8] formerly labeled ΔE^0 as the "steric-interaction" energy, but BB identify it as the sum of "electrostatic" (ΔV_{elstat}) and "Pauli or steric repulsion" (ΔE_{Pauli}) contributions, where "ΔV_{elstat}" is evaluated (rather inconsistently) as the Coulombic interaction between the interpenetrating fragment densities $\rho_A + \rho_B$ (not the same as the density of Ψ^0, owing to the non-vanishing overlaps between Ψ^A, Ψ^B). "ΔE_{Pauli}" is then evaluated by difference from ΔE^0, and a final "orbital-interaction" term ΔE_{oi} is evaluated by difference from the actual fragment binding energy ΔE to give the basic BB–KM energy decomposition [Eq. (3)]. The same overlap inconsistencies that render the electrostatic label questionable are of course propagated into the Pauli and orbital-interaction labels.

$$\Delta E = \Delta E_{Pauli} + \Delta V_{elstat} + \Delta E_{oi} \tag{3}$$

The BB–KM labeling ambiguities naturally propagate into Bickelhaupt and Baerends' verbal arguments. The issue of verbal imprecision is quite material in the present case, for it has been shown[13] that the ethane barrier can be made to appear or disappear by slightly varying the treatment of nonorthogonality in a manner that lies wholly within the uncertainties of the verbiage. (The fact that overlap ambiguities involve the unfilled as well as filled fragment orbitals will be discussed below.) The imprecision of terminology is therefore of the same order as the phenomenon to be analyzed.

The inaccuracies of the BB–KM labels can also be judged by considering the simplest case of H_2. In this case the "unperturbed" Ψ^0 wavefunction is practically equivalent (differing at most by a possible triplet spin contamination term) to the original Heitler–London valence bond (VB) wavefunction, with the spatial part constructed from the product of overlapping hydrogen-atom orbitals. The apparent conclusion that a Heitler–London-type wavefunction contains no "orbital-interaction component" is implausible, casting profound doubt on the BB–KM definitional scheme.

Critique of Four-Electron Destabilizing Rationale

Let us nevertheless pass over these difficulties and proceed directly to the original 4e destabilizing MO diagram (Figure 1) that was the intended goal of BB–KM development. For this purpose we can agree to substitute Kohn–Sham MOs and matrix elements for the presumed SCF–MOs of earlier treatments, as BB suggest is valid. We can also stipulate the relevance for the ethane case of analyzing the energies E_1, E_2 of doubly degenerate *e*-type MOs (e'', e' in D_{3d} geometry, or e_g, e_u in D_{3h}), which are recognized[14] to carry the major torsional dependence. With these stipulations we shall now consider the possible physical interpretation (if any) that may be assigned to the "perturbation diagram" Figure 1. We shall also address how the *same* torsional dependence of E_1, E_2 can be alternately interpreted, in a more consistent and accurate perturbative framework, in hyperconjugative terms.

It is useful to first outline the hyperconjugative "two-electron (2e) stabilizing" rationale in a manner that can be most directly contrasted with the four-electron destabilizing rationale of Figure 1. Figure 2 presents the corresponding hyperconjugative diagram, showing how a doubly occupied orbital ϕ_a (e.g., σ_{C-H}) interacts with an unfilled orbital ϕ_{b*} (e.g., the vicinal $\sigma^*_{C'-H'}$) of energy $\varepsilon_{b*} = \langle \phi_{b*} | \mathcal{H} | \phi_{b*} \rangle$, with associated interaction and overlap matrix elements $h_{ab*} = \langle \phi_a | \mathcal{H} | \phi_{b*} \rangle$, $S_{ab*} = \langle \phi_a | \phi_{b*} \rangle$. An analysis similar to that for Figure 1 (see Supporting Information Section A.2 for details) leads to the familiar expression for the two-electron stabilization energy ΔE_{2e} [Eq. (4)] for $\phi_a \rightarrow \phi_{b*}$ (vicinal $\sigma_{C-H} \rightarrow \sigma^*_{C'-H'}$) interaction.

$$E_{2e} = -2\frac{h_{ab*}^2}{\varepsilon_{b*} - \varepsilon_a} \tag{4}$$

(Note that Equation (4) is independent of overlap S_{ab*}, although the expression is formally correct up through terms of order $O(S_{ab*}^2)$ To express ΔE_{2e} in a form somewhat more parallel to ΔE_{4e}, we can employ a Mulliken-type approximation to express the approximate proportionality of h_{ab*} to the overlap S_{ab*} [Eq. (5)] where k is a constant of order unity in atomic units.

$$h_{ab*} = -k\, S_{ab*} \tag{5}$$

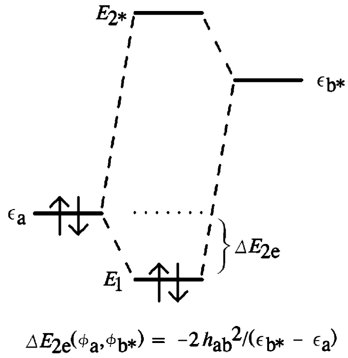

Figure 2. Two-electron stabilizing interaction (See Supporting Information Section A.2) for filled orbital ϕ_a and unfilled orbital ϕ_{b*} (taken orthogonal, but leading to the same splitting diagram, to leading order in S_{ab*}, whether ϕ_a, ϕ_b are orthogonal or nonorthogonal).

We can also recognize that the orbital energy difference $\varepsilon_{b*} - \varepsilon_a$ is nearly constant (torsionally insensitive) and of order unity in atomic units (1 a.u. ≈ 627 kcal mol^{-1}). Hence, we can rewrite Equation (4) in the approximate form given by Equation (6) (where k' is a new composite constant of order unity) to display the clear contrast with ΔE_{4e} in Equation (2).

$$\Delta E_{2e} \simeq -2\,k' |S_{ab*}\, h_{ab*}| \tag{6}$$

On a purely numerical level, Equation (1) or Figure 1 present no paradox, for matrix diagonalization in a chosen basis is a purely mathematical operation with no physical or chemical interpretation per se. The difficulty arises when one attempts to attach "perturbative" significance to the splitting diagram. As expressed by Bickelhaupt and Baerends (ref. [5], p. 4), the BB–KM analysis aims to provide an improved description of "changes of the one-electron energies of the orbitals in response to the perturbations" by means of such qualitative MO diagrams, while freeing them "from the double odium of inaccuracy and frequent empiricism." However, the difficulties of achieving a logically and physically consistent interpretation of these diagrams go far deeper.

What are the objections to such a "perturbative" interpretation of Equation (1) and Figure 1? Two major difficulties can be identified, the first quite general and the second somewhat specific to the ethane barrier problem:

1) If the orbitals ϕ_a and ϕ_b are overlapping, they cannot be considered to be the eigenfunctions of any underlying Hermitian Hamiltonian operator with energies ε_a, ε_b. Thus, there is no imaginable physical (Hermitian) Hamiltonian $\mathcal{H}^{(0)}$ that can serve as the "unperturbed system" for such analysis.[15]
2) Overlap integrals S_{ab*} between filled and unfilled orbitals are often comparable to those S_{ab} between filled orbitals; in such cases (as for ethane), it is physically and numerically inconsistent to include one type of overlap without the other.

We can judge from the first objection that the "unperturbed Hamiltonian" which leads to the outer levels of the splitting diagram (Figure 1) must suffer from the profoundly unphysical pathologies of non-Hermitian operators (such as non-conservation of probability and violation of Fermi–Dirac commutation relations[9b]). We can also judge that the second objection is highly relevant in ethane by evaluating the numerical overlaps between vicinal C–H bond and antibond orbitals, for example, $S_{ab} = -0.0847$, $S_{ab*} = -0.0743$ calculated at the RHF/6-31G* level in staggered geometry, a difference of less than 15%.[16] The superficial 4e-destabilizing interpretation of Figure 1 must therefore be reformulated to take account of both $\phi_a - \phi_b$ and $\phi_a - \phi_{b*}$ interactions as well as to remove the overlap that prevents consistent Hermitian formulation of an unperturbed $\mathscr{H}^{(0)}$ system Hamiltonian.

The first difficulty can be removed by employing Löwdin's symmetric orthogonalization procedure,[17] which leads to orthonormal orbitals $\bar\phi_a$, $\bar\phi_b$ that differ as little as possible (in the least-squares sense) from ϕ_a, ϕ_b. The matrix diagonalization problem now takes the form of Equation (7) where $\bar\varepsilon_a = \langle \bar\phi_a | \mathscr{H} | \bar\phi_a \rangle$, $\bar\varepsilon_b = \langle \bar\phi_b | \mathscr{H} | \bar\phi_b \rangle$, $\bar h_{ab} = \langle \bar\phi_a | \mathscr{H} | \bar\phi_b \rangle$.

$$\underline{\underline{H}} = \begin{pmatrix} \bar\varepsilon_a & \bar h_{ab} \\ \bar h_{ab} & \bar\varepsilon_b \end{pmatrix} \xrightarrow{\text{diagonalize}} \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \tag{7}$$

(Recall that the final MO energies E_1, E_2 are unchanged, since we have only performed a non-singular basis transformation.) The resulting splitting diagram (see Supporting Information Section A.3 for details) is shown in Figure 3, which leads to no net energy change when the MOs are fully occupied [Eq. (8)].

$$\Delta E_{4e}(\bar\phi_a, \bar\phi_b) = 0 \tag{8}$$

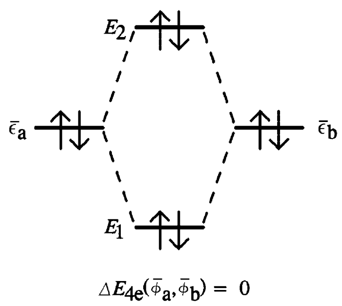

Figure 3. Four-electron nonstabilizing interaction (Supporting Information Section A.3), expressed in terms of orthogonalized unperturbed orbitals $\bar\phi_a$, $\bar\phi_b$ (for which there exists a valid Hermitian $\mathscr{H}^{(0)}$).

A proper physical (Hermitian) perturbative interpretation can now be given for the splitting diagram in Figure 3, but the physical "effect" on the torsion barrier has vanished!

However, as noted in Objection (2) above, an accurate description of the actual MO energy levels E_1, E_2 must actually involve the unfilled ϕ_{b*} ($\sigma^*_{C'-H'}$) as well as filled ϕ_b ($\sigma_{C'-H'}$) neighbor orbitals of ϕ_a. Let us therefore extend the basis to three orbitals,[18] transforming these to orthonormal form by the Löwdin symmetric orthogonalization procedure as before [Eq. (9)]. To leading order in the overlaps S_{ab}, S_{ab*},

$$(\phi_a, \phi_b, \phi_{b*}) \xrightarrow{\text{Löwdin}} (\bar\phi_a, \bar\phi_b, \bar\phi_{b*}) \tag{9}$$

the relationship between nonorthogonal and Löwdin-orthogonalized basis orbitals is found to be (see Supporting Information Section A.4 for details) given by Equations (10a–c)].

$$\phi_a = \bar\phi_a + {}^1\!/_2\, S_{ab}\, \bar\phi_b + {}^1\!/_2\, S_{ab*}\, \bar\phi_{b*} \tag{10a}$$

$$\phi_b = \bar\phi_b + {}^1\!/_2\, S_{ab}\, \bar\phi_a \tag{10b}$$

$$\phi_{b*} = \bar\phi_{b*} + {}^1\!/_2\, S_{ab*}\, \bar\phi_a \tag{10c}$$

Only the expressions for ϕ_a, ϕ_b are needed to make comparisons with the original splitting diagram in Figure 1. Substitution of these quantities into the original matrix diagonalization problem, Equation (1), leads to the splitting diagram shown in Figure 4, in which the net perturbative effect, denoted $\Delta E_{4e}(\bar\phi_a, \bar\phi_b, \bar\phi_{b*})$ is now of stabilizing form [Eq. (11)].

$$\Delta E_{4e}(\bar\phi_a, \bar\phi_b, \bar\phi_{b*}) = -2|S_{ab*}\, h_{ab*}| \tag{11}$$

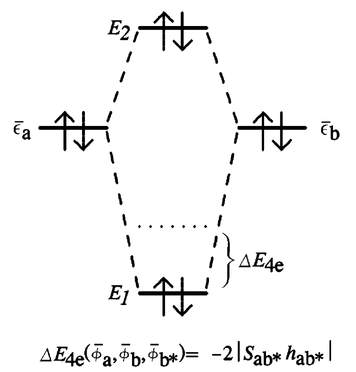

Figure 4. Four-electron stabilizing interaction (see Supporting Information Section A.4), for a proper three-term description of E_1, E_2 in terms of Löwdin-orthogonalized basis orbitals $\bar\phi_a$, $\bar\phi_b$, $\bar\phi_{b*}$).

Comparison with Equation (6) shows that this stabilizing effect is essentially identical to that predicted by the two-electron $\phi_a \rightarrow \phi_{b*}$ hyperconjugative interaction! The clear implication is that the numerical values are equivalent because the physical effects are equivalent. We can therefore conclude that hyperconjugative $\sigma_{C-H} \rightarrow \sigma^*_{C'-H'}$ interactions are responsible for the torsional variations of E_1, E_2 in each case, whether deeply concealed as in Figure 1 (by orbital overlap and superficial "bond" labels that are inadequate to express the ambiguities of nonorthogonal orbital composition), or clearly isolated and identified as in Figure 2.

We re-emphasize that Figure 1, Figure 2, Figure 3, and Figure 4 describe the same final MO energies E_1 and E_2 and torsional variations, merely referred to different "unperturbed systems" $\mathscr{H}^{(0)}$ (manifestly non-Hermitian in Figure 1, Hermitian in other cases). The fact that four-electron destabilization (Figure 1) and two-electron stabilization (Figure 2) can be ascribed a common physical origin implies that the former is somewhat superfluous in this case. The key distinction between the two "effects" is that the former is explicitly overlap-dependent (with resultant lack of unitary invariance to basis transformations), and thus vanishes as soon as ϕ_{b^*} mixing is prevented by choosing an orthogonal basis, whereas the latter is not. (As remarked in the Introduction, the unphysical nature of the supposed four-electron destabilizing effect is also indicated by the fact that it persists even if the interaction $h_{ab} = 0$.) It is remarkable that this somewhat flimsy theoretical construct has enjoyed such beguiling influence on a generation of organic chemists and their textbook writers.

True Steric Effects?

For comparison, it is useful to examine the case where interactions with unfilled orbitals ϕ_{b^*} are truly negligible compared to those with filled orbitals ϕ_b. An example is the interaction of two helium atoms, each in their $(1s)^2$ ground state. The nearest unfilled orbital is $2s$, too high in energy and too radially and angularly diffuse to serve as an effective acceptor orbital. We may therefore safely neglect the interactions of filled donor orbitals ϕ_a, ϕ_b with acceptor orbitals ϕ_{a^*}, ϕ_{b^*}, which reduces the problem to 2×2 form. Although ϕ_a, ϕ_b are nodeless $1s$ orbitals at infinite separation, at finite separation they evolve into the corresponding orthogonalized orbitals $\bar{\phi}_a$, $\bar{\phi}_b$ that preserve the Pauli exclusion principle. Weisskopf[19] has lucidly described the manner in which this orbital orthogonalization leads to the "kinetic-energy pressure" that opposes interpenetration of matter. As the orbitals ϕ_a, ϕ_b begin to overlap, the physically required orthogonalization leads to additional oscillatory and nodal features in the orbital waveform, which correspond to increased wavefunction curvature and kinetic energy, the essential "destabilization" that opposes interpenetration. The energies $\bar{\varepsilon}_a$, $\bar{\varepsilon}_b$ of the Pauli-preserving orbitals $\bar{\phi}_a$, $\bar{\phi}_b$ are thereby raised with respect to the long-range asymptotic values ε_a, ε_b [Eq. (12a,b)].

$$\bar{\varepsilon}_a = \varepsilon_a + |S_{ab}\,h_{ab}| \qquad (12a)$$

$$\bar{\varepsilon}_b = \varepsilon_b + |S_{ab}\,h_{ab}| \qquad (12b)$$

As in Figure 3, the MO energy levels E_1, E_2 are split symmetrically with respect to the proper physical orbital energies $\bar{\varepsilon}_a$, $\bar{\varepsilon}_b$, but the energy raising in Equations (12a,b) gives an apparent unsymmetrical pattern (see Figure 1) when expressed with respect to the long-range asymptotic values ε_a, ε_b. This situation is completely consistent with Coulson's original remark.[4]

The Weisskopf picture of steric repulsion is the conceptual and numerical foundation of the Natural Steric Analysis method,[20] as implemented in the general NBO analysis program.[21] This method was employed by Pophristic and Goodman[2] to evaluate the ethane barrier steric effects directly (not by difference from a putative "electrostatic" contribution, as in the BB method). Consistent with the hyperconjugative picture[13b] (and results of other workers[22]) the "steric effect" is found to be of much smaller magnitude and opposite sign, acting to favor the eclipsed conformation![23] (The principal steric effect appears to involve the "backside" lobes of the C–H bond orbitals, which protrude toward one another in eclipsed conformation but sidestep one another in staggered conformation.) Thus, the steric rationalization of ethane barriers is doubly nonsensical.

Of course, as the steric bulk of pendant groups increases, "true" steric effects can increasingly dominate the conformational potential. Nevertheless it remains true that hyperconjugative delocalizations impose an innate preference of the skeletal geometry for staggered conformations,[24] subject to modulation by steric or coordinative interactions between more complex pendant groups, but exposed in relatively pure form in ethane and ethane-like molecules.

Concluding Remarks

In focussing on the logic of the BB method, we have bypassed details of the NBO-based algorithms for evaluating steric and hyperconjugative contributions; Supporting Information Section A.5 replies to Bickelhaupt and Baerends' two specific technical points on NBO methodology. We emphasize that the bond-antibond picture of barrier origins is rather insensitive to details of bond-orbital construction, and indeed was originally developed[13b] and critically tested[13a] in the framework of crude bond-orbital models[25] of pre-NBO vintage. Nevertheless, NBOs have become the preferred method for quantifying and visualizing hyperconjugative interactions in modern ab initio (single- or multi-configurational) and density functional descriptions, as illustrated in Figure 5.

To summarize, we conclude that proper mathematical formulation of the four-electron destabilizing-interaction diagram (Figure 1) exposes the superficiality of the supposed steric interpretation of the E_1, E_2 torsional variations in ethane, and demonstrates that these variations should instead be attributed to hyperconjugative two-electron stabilizing interactions (Figures 2 and 5) that are easily obscured through loose treatment of nonorthogonality. While Figure 1 may be a useful mnemonic for representing 2×2 matrix diagonalization in a nonorthogonal basis set, it should not be envisioned as a physical interpretation of any imaginable physical

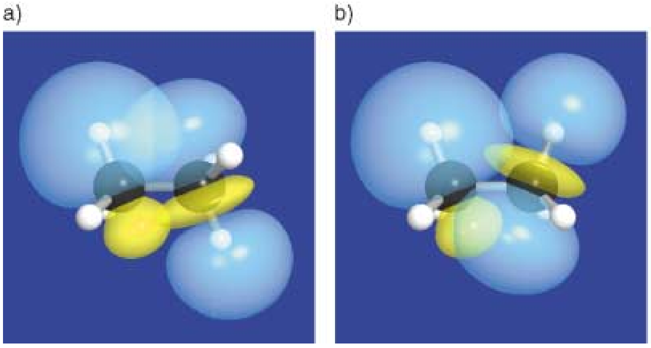

Figure 5. Vicinal σ_{C-H}–$\sigma^*_{C'-H'}$ NBO interactions in a) staggered (-2.59 kcal mol^{-1}) and b) eclipsed (-0.89 kcal mol^{-1}) conformers of ethane (optimized, B3LYP/6-311++G** level), which show the more favorable 2e stabilization $\Delta E_{2e}(\sigma_{C-H}\rightarrow\sigma^*_{C'-H'})$, Equation (4), in the staggered case.

process. By exhibiting the mathematical relationship that converts a four-electron destabilizing effect into a two-electron stabilizing effect, we have demonstrated explicitly that these two "effects" generally share a common mathematical origin. In this circumstance, attempts to assign distinct physical interpretations to Figures 1 and 2 are illusory.

The preceding arguments essentially echo and complement the numerical conclusions that were drawn long ago[13] concerning earlier versions[25] of the "Pauli repulsions" rationale for ethane barriers. Because this literature and its implications seem to have largely escaped the notice of qualitative MO theory adherents, it seemed preferable to address the BB case directly in the language and iconography that is apparently still favored by many organic-chemistry textbook writers.

It should be emphasized that these criticisms make no reference to the numerical validity of standard LCAO-MO variational calculations in nonorthogonal basis sets. Because these calculations are invariant with respect to non-singular transformations that span the same Hilbert space, there can be no numerical distinction between one type of basis set or another; the choice is dictated solely by numerical convenience. Nor do these arguments detract from the general usefulness of Mulliken-type approximations [cf. Eq. (5)] to visualize bonding interactions in terms of orbital overlap (that is, in terms of pre-orthogonal PNBOs that differ from orthonormal NBOs only in omission of the final interatomic orthogonalization;[26] see Figure 5). Such overlap imagery can be a powerful conceptual guide to the actual Hamiltonian interaction strengths, without encouraging the frequent misconception that spatial orbital overlaps (rather than kinetic and potential energy terms in the Hamiltonian operator) are somehow "causing" chemical bonding.

The recognition that energy-level variations which are commonly attributed to four-electron destabilizing effects can instead be understood in terms of hyperconjugative $\phi_{a}-\phi_{b*}$ interactions suggests how one can ultimately simplify and unify the understanding of phenomena that might otherwise seem to require distinct "effects." In effect, the stability of the staggered conformer can be attributed to resonance-type delocalization of the form (Figure 6) which imparts slight double-bond character to the C–C torsional bond and is maximized in antiperiplanar alignments.[27] The ethane-like rotation barriers are thus seen to have an intimate connection to anomeric and gauche effects, anionic hyperconjugation, stereoelectronic beta-elimination, and other conjugative and hyperconjugative phenomena in which $\phi_{a}-\phi_{b*}$ donor–acceptor (generalized Lewis base–Lewis acid) interactions play a dominant role.[28] The four-electron destabilizing concept therefore seems to play a somewhat dubious and superfluous role in the present theory of torsional and stereoelectronic phenomena. Judicious de-emphasis of this concept would have the desirable effect of promoting conceptual economy and heightening general appreciation of the pervasive role of conjugative and hyperconjugative effects in chemistry.

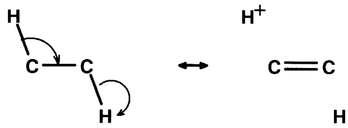

Figure 6. Resonance-type hyperconjugative delocalization in ethane

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