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Dissecting the Hindered Rotation of Ethane

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The existence of a rotational barrier of ca. 3 kcal mol⁻¹ around the C–C single bond in ethane has been known^[1] since the early studies of Ebert,^[2] Wagner,^[3] Eucken and Weigert^[4] and Pitzer^[5] done in the 1930s. Even the simplest ab initio methods are able to reproduce this fundamental result. However, the physical origin of this hindered rotation is still under controversy in the literature. There are two effects that have been regarded as responsible for the rotational barrier: a larger steric repulsion in the eclipsed conformation^[6–10] and an enhanced stabilization of the staggered conformation due to hyperconjugation.^[11–16] Clearly, the two effects (and possibly some other ones) coexist in ethane, so in order to quantify the magnitude of one of them one must be able to *switch off* the other in the model calculation.

The steric repulsion still remains the most popular explanation of the hindered rotation of ethane. This effect is often understood as the increase in energy that accompanies the antisymmetrization of a wave function originally formed by strictly localized descriptions of two methyl groups brought up to the final ethane geometry where they overlap. This so-called Pauli repulsion is considered to be more important for the eclipsed conformation,^[7] where the overlap between the occupied σ_{C-H} molecular orbitals is larger, thus giving rise to a hindered rotation. The non-orthogonality between the molecular orbitals (MOs) of the two fragments seems to be the main source of controversy of such models. It has been argued that a zeroth-order unperturbed system formed by two non-orthogonal sets cannot be put in correspondence with a Hermitian Hamiltonian, raising doubts about any physical argument obtained from a perturbative approach using such a model.^[19] (We cannot accept this point of view, which would exclude all the perturbation theories of intermolecular interactions as being illegitimate.)

The hyperconjugation^[20] effect is due to interactions/delocalizations between electrons of vicinal C–H bonds mainly through the C–C bond. In an MO picture, this corresponds to favorable two-electron two-orbital interactions between the occupied σ_{C-H} orbital of one methyl group and the virtual antibonding σ^*_{C-H} orbital of the other. This also involves orbital σ^*_{C-C} .^[21] The electron delocalization effect can easily be assessed in valence bond (VB) theory calculations^[8–10] by adding/

removing the appropriate resonance structures from the wave function. In an MO calculation it is not that simple due to the delocalized nature of the MOs. The hyperconjugation effect is estimated by constructing the wave function from sets of MOs localized in methyl moieties. The way such MOs are constructed, in particular whether they are variationally optimized,^[22] apparently led to opposite conclusions about the role of the hyperconjugation in the rotational barrier.^[10]

Another factor to be taken into account is the geometry relaxation that accompanies the internal rotation, and in particular the change in the C–C distance. It is somewhat striking that the C–C bond is significantly shorter in the staggered conformation than in the eclipsed one although this bond is formally not changing during the rotation. This effect already appears at the simplest minimal basis SCF level of theory: at the STO-6G level one gets C–C bond lengths equal to 1.535 Å and 1.545 Å, respectively. At the same time the effect of geometry relaxation on the height of the barrier is minor. Nonetheless, previous studies^[23,24] concluded that different answers can be obtained for the relative importance of the steric repulsion and the hyperconjugation effect depending on whether the geometry relaxation has been considered or not.

Previous energy decomposition analyses relied, in one way or another, on the definition of two methyl fragments. However, in the last years there have been a growing interest in other kinds of energy partitioning schemes,^[25] closely related to population analysis and bond-order techniques. Such schemes allow expressing the total energy of a system, exactly or up to a good accuracy, as a sum of atomic and diatomic contributions, as given by Equation (1):

$$E_{\text{tot}} = \sum_A E_A + \sum_{A<B} E_{AB} \quad (1)$$

The diatomic terms naturally reflect the attractive or repulsive interactions between the atoms in the molecule. The one-center terms correspond to the effective energy of each atom in the molecule; its value relative to that of the corresponding free atom accounts for the promotion that occurs upon bond formation. In this sense, it is important to recall that the one- and two-center contributions are static parameters.^[26] They measure to which extent the energy of a given atom or atomic pair contributes to the total molecular energy at that geometry and with the wave function used at that point. Thus, the diatomic values cannot be put into direct correspondence with the dissociation energies, as dissociation involves changes in both geometry and wave function. The main advantage of this methodology for the present case is that one can decompose all energetic interactions within the molecule on the basis of a single ab initio calculation, without recurring to an arbitrary

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(promolecule) model or to perturbative approaches which are also, in general, restricted to just two interacting fragments.

In recent years one of us has developed several schemes of Hilbert space partitioning of the Hartree–Fock molecular energy. (Since the rotational barrier can be described well without the aid of electron correlation, there is no need to consider electron correlation herein.)

In the first scheme, called chemical energy component analysis (CECA),^[26] the sum of the one- and two-center energy components usually reproduces closely, but not exactly, the corresponding molecular energy. For that reason and in the present work, we have implemented an alternative exact version of CECA (we shall denote it CECA_{exact}). We provide a brief description of the method in the Computational Methods section.

It is worth mentioning that very recently Pendas and co-workers^[27] have tackled the problem of the ethane barrier and other stereoelectronic effects by using a one- and two-center energy decomposition scheme at the Hartree–Fock level in the framework of Bader's atoms in molecules (AIM)^[28] three-dimensional analysis. Their aim, however, has been to group the appropriate contributions arising from adiabatic and diabatic states in order to let them correspond to some extent with quantities like Pauli repulsion or orbital interactions. We believe that the one- and two-center components provided by such energy decompositions can themselves provide very useful information about the process and can also be put into correspondence with the steric and hyperconjugative effects.

In our analysis, lacking any reference state, we tentatively identify steric repulsion effects by the change in the sum of the vicinal hydrogen–hydrogen energy components, while the effects of hyperconjugation can be judged through the changes in the C–C and C–H binding energies—partial transfer of electrons from one bond to another leads to minor changes in bond orders and bond energies.

There is another aspect of this problem which apparently has not received proper attention. It is known that the 2s atomic orbitals of the carbon are more populated in the SCF wave functions than are the 2p ones, in accordance with the fact that they are of lower energy in the free atom. However, if one builds up a wave function by starting from strictly localized molecular orbitals (SLMOs) in which the bonding orbitals are constructed by making use of the four orthogonal sp³ hybrids, then as a first approximation one obtains equal population of the four orbitals 2s, 2p_x, 2p_y and 2p_z. The final SCF solution can be interpreted in the SLMO framework by considering that each SLMO gets some admixture of virtual orbitals of other bonds and ultimately their collective effect leads to an increase in the s-population. (Owing to the directional character of the p-orbitals, the net effect for such different admixtures leads to adding the s-components and cancelling the p ones.)

In the standard formalism it is difficult to distinguish between delocalizations ultimately connected with correcting the s- and p-population ratios and the "true" hyperconjugation effects which may act between the different methyl groups of the ethane. However, one may utilize the fact that the require-

ment of the orthogonality of molecular orbitals is only an issue of mathematical convenience. The single-determinant wave function is completely determined (up to a physically unimportant constant factor) by the *subspace* of the occupied orbitals. One may select any—orthogonal or non-orthogonal—basis (i.e. the MOs) in that subspace; the use of non-orthogonal orbitals makes the calculations a little more involved. We shall use this property to introduce the increased s-population of the carbon atomic orbital at the very beginning, by using non-orthogonal hybrids with increased s-character relative to the standard sp³ ones.

Herein we take advantage of these methodologies to shed light on the origin of the rotational barrier of ethane. We shall focus not just on the debate on steric repulsion vs hyperconjugation stabilization, but also on how the subtle energetic difference between the staggered and eclipsed conformation manifests through the corresponding atomic and diatomic energy terms.

Our aim has been to get a clear picture of the chemistry of the process, rather than to obtain accurate quantitative values of the rotational barrier. Hence, we have used a minimal basis, namely the STO-6G, combined with different models in a single-determinant wave function. Nevertheless, the minimal basis calculations already reproduce the experimental value^[5] of the barrier of 2.875 kcal mol⁻¹ with surprising accuracy, and are much more suitable to qualitative interpretations than more extended ones.

We have calculated energy profiles for different values of the (H_a–C_a–C_b–H_b) dihedral angles between two equivalent eclipsed conformations for the four models described in the Computational Methods section, namely two SLMO ones, the Pure sp³ and Optimized sp³, and two Hartree–Fock. In the case of Hartree–Fock we have calculated two energy profiles: an Unrelaxed profile in which the geometry was the same as used in the SLMO calculations, that is, the idealized tetrahedral geometry for the two methyl groups has been kept fixed along the rotation, and a Relaxed one in which all geometrical parameters were optimized for each dihedral angle.

The four energy profiles are displayed in Figure 1. All profiles reproduce the rotational barrier semi-quantitatively. The value obtained at the HF/STO-6G level, including full geometry relaxation, is 2.88 kcal mol⁻¹, very close to best theoretical estimates. The very simple SLMO models with idealized tetrahedral geometries predict values of 2.37 and 2.49 kcal mol⁻¹ for the Pure and Optimized sp³ models, respectively. These values represent ca. 75% of the value obtained at the Unrelaxed Hartree–Fock level with the same geometry constraints (3.20 kcal mol⁻¹). It is noticeable that the quite simple SLMO models, even the Pure sp³, can recover most of the barrier height that can be calculated with the inclusion of orbital delocalization. The total energy obtained with the Pure sp³ hybrids is quite far from the Optimized sp³ one, which is roughly 0.045 a.u. lower, and yet the energy profile is almost indistinguishable. These observations already seem to point out the predominant role of steric repulsion versus the hyperconjugation effect.

Also, it is worth mentioning that the Optimized sp³ wave function, which probably has never been considered before,

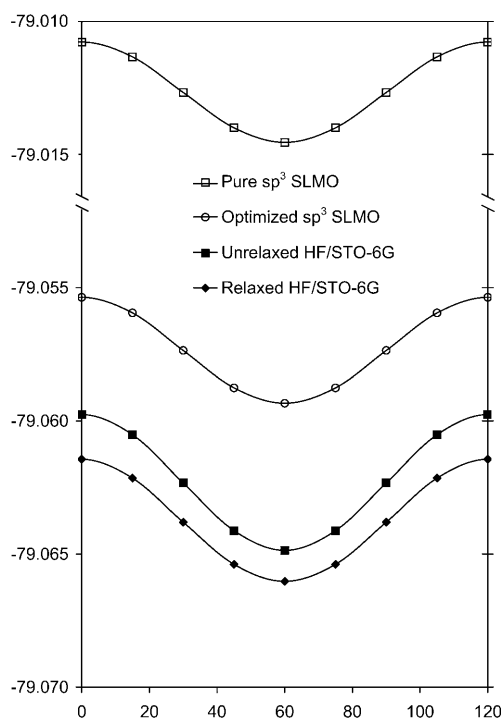


Figure 1. Potential energy barrier of the ethane molecule calculated with four different theoretical models.

reproduces the energy of the HF wave function very closely. That means that practically all the delocalization/hyperconjugation terms of any conventional analysis emerge in such a way as to enable the s-orbital to be more populated than the p-orbitals, but being at the same time quite irrelevant as far as the shape of the barrier is concerned.

One could attribute the difference between the height of the SCF potential curve with the Unrelaxed geometry ($3.2 \text{ kcal mol}^{-1}$) and that of the Optimized sp^3 curve ($2.49 \text{ kcal mol}^{-1}$) to the true delocalization effects. However, even that role of delocalization is in some sense overestimated. The point is that the barrier given by the fully relaxed HF method is $2.88 \text{ kcal mol}^{-1}$, that is, it has a value between these two numbers. That is because the deviation of the C–C–H angle from the ideal tetrahedral value is about half a degree larger in the eclipsed geometry than in the staggered one. That means that for the idealized geometry and fully optimized wave function the molecule is a little more strained in the eclipsed conformation, which leads to a slightly overestimated value of the barrier on the unrelaxed SCF curve.

In order to get deeper insight into the nature of the rotational barrier, we have performed an energy decomposition analysis in terms of one- and two-center chemical components for several models along the rotation profile. For sake of clarity, we are considering the changes in the sums of one-center energy contributions of the carbon and hydrogen atoms (ΔE_{C} and ΔE_{H} , respectively) along the profile, and those of three groups of the two-center energy components ΔE_{CC} , ΔE_{CH} and ΔE_{HH} . The first represents the single C–C two-center interaction; the second contains the six C–H interactions between

bonded atoms and the last one includes all the repulsion contributions between H atoms in the vicinal position. Of course, there are also two-center vicinal interactions between C and H atoms and the repulsions between geminal H atoms; these terms, however, have less chemical relevance and remain almost constant upon rotation, so we need not to discuss them explicitly.

We start by considering the change on the energy components derived from the $\text{CECA}_{\text{exact}}$ analysis for the simplest Pure sp^3 model (Figure 2a) and include stepwise the different effects that lead to the final fully relaxed profile. Furthermore, the one-center atomic energy components remain quite constant along this profile. This is very convenient in order to simplify the chemical analysis of the process, as it is not easy to in-

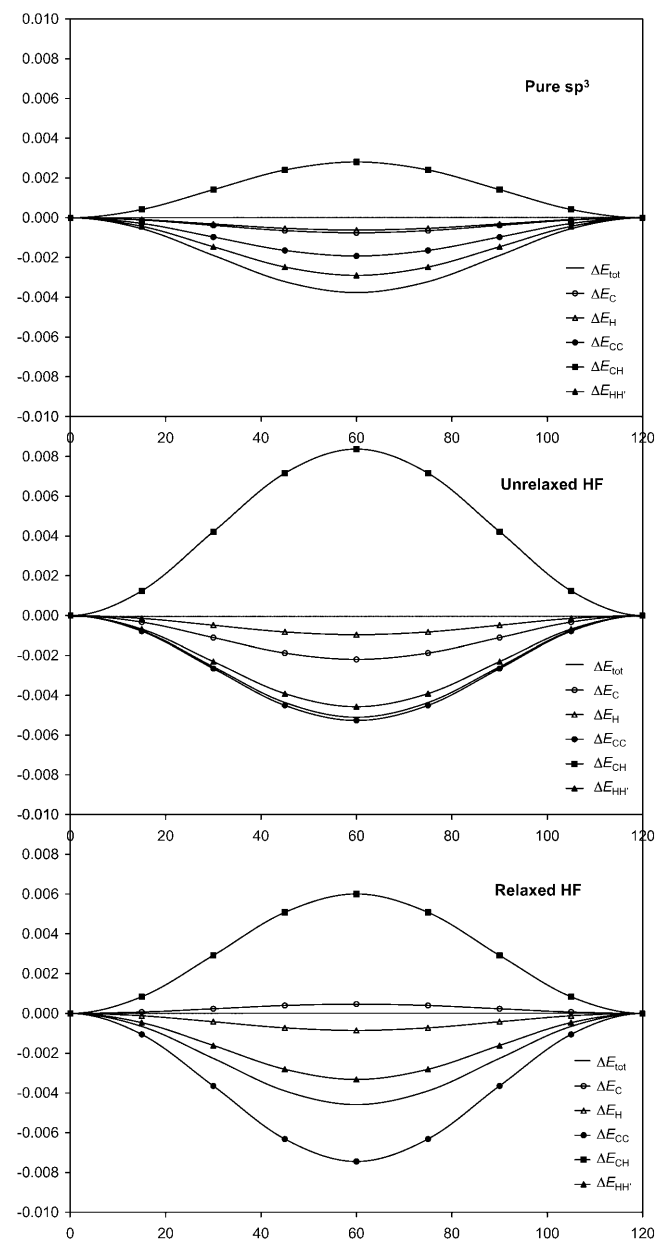


Figure 2. Energy components (a.u.) for the rotational barrier with three theoretical models.

interpret the changes in the intraatomic energies in simple terms. As far as the diatomic contributions are concerned, we can see that in the staggered conformation the attractive C–C interaction is slightly more negative, indicating an enhancement of the bonding interaction. Similarly, the repulsion between the H atoms decreases, indicating a lower steric repulsion. These energy changes are partly counterbalanced by a destabilization of the C–H bonding interaction, which amounts to roughly the net energy change for the rotation process (ΔE_{tot}) but with opposite sign. The destabilization of the C–H bonds and enhancement of the C–C bonding energy in the staggered conformation can be explained by non-orthogonality effects, which mimic in some sense the delocalization: if two orbitals overlap with each other, each may be said to contain some admixture of the other. This effect clearly resembles some aspects of the hyperconjugation picture, and what one can do is to determine how it is enhanced when *true* orbital delocalization is allowed. The net effect of these two non-orthogonality components is very small (ca. 1 mH) and is *opposite* to the net global energetic effect (which we recall already reproduces 80% of the true—fully relaxed HF—barrier).

Noteworthy, the same analysis for the Optimized sp^3 energy profiles yields almost indistinguishable curves for the variation of the chemical components (results not reported). This indicates that the large gain in energy upon increase of the s-content of the hybrids is not only nearly independent of the mutual orientation of the two methyl groups, but so is also its redistribution among the chemical bonds. This shows how ingenious the original sp^3 model is in reflecting the *fundamental* stereochemical effects.

In Figure 2b we report the energy component profiles when the *true* orbital delocalization is allowed by means of a Hartree–Fock optimization of the molecular orbitals at the same idealized geometry (Unrelaxed HF model). The first observation is that, as expected, the two opposite effects associated with the hyperconjugation are enhanced. The destabilization of the C–H bonds in the staggered conformation is about three times larger than in the SLMO model (at the same geometry) and similar behaviour is observed for the C–C bond energy gain, partially compensating it. The net delocalization effect—the sum of ΔE_{CH} and ΔE_{CC} terms—is about 3 mH. It is of the same order as the global energetic effect (5 mH) but again in the opposite direction. The repulsion between the H atoms is also increased as compared to the pure sp^3 curve, but not as much as the previous two components. The profile for the ΔE_{HH} contribution is very similar to that of the net total energy as all other terms effectively cancel. It is also worth mentioning that allowing for delocalization, yet keeping the same idealized geometry, produces larger changes in the intra-atomic components, especially for carbon atoms. Both intra-atomic energy contributions are more negative at the staggered conformation and account for half of the total barrier. This makes the picture of this model rather difficult to analyze in clear-cut chemical terms.

Finally, we can take into account both electron delocalization and geometry relaxation effects in the model (Figure 2c). In this case the intra-atomic contributions show little depend-

ence on the mutual orientation of the methyl groups and also almost perfectly cancel. The change in the C–C distance along the profile allows for a larger enhancement of the C–C bonding energy in the staggered conformation. This sole contribution is more than 50% larger than the global energetic effect itself. On the contrary, the weakening of the C–H bonds in the staggered conformation is slightly reduced by the geometry relaxation, so that the final net effect of the changes in the C–C and C–H energy components is in same direction as the global net effect, but is practically cancelled. The contribution of the steric repulsion between H atoms is slightly reduced by geometry relaxation, as the CCH angles decrease in the eclipsed conformation keeping the H atoms of different methyl groups further apart. Nevertheless, this repulsion still accounts for more than 70% of the height of the barrier, and more importantly, it has been present at roughly the same magnitude in all models. The inclusion of the net effect of the delocalization in terms of C–C and C–H energy contributions accounts for the remaining 30% of the barrier value.

The absolute energetic quantification of the hyperconjugation is a difficult and rather arbitrary task as it is strongly dependent on the nature of the diabatic reference state. In our case we do not make explicit use of such reference states and therefore we feel we cannot provide an estimate of it. However, what is really relevant for the barrier is the difference between hyperconjugation contributions between the two conformers, and this could be assimilated in our approach by the difference on respective $\Delta E_{\text{CC}} + \Delta E_{\text{CH}}$ values. Our estimate of $0.9 \text{ kcal mol}^{-1}$ in favor of the staggered conformation is in very good agreement with the recent values obtained by Pendas^[27] ($0.6 \text{ kcal mol}^{-1}$), Gao^[10] ($0.8 \text{ kcal mol}^{-1}$) and Bickelhaupt^[7] ($0.4 \text{ kcal mol}^{-1}$).

Thus, we can conclude that the hyperconjugation/delocalization effects are indeed very important for the rotational barrier. They give rise to individual energy components (namely the enhancement of the C–C bond and the weakening of the C–H bonding energy) which are larger in absolute value than the steric repulsion between the two methyl groups. This is the case even if simple SLMOs are used, due to non-orthogonality effects which mimic delocalization. However, the relatively large terms originating from hyperconjugation cancel almost completely. In that sense one may claim that the simple picture of attributing the barrier to the repulsion between the hydrogen atoms is indeed legitimate.

Computational Methods

We now describe the four models with increasing complexity that we have considered herein. The first model corresponds to a very simple wave function built up from strictly localized molecular orbitals (SLMOs) formed from directed hybrid orbitals of the C atoms and the 1s orbital of the H atom (Hoyland's^[29] model). An idealized geometry with $R(\text{C–C}) = 1.54 \text{ \AA}$, $R(\text{C–H}) = 1.07 \text{ \AA}$, idealized tetrahedral angles and pure sp^3 orbitals was used. The only parameter optimized (manually) accounted for the (minor) polarity of C–H bonds. Herein, we refer to this model as Pure sp^3 .

The second model is very similar to the first one, except that the atomic hybrids were subjected to optimization of the *s*-content, giving up their orthogonality. First a minor mixing between the 1s and 2s STO-6G basis orbitals was introduced, based on an inspection of the SCF orbitals. Thus the original 1s was replaced by the linear combination $\chi_{1s} + 0.025\chi_{2s}$ and the new 2s orbital was obtained by Schmidt-orthogonalization to the modified 1s orbital. The new hybrids had the *s*-coefficient increased with a factor of 1.73 relative to the ideal sp^3 hybrids, selected by manual optimization of the total molecular energy. The optimization of the *s*-content of the hybrids permitted the recovery of almost exactly the *s*-population of the carbon atoms calculated at the same geometry, but using fully optimized SCF orbitals. The same composition was used for the hybrids used to build up the C–H and the C–C bonds, because it has been found that their separate optimization improves the total energy by less than 50 μ Hartrees. Herein, we refer to this model as Optimized sp^3 .

It may be worth mentioning that in most cases one uses localized molecular orbitals that are required to be orthogonal to each other. However, by using non-orthogonal SLMOs we can get rid of those “tails” of the standard localized orbitals which are solely due to the arbitrary requirement of the orthogonality, but do not correspond directly to some true physical interactions causing delocalization. This permits us to distinguish between “mathematical” and “physical” delocalization effects. That is of importance when one wishes to discuss the role of hyperconjugation on the ethane barrier.

We did not perform explicit orthogonalization of the SLMOs constructed in the first and second models, instead we directly calculated the “density matrix” **D** by using the inverse of the matrix σ describing the overlap of the occupied SLMOs [see Eq. (VII.34) in ref. [30]]:

$$\mathbf{D} = 2 \sum_{ij}^{\text{occ.}} \mathbf{c}_i (\sigma^{-1})_{ij} \mathbf{c}_j^\dagger \quad (2)$$

where \mathbf{c}_i is the column vector of the coefficients of the *i*th SLMO in terms of the whole basis. The density matrix obtained in that manner has been used for calculating the different energetic quantities.

Apart from the previous two models using strictly localized orbitals (therefore excluding most delocalization effects between the two methyl units) we have also used standard SCF calculations with variationally optimized canonic Hartree–Fock orbitals with and without geometry constrains.

On the other hand, the molecular energy decomposition schemes in terms of one- and two-center components are not uniquely defined for a number of reasons. First, there is some arbitrariness in the definition of the atom in the molecule. Like in population analyses, there are different methods to define them, leading to different decomposition schemes. Thus, the analysis can be carried out either in the Hilbert space of atom-centered basis orbitals or directly in the three-dimensional (3D) physical space. The Hilbert-space-based methods are very useful and clearly defined when the basis set used in the calculation possesses pronounced atomic character. The Hilbert

space decompositions also have the advantage that it can be exact, that is, the one- and two-center components sum exactly to the total molecular energy. 3D space^[31–34] is exact only formally. As the analyses usually involve numerical integrations, there is always a numerical error associated with the decomposition. In the particular case of the ethane, the energy differences taking place along the hindered rotation are of the same order as the integration errors inherent in a 3D-space-based decomposition analysis. Hence, we had to limit ourselves to Hilbert-space-based methodologies. Herein we have considered minimal basis model calculations, so the Hilbert space analysis seems to be the adequate one.

Furthermore, the fact that each basis orbital is assigned to one of the atoms does not lead to a unique decomposition of the molecular energy into atomic and diatomic components. In this respect, exceptions are the semiempirical theories in which only one- and two-center integrals are used, which leads to a natural decomposition of the energy into monoatomic and diatomic terms. The analogous Clementi analysis of the ab initio results^[35] led to large three- and four-center terms lacking any chemical significance, and has been abandoned from that reason.

As mentioned before, in the last years one of us has developed several such Hilbert-space-based partitioning schemes for the Hartree–Fock molecular energy. In the first scheme called CECA,^[26] the three- and four-center energy components have been compressed into one- and two-center ones as much as it is possible by performing appropriate projections. This essentially means that the three- and four-center integrals are subject to the projective integral approximations first introduced in the framework of the chemical Hamiltonian approach.^[36] The sum of the one- and two-center energy components usually reproduces closely, but not exactly, the respective molecular energy. (The CECA energy components sum strictly to the exact energy for the diatomics only.) Owing to the approximations involved, the original CECA scheme could hardly be used to study such tiny effects as those occurring when the ethane rotation barrier is considered. For that reason, we have implemented an exact version of CECA (we denote it CECA_{exact}) which has not yet been described previously in ref. [25]. That scheme has been constructed on the basis of the comparison of the exact and approximate versions of some other energy decomposition schemes^[25, 37, 38] in the following manner.

Therein^[25] an exact energy decomposition scheme (denoted by E1 therein) has been developed, in which the different energy terms are assigned to the individual atoms or pairs of atoms merely on the basis of considering to what center the orbital(s) in the respective “ket” of the integral do belong—and what nucleus is involved in the case of electron–nuclear attraction terms. One can now introduce the same integral approximations as used in CECA, and get an approximate scheme (denoted by A1 in ref. [25]), the overall error for which is exactly the same as for CECA. The individual energy components of A1 are close but not identical to those in CECA, owing to the more complex analysis used in the latter scheme, leading to redistribution of some minor terms between the monoatomic and diatomic energy components. However, the

integral approximations distinguishing the schemes E1 and A1 do not involve those terms by which the schemes CECA and A1 differ. The difference between the given one- or two-center terms of the exact E1 and approximate A1 schemes, respectively, represent correction terms that may also be assigned to the same atom(s) in question. Adding them to the respective CECA energy components, we get the desired components of the CECA_{exact} scheme. For a detailed discussion of the formalism and the explicit formulae of the energy components we refer to ref. [25].

The chemical components arising from the alternative energy decomposition scheme (E1) provide a similar chemical picture of the rotation. The main difference between the two schemes is that in the case of the E1 method the differences of the one-center atomic components are bigger, which makes the chemical analysis much more difficult. This is because some chemically relevant two-center energy components are formally regrouped to the individual atomic ones in the E1 scheme. This illustrates the inadequacy for chemical analysis of methods based solely on atomic contributions, such as Bader's original AIM^[28] or that of Mandado et al. based on Hirshfeld atoms.^[39] Chemists tend to think in terms of atoms forming a molecule, but specially of the interactions between them. The net energy of one atom in a molecule is a result of a subtle balance between the positive and negative interactions with the rest of atoms, and the latter are precisely that which bears chemical information. Therefore, in this sense the CECA_{exact} method seems to be more suitable for the analysis of energy components in chemical terms.

Finally, it is worth mentioning that in both the CECA_{exact} and E1 schemes the kinetic energy is considered as a part of the atomic one-electron Hamiltonian, similarly to the case of 3D space decomposition schemes using disjoint atomic domains like Bader's atoms.^[28,31,32,34] As discussed in ref. [38], if the kinetic energy also contributes to the two-center terms, the values of the one- and two-center components are on the "chemical scale" at the equilibrium geometries. However, in other points of the potential energy surface the different energy components can behave in a completely non-physical way.^[38] This was the case in our calculations, too, and for that reason we have not considered such a possibility herein.

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