

An inequality formulation of conformational energy differences

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A theoretical analysis has been performed of the effects of geometry optimization upon computed barriers to rotation and pyramidal inversion. It is shown that, where ΔE is the true energy difference between the energy minimum and the transition state for a particular conformational process, (barrier using the optimized geometry of the lower state) $> \Delta E >$ (barrier using the optimized geometry of the higher state). Some numerical tests of this inequality are discussed. These reveal certain limitations upon the assumption that an optimized geometry is transferable from one basis set to another.

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On a effectué l'analyse théorique des effets de l'optimisation de la géométrie sur les barrières calculées pour la rotation et pour l'inversion pyramidale. On a montré que, lorsque ΔE est la vraie différence d'énergie entre l'énergie minimum et l'état de transition pour un processus conformationnel déterminé, (la barrière utilisant la géométrie optimisée de l'état le plus bas) $> \Delta E >$ (la barrière utilisant la géométrie optimisée de l'état le plus élevé). On discute de quelques essais numériques de cette inéquation. Ceux-ci relèvent certaines limitations concernant l'hypothèse qu'une géométrie optimisée est transférable d'une base à une autre.

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Introduction

A number of workers have suggested recently (1) that the conventional explanation of the first and second of Hund's rules² may be incorrect, because this explanation overemphasizes effects of electron-electron repulsion upon energy differences within a multiplet (2). While there is no doubt that electron repulsion is largest in the state having the lower energy, for neutral systems nuclear-electron attraction is also largest (most negative) in the state having the lower energy, and this attractive term is always the dominant component in a Hund multiplet.

To rationalize this result, Colpa (3) proposed a reformulation of the theory of Hund's rules in which certain unnecessary assumptions concerning the role of electron repulsion were deleted. In the Restricted Hartree Fock (RHF) scheme, this reformulation has the mathematical form

of a series of inequalities. In the case of the singlet-triplet energy difference of an open shell $\pi\pi^*$ excited configuration, the appropriate inequality is

$$[1] \quad 2K_{\pi\pi^*}^S \leq \Delta E_{\text{RHF}} \leq 2K_{\pi\pi^*}^T$$

in which ΔE_{RHF} is the energy difference between the exact RHF energy levels, and $K_{\pi\pi^*}^S$ and $K_{\pi\pi^*}^T$ are the exchange integrals for the exact RHF π and π^* orbitals of the singlet and triplet states, respectively.

As has been shown elsewhere (4), $2K_{\pi\pi^*}^S$ and $2K_{\pi\pi^*}^T$ are the energy differences which result when both states are described by singlet or by triplet RHF orbitals, respectively. These energy differences correspond to the use of a "frozen" orbital model which maintains the identity of orbitals in different states. According to the inequality of eq. 1, the true energy difference in the RHF approximation lies between the values of the two differences obtained with the frozen orbital approximation.

The significance of such work is that it provides insight into why an energy difference computed within a particular frozen orbital approximation may either underestimate or overestimate the true energy difference, according

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²Hund's first rule states that, for a given configuration in an atom, the state of lowest energy is the state with the highest multiplicity. The second rule states that, within the manifold of states with the same multiplicity, the state with the largest angular momentum quantum number has the lowest energy.

to the particular frozen orbital model which is selected. This situation has a parallel in the computation of conformational energy differences. Much work, especially by Veillard (5), has shown that full geometry optimization along the reaction coordinate is necessary to reproduce barriers to torsion about bonds or pyramidal inversion at a tricoordinate centre. The purpose of the present work is to demonstrate, by means of an inequality formulation of the problem, the relationship between barriers computed within a particular rigid rotor model and the true value of the barrier.

Theory

For the analysis of rotation in ethane, we employ a two-symbol descriptor to represent the state of the molecule. The first symbol describes the conformation, *i.e.*, staggered or eclipsed. The second (bracketed) symbol refers to the particular optimized geometry employed to describe this conformation.³ Thus St(St) describes a staggered conformation with CC and CH bond lengths and HCH angles optimized for this conformation; this is the true equilibrium situation for the staggered conformation. In the same way, Ecl(St) describes an eclipsed conformation which has the CC and CH bond lengths and HCH angles of the staggered conformation. The energies of the various states are given by $E_{\text{St(St)}}$, etc.; and $\Delta E = E_{\text{Ecl(Ecl)}} - E_{\text{St(St)}}$ is the energy difference between the true equilibrium conformations Ecl(Ecl) and St(St).

The transformation from St(St) to Ecl(Ecl) can be supposed to proceed in two stages. In the first, rotation takes place within a rigid rotor model, *i.e.*, $\text{St(St)} \rightarrow \text{Ecl(St)}$. The energy difference associated with this process is designated $B(\text{St})$. In the second step, the state Ecl(St) relaxes to its true equilibrium geometry Ecl(Ecl).

Since

$$E_{\text{Ecl(St)}} \geq E_{\text{Ecl(Ecl)}}$$

it follows that

$$E_{\text{Ecl(St)}} - E_{\text{St(St)}} \geq E_{\text{Ecl(Ecl)}} - E_{\text{St(St)}}$$

i.e.

$$[2] \quad B(\text{St}) \geq \Delta E$$

³It is known (5) that the CC and CH bond lengths as well as the HCH angles of the staggered and eclipsed conformations of ethane are not the same.

Proceeding analogously for the transformation from Ecl(Ecl) to St(St), with $B(\text{Ecl})$ the energy difference for the step $\text{Ecl(Ecl)} \rightarrow \text{St(Ecl)}$, and noting that

$$E_{\text{St(Ecl)}} \geq E_{\text{St(St)}}$$

leads to

$$E_{\text{Ecl(Ecl)}} - E_{\text{St(Ecl)}} \leq E_{\text{Ecl(Ecl)}} - E_{\text{St(St)}}$$

i.e.

$$[3] \quad B(\text{Ecl}) \leq \Delta E$$

Combining [2] and [3] gives

$$[4] \quad B(\text{St}) \geq \Delta E \geq B(\text{Ecl})$$

One can easily generalize the proof of this inequality to

$$[5] \quad \text{Barrier for lower state rigid rotor} \geq \Delta E \geq \text{Barrier for higher state rigid rotor}$$

Equations similar to [4] and [5] are also derived readily for an inversion barrier.

It is evident that these inequalities are formally similar to the inequality of [1]. However, there are important differences: eq. 1 is rigorously correct within the RHF scheme; but eqs. 4 and 5 will apply to exact wavefunctions, to Hartree Fock (HF) wavefunctions, or even to approximate HF wavefunctions, so long as the equilibrium geometry is computed exactly within the particular approximation selected. These geometries will, of course, be somewhat different within the various approximations. Some numerical tests of [5] follow in the next section.

Numerical Tests of the Theory

Table 1 summarizes the results of computations on ethane employing a minimal (STO-3G) and an extended (4-31G) basis set (6) with Gaussian 70 (7). The energy differences computed with the extended basis set are $B(\text{St}) = 2.90$ kcal/mol, $\Delta E = 2.77$ kcal/mol, and $B(\text{Ecl}) = 2.64$ kcal/mol, in agreement with [4].⁴

The calculations just described are relatively expensive in terms of costs of computer time, because of the need to optimize the geometry of both states. It has, therefore, become customary (8) to compute the optimized geometry with the STO-3G basis set and then calculate energy differences with the 4-31G basis set, the assump-

⁴Veillard (5) has reported $\Delta E = 3.07$ kcal/mol.

TABLE 1. Total energies and rotational barriers in ethane

Conformation	Energy ^a	
	Staggered optimized parameters (St)	Eclipsed optimized parameters (Ecl)
<i>Minimal basis set</i> (optimization with the minimal basis set)		
Staggered	-78.306138 ^b	-78.305778 ^c
Eclipsed	-78.301493 ^b	-78.301525 ^c
Difference	$B(\text{St}) = 2.92 > \Delta E = 2.90 > B(\text{Ecl}) = 2.67^d$	
<i>Extended basis set</i> (optimization with the minimal basis set)		
Staggered	-79.115732 ^b	-79.115466 ^c
Eclipsed	-79.111189 ^b	-79.111297 ^c
Difference	$B(\text{St}) = 2.85 > \Delta E = 2.78 > B(\text{Ecl}) = 2.62^d$	
<i>Extended basis set</i> (optimization with the extended basis set)		
Staggered	-79.115927 ^e	-79.115726 ^f
Eclipsed	-79.111302 ^e	-79.111514 ^f
Difference	$B(\text{St}) = 2.90 > \Delta E = 2.77 > B(\text{Ecl}) = 2.64^d$	

^aTotal energies in hartrees; 1 hartree = 627.71 kcal/mol.

^b $r_{\text{CC}} = 1.5452 \text{ \AA}$; $r_{\text{CH}} = 1.0858 \text{ \AA}$; $\angle \text{CCH} = 110.66^\circ$

^c $r_{\text{CC}} = 1.5587 \text{ \AA}$; $r_{\text{CH}} = 1.0849 \text{ \AA}$; $\angle \text{CCH} = 111.02^\circ$

^dEnergy differences in kcal/mol.

^e $r_{\text{CC}} = 1.5300 \text{ \AA}$; $r_{\text{CH}} = 1.0834 \text{ \AA}$; $\angle \text{CCH} = 110.07^\circ$

^f $r_{\text{CC}} = 1.5412 \text{ \AA}$; $r_{\text{CH}} = 1.0828 \text{ \AA}$; $\angle \text{CCH} = 111.64^\circ$

tion being made that the optimized geometry does not change appreciably as the basis set is changed. Equation 4 can be employed to assess the validity of this procedure and the assumption of transferability of geometry from one basis set to another. In this connection, it is useful to note that, for a problem such as the rotational barrier of ethane, one should expect that

$$[6] \quad E_{\text{Ecl}(\text{St})} - E_{\text{Ecl}(\text{Ecl})} \simeq E_{\text{St}(\text{Ecl})} - E_{\text{St}(\text{St})}$$

because both sides of this approximate equality refer to relaxation to an equilibrium geometry; and the same bonds and valence angles are involved.

When eq. 6 is a strict equality, we have

$$[7] \quad \Delta E = \frac{1}{2}(B_{\text{St}} + B_{\text{Ecl}})$$

The computations on ethane with the 4-31G basis set obey eq. 7 very closely; the average of $B(\text{St})$ and $B(\text{Ecl})$ is 0.004416 hartree, as compared to $\Delta E = 0.004413$ hartree.

In contrast to these results, a computation on ethane with the STO-3G basis set and a single optimization cycle led to the energy differences $B(\text{St}) = 2.92$ kcal/mol, $\Delta E = 2.90$ kcal/mol, and $B(\text{Ecl}) = 2.67$ kcal/mol. Although these data still obey [4], it is clear that [7] is not obeyed.

A further analysis showed that [6] was not obeyed and that $E_{\text{Ecl}(\text{St})} \sim E_{\text{Ecl}(\text{Ecl})}$. This analysis of rotation in ethane thus shows that a single optimization cycle at the STO-3G level is insufficient. Using the geometries computed by one STO-3G optimization cycle, the energy differences computed at the 4-31G level are $B(\text{St}) = 2.85$ kcal/mol, $\Delta E = 2.78$ kcal/mol, and $B(\text{Ecl}) = 2.62$ kcal/mol. Equation 4 is again obeyed; however, ΔE is not the average of $B(\text{St})$ and $B(\text{Ecl})$, although the deviation is less marked than for the STO-3G results.

Table 2 summarizes computations on pyramidal inversion in ammonia. These show that the geometry computed with an STO-3G basis set cannot be used to calculate 4-31G energy differences. In this case, the inequality of [5] should be

$$[8] \quad B(\text{optimization at pyramidal geometry}) \geq \Delta E \geq B(\text{optimization at planar geometry})$$

The energy differences computed with STO-3G optimized geometries and the STO-3G basis set are $B(\text{pyr}) = 12.50$ kcal/mol, $\Delta E = 11.13$ kcal/mol, and $B(\text{plan}) = 9.78$ kcal/mol, in agreement with [8]. However, when these geometries are

TABLE 2. Total energy and inversion barriers in ammonia

Conformation	Energy ^a	
	Pyramidal optimized parameters (Py)	Planar optimized parameters (Pl)
<i>Minimal basis set</i> (optimization with the minimal basis set)		
Pyramidal	-55.455390 ^b	-55.453250 ^c
Planar	-55.435481 ^b	-55.437665 ^c
Difference	$B(\text{Py}) = 12.50 > \Delta E = 11.13 > B(\text{Pl}) = 9.78^a$	
<i>Extended basis set</i> (optimization with the minimal basis set)		
Pyramidal	-56.099081 ^b	-56.100586 ^c
Planar	-56.100260 ^b	-56.104912 ^c
Difference	$B(\text{Py}) = -0.74 > \Delta E = -3.66 > B(\text{Pl}) = -2.71^a$	
<i>Extended basis set</i> (optimization with the extended basis set)		
Pyramidal	-56.106692 ^d	-56.106613 ^e
Planar	-56.105948 ^d	-56.105997 ^e
Difference	$B(\text{Py}) = 0.49 > \Delta E = 0.44 > B(\text{Pl}) = 0.39^a$	

^aSee Table 1.^b $r_{\text{NH}} = 1.0318 \text{ \AA}$; $\angle \text{HNH} = 104.77^\circ$ for pyramidal structure.^c $r_{\text{NH}} = 1.0052 \text{ \AA}$; $\angle \text{HNH} = 120.00^\circ$ for planar structure.^d $r_{\text{NH}} = 0.991 \text{ \AA}$; $\angle \text{HNH} = 115.8^\circ$ for pyramidal structure.^e $r_{\text{NH}} = 0.986 \text{ \AA}$; $\angle \text{HNH} = 120.00^\circ$ for planar structure.

used to calculate the energy differences with the 4-31G basis set, negative barriers are observed, *i.e.*, $B(\text{Pyr}) = -0.74 \text{ kcal/mol}$, $\Delta E = -3.66 \text{ kcal/mol}$, and $B(\text{plan}) = -2.71 \text{ kcal/mol}$. In addition, these negative barriers do not satisfy [8].

The barriers computed with the 4-31G basis set and 4-31G optimized geometry do satisfy [8]. However, ΔE is lower than the experimental value (5.9 kcal/mol) (9). The experimental ΔE for ammonia has been reproduced with a very extended basis set which included *d*-type polarization functions on nitrogen and *p*-type functions on hydrogen (10).

Our results are thus entirely in accord with the view (10, 11) that barriers to pyramidal inversion are extraordinarily sensitive to the nature and quality of the basis set as well as the nature of the geometry optimization scheme employed. At the same time, the inequality formulation of the problem suggests that the qualitative comparison of barriers to pyramidal inversion of a series of closely related molecules should be valid, provided that geometry optimization of both the pyramidal and planar conformations is performed, and the same basis set is employed for the geometry optimization and the computation of energy differences.

It is, perhaps, useful to recognize that inequalities of the type discussed in this paper will exist regardless of the nature of the optimization that is performed, so long as both the upper and lower states are optimized in the same way. The present example of geometry optimization can, therefore, be regarded as a subset of a more complete optimization scheme in which basis set optimization would be included. However, basis set optimization is usually not practical for polyatomic molecules, and our numerical examples were restricted to geometry optimization using the standard STO-3G and 4-31G basis sets.

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