Conformation Analysis in Light of Localization and Delocalization*

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The role of electron delocalization in conformational effects, especially in giving rise to barrier forces is discussed in the bond orbital framework. Using orthogonal bond orbitals, the effects of through space and through bond delocalization interactions is demonstrated; numerical examples show the predominant role of through space delocalization. The total energy obtained by strictly localized orthogonal bond orbitals is shown to be rather independent of the relative orientations of the bonds. Second order perturbative delocalization energy corrections are interpreted as bond-bond pair potentials within the orthogonal basis. On the contrary, nonorthogonal bond orbitals lead to an energy expression which is very sensitive to the bond orientations even if one neglects completely electron delocalization. The origin of the barriers is discussed in terms of nonempirical bond-bond pair potentials.

INTRODUCTION

»It is our opinion that too much effort has gone into a search for a simple explanation to this phenomenon...«,[1] wrote Hoffman in 1963 discussing the Extended Hückel results on the ethane barrier. In this contribution, joining to the above observation partly, we stress that there exists no unique explanation to the origin of barrier forces, because the same physical effect can be described by different »reasons« in different mathematical frameworks. On the other hand, we feel that in a given mathematical formalism it is worthwhile to look for the possible simplest explanation to any phenomenon if one wants to understand something about the effects, not only to calculate them simply.

Concerning the theory of barriers to internal rotations, two different quantum chemical models will be discussed. The first one works with orthogonal atomic orbitals; as known, all the ZDO theories such as CNDO/2, PCILO, INDO, etc. work within a atomic basis which is tacitly assumed to be Löwdin-orthogonalized. In the second model, which is the usual one in the *ab initio* framework, the basis overlap effects are treated explicitly.

In both models we adopt the bond orbital framework. A strictly localized bond orbital, SLBO, possesses two hybrid atomic orbitals, except lone pairs which are left as single hybrids.

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The wave function constructed from SLBOs represents only a rough approximation to the exact Hartree-Fock wave function for the same molecule. Because of the two-center character of the SLBOs, they do not account for the electron delocalization effects; tails are to be added to SLBOs in order to describe delocalization. The exact (SCF) localized molecular orbitals contain always some tails. Concerning the problem of conformational energy differences, one can investigate whether the tails are important in calculating them or not. Reformulating this question, one can ask whether electron delocalization is important or not. As we will see, the answer depends on the fact that we have orthogonal or nonorthogonal set of SLBOs.

Using orthogonal SLBOs, a number of earlier and recent investigations[2-11] pointed out that the tails are of extreme importance in accounting for barriers to internal rotations. According to England and Gordon,[2-4] the origin of barriers is connected to the interaction of an SLBO with its own tail. In the »σ—σ* theory« of Brunck and Weinhold[5] this observation is reformulated so that the barriers arise due to vicinal bond-antibond interactions. This fact is supported also by the observation that the zeroth order wave function in PCILO fails to predict barriers; at least a second order perturbation energy is needed to account for them.[6] Based on the fact that the tails are important but small, Surján and Mayer[8] proposed a linearized SCF procedure which can be used in conformation analysis of large molecules.[10] The main point in the linearized SCF theory is that one can neglect every terms in the SCF equations written in the bonding-antibonding basis of SLBOs, which contains second or higher powers or products of tails. The rather high accuracy of the linearized SCF method in calculating barriers to rotations has been understood recently bu Surján et al.[11] by making distinctions between through space and through bond delocalization interactions. As a matter of fact, a linearized theory generates tails originating from direct through space interactions between bonding and antibonding orbitals, and the resulting tail formula shows a very high orientation sensitivity.[11] On the other hand, the tails not accounted for in the linearized SCF model can be obtained by considering through bond delocalization corrections.[11] The through bond tails can influence strongly the total energy but, as a consequence of the relevant tail formula, through bond effects contribute to the energy by a term which is rather independent to the orientation of bonds. As an illustration, we will present some numerical results on rotational barriers as obtained by the linearized SCF approximation compared with a method taking into account through bond delocalization effects.

Because the numerical realizations of the above theories were performed within a semiempirical ZDO formalism, the work of Corcoran and Weinhold[9] was of crucial importance in generalizing these ideas. These authors could show that, even in an *ab initio* scheme, orthogonal bond orbitals cannot give correct barriers without taking into account delocalization corrections. For instance, the bond orbitals of ethane, built up from Löwdin-orthogonalized atomic orbitals, lead to a barrier of wrong sign. Thus the electron delocalization is very important even in the *ab* initio scheme if one has orthogonal bond orbitals.

The above considerations lead to the general conclusion that, using orthogonal basis set, the origin of the barriers is connected to through space delocalization interactions between bonding and antibonding orbitals.

Let us review now the case when the SLBOs are non-orthogonal. It has been known for a long time, that in this approach the barriers of simple molecules can be calculated without any delocalization correction in an approximation of accuracy 10—20⁰/o. The most important references on this field are (12—15). This finding indicates that the electron delocalization is not a »physical« reason of the barriers but only a possible way of interpretation in the language of orthogonal orbitals. It was recently argued by Corcoran and Weinhold,[9] that, using nonorthogonal SLBOs, the necessary bond-antibond mixture is implicitly incorporated as an orthogonality effect.

It was also observed that the polarity of SLBOs influences weakly the obtained barrier values. Satisfactory approximation can be obtained by completely unpolarized bonding orbitals,[5,9,12] showing the unimportance of pure electrostatic effects in giving rise to barrier forces. Additionally, it is known also that pure exchange contributions to rotational barriers are small,[16] showing that the origin of the barriers can be explained in the nonorthogonal case by the overlap repulsion.

Based on these ideas, we will present here derivations of simple bond-bond pair potentials the changes of which are responsible for the barriers to internal rotations around single bonds.

Bond-bond Pair Potentials in the Orthogonal Basis

In order to derive the pair potential in the orthogonal case, let us study first the energy expression for the strictly localized wave function (more precisely: the wave function built up from SLBOs). This obviously reads:

$$E_o = E_{nucl} + 2 \sum_i H_{ii} + 2 \sum_{ik} (ii \mid kk) - \sum_{ik} (ik \mid ik) \qquad (1)$$

Here E_{nucl} is the nuclear repulsion energy, the summation indices run over all the doubly occupied SLBOs, we adopt the (11|22) convention for the two-electron integrals, and H is the core. Due to the strictly localized character of the MOs the exchange part of the energy (the last term in (1)) can be simplified in the ZDO approximation and the relevant expression becomes

$$E_o = E_{nucl} + 2 \sum_i H_{ii} + 2 \sum_{ik} (ii \mid kk) - \sum_i (ii \mid ii) \qquad (2)$$

We will point out that E_o is rather independent of the relative bond orientations.

Realizing that the electron-nuclear attraction energies are present in H_{ii}, one can conclude that the terms in (2) are either independent of the relative orientations of the bonds, or they cancel each other to a high extent. The latter is the case with the terms which describe the net electrostatics of the molecule. For neutral and unpolar systems, such as e. g. ethane, the electrostatic effects have negligible role in giving rise to barrier forces.[12] Thus E_o changes only slightly if the orientations of bonds are changed in a molecule. This fact is well illustrated in Table I where it seems that the SLBO approximation leads to unreasonably small barriers.

Table I shows also that through bond and through many bond interactions[11] are unimportant in calculating the barriers: the linearized SCF approximation gives accurate results. As we have already mentioned, the linearized SCF approximation accounts for the through space electron delocalization, thus the latter must be responsible for the barrier. This kind of delocalization can be described most simply by perturbing the SLBOs in the same manner as it is done in the PCILO method.[8,17] The relevant second order energy correction is:

$$E^{(2)} = - \sum_{ik} \frac{H^2_{ik*}}{H_{k*k*} - H_{ii} - (ii \mid k*k*)} \tag{3}$$

This formula is valid under the ZDO approximation.

The perturbed total energy can be written as $E = E_o + E^{(2)}$. Based on the above discussion, the only orientation dependent term in E is $E^{(2)}$. Therefore, with respect to an internal rotation in the rigid rotor approximation the total energy has the form

$$E = const + \sum_{ik} V_{ik} \tag{4}$$

V_{ik} representing the bond-bond interaction potential which is not else than the second order delocalization energy correction:

$$V_{ik} = - \frac{H^2_{ik*}}{H_{k*k*} - H_{ii} - (ii \mid k*k*)} \tag{5}$$

The orientation dependency of V_{ik} arises primarily from H_{ik*} in the numerator of (5); the denominator is more-or-less insensitive to rotations.

This pair potential describes a bond-antibond interaction corresponding to a $\sigma \rightarrow \sigma^*$ delocalization effect which is not else than the »origin« of the barrier in this mathematical framework. In the next Section we will discuss the origin of the barriers in another formalism.

TABLE I

Barriers to Internal Rotations in the Rigid Rotor Approximation by Different Methods (kcal/mol)*

molecule	a	b	c	d	e	f
$H_3C{-}NH_2$	0.21	1.56	1.56	1.56	2.0[11]	2.1—2.4[v]
$H_3C{-}OH$	0.13	0.77	0.77	0.79	1.1[iii]	1.1[vi]
$H_3C{-}CH_3$	0.24	2.29	2.26	2.27	2.9[i]	2.5—3.3[iv]

* 1 kcal = 4.186 joule
a: strictly localized orbitals; b: linearized *SCF* approximaiton, see Refs [8,10]; c: delocalized MOs considering through space and through bond interactions, see Ref. [11]; d: full SCF result; e: experiment; f: ab initio. The calculations a—d were performed within the CNDO/2 scheme. The total energies in methods b and c are calculated as correct expectation values by the MOs with the corresponding delocalization correction.
  (i): refs. [21—23]
  (ii): ref. [29]
  (iii): ref. [30]
  (iv): refs. [24—28]
  (v): refs. [31, 32]
  (vi): ref. [32]. For a more detailed review on barrier calculations of these molecules see e. g. [33] and references therein.

The Bond-bond Pair Potential Using Nonorthogonal Strictly Localized Bond Orbitals

The situation is quite different if one has bond orbitals which overlap. This is the case e. g. in an SCF *ab initio* framework. As we have already mentioned, in that case it is not necessary to take into account electron delocalization effects, because the origin of the barrier forces is now connected to the overlap repulsion. This finding permits us to derive a simple approximate but nonempirical form of the bond-bond interaction potential.[18]

To begin with, let us recall the energy expression of a molecule using nonorthogonal molecular orbitals:[19]

$$E = E_{nucl} + 2 \sum_{ik} H_{ik} S_{ik}^{-1} + \sum_{ijkl} [2 S_{ij}^{-1} S_{kl}^{-1} - S_{ik}^{-1} S_{jl}^{-1}] (ij \mid kl) \qquad (6)$$

where S^{-1} is the inverse of the overlap matrix of the molecular orbitals. The summation indices run over the occupied orbitals. Again, the core H contains the kinetic energy operator Δ and the nuclear-electron attraction.

By introducing some further approximations, we would like to bring (6) into a more compact form. Having strictly localized bond orbitals, the use of the Mulliken approximation for the two-electron integrals can be justified.[18] As a matter of fact, due to the strictly localized character, our bond orbitals correspond to a quite compact charge distribution in the space, similarly to a single atomic orbital for which the Mulliken scheme was proposed.[20] Moreover, if we introduce the Mulliken approximation in the bond orbital basis instead of in the atomic orbital one, the large three- and four center integrals containing intrabond overlaps remain unapproximated.

On the basis of the same arguments, we can use the Mulliken scheme also for the matrix elements of the electron-nuclear attraction operator. Finally, the inverse overlap matrix can be expanded into a power series up to the second order. By introducing these approximations, the relevant formula for the total energy becomes:[18]

$$E = E_{nucl} + 2 \sum_i \{ \sum_{k(\neq i)} (ii \mid kk) - \sum_a Z_a \langle i \mid r_a^{-1} \mid i \rangle \} + \sum_i [\Delta_{ii} + (ii \mid ii)] +$$

$$+ \sum_i \sum_{k(\neq i)} [S_{ik} \Delta_{ik} + (S_{ik})^2 \Delta_{ii} + \frac{1}{2}(S_{ik})^2 \{ (ii \mid kk) - (ii \mid ii) \}] \qquad (7)$$

Let us now analyse this energy formula with respect to the orientation sensitivity. The first row contains the pure electrostatic effects which, as we have already discussed, have no significant contribution to barriers to rotations of molecules under study. In the second row there are matrix element of diagonal type which are completely orientation independent. Accordingly, the total energy reads:

$$E = const + \sum_{ik} U_{ik} \qquad (8)$$

where U_{ik} is the bond-bond pair potential in the »nonorthogonal« framework; the changes of which are responsible for giving rise to barrier forces:

$$U_{ik} = S_{ik} \{ \Delta_{ik} + S_{ik} (\Delta_{ii} + \Delta_{kk})/2 + \frac{1}{2} S_{ik} [(ii \mid kk) - [(ii \mid ii) + (kk \mid kk)]/2] \} \qquad (9)$$

In writing down (9), we symmetrized the orientation dependent part (third row) of (7) with respect to the labels i and k.

In analysing this result, the following points are worth mentioning:

(i) every term in the pair potential depends on the interbond overlap S_{ik}. This shows the central importance of the overlap repulsion in giving rise to barriers.

(ii) Δ_{ik} is also of the same order of magnitude as S_{ik}, thus every term in (9) is of the second order in the interbond overlap. This emphasizes how fine effects are to be accounted for if one wants to calculate the barriers.

(iii) The two-electron integrals in the pair potential arise from the expectation value of the exchange operator. However, there are integrals of different sign thus they can compensate each other to some extent — this confirms the finding of Christiansen and Palke[16] that pure exchange contributions to barriers are small.

(iv) Kinetic energy matrix elements are also present in U_{ik}, both of diagonal and offdiagonal type. As far as we know, the role of kinetic energy intergrals has not been emphasized in connection with rotational barriers.

CONCLUSION

In this contribution the role of electron delocalization in giving rise to barrier forces was reviewed. Earlier numerical results show that (i) direct delocalization effects are important only if one works with orthogonal strictly localized bond orbitals, while (ii) applying transferable nonorthogonal bond orbitals the barriers arise mainly due to overlap effects. Based on these observations, we presented simple derivations of approximate bond-bond interaction potentials describing barriers to internal rotations, which have quite different forms in the two cases (i) and (ii). This difference stresses that the same physical phenomenon can be attributed to quite different hints if the corresponding mathematical frameworks are different.

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SAŽETAK

Konformacijska analiza s aspekta lokalizacije i delokalizacije

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Pomoću veznih orbitala razmatrana je uloga elektronske delokalizacije u konformacijskim efektima, posebno u smislu doprinosa barijernim silama. Uz pomoć ortogonalnih veznih orbitala prikazani su efekti delokalizacijskih interakcija kroz prostor i kroz vezu; numerički primjeri pokazuju dominirajuću ulogu delokalizacije kroz prostor. Ukupna energija dobivena striktno lokaliziranim veznim orbitalama pokazuje se prilično neovisnom o relativnoj orijentaciji veza. Korekcije drugog reda u perturbiranoj delokalizacijskoj energiji interpretirani su kao potencijali parova veza-veza u ortogonalnoj bazi. Nasuprot, iz neortogonalnih veznih orbitala slijedi izraz za energiju koji je vrlo senzitivan na orijentacije veza, čak ako se potpuno zanemari elektronska delokalizacija. Porijeklo barijera diskutirano je na osnovi neempirijskih potencijala parova veza-veza.