

## Delocalization Corrections to the Strictly Localized Molecular Orbitals: A Linearized SCF Approximation

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An explicit formula is derived for calculating the delocalization corrections (tails) to be added to the strictly localized bond orbitals. It was obtained by solving analytically the SCF problem for the interbond interactions in a linearized approximation. The model calculations at the CNDO/2 level show that this simple approach is sufficient to account for the molecular conformations.

**Key words:** Localized orbitals – Tails of  $\sim$  – Delocalization corrections to  $\sim$  – linearized SCF approximation.

In recent years there is a considerable interest in analysing and constructing molecular wave functions in terms of strictly localized molecular orbitals (SLMOs) corresponding to individual bonds, lone pairs, etc. [1–13]. Different procedures have also been proposed for calculating the small delocalized components (tails) always present in the SCF localized orbitals. (As pointed out in [8, 13, 14], the usual, orthogonal SLMOs without delocalization corrections are not able to account for conformational effects, etc.) These procedures usually apply the SCF perturbation theory [3, 6, 11]. In this approach the tails generated in the given order appear in the perturbation expression for the next order, leading to an iterative procedure (The simple perturbation theory is adequate only in an extended-Hückel type formalism [1, 15, 16], or if one departs from the single determinant wave function as in the PCILO method [17].)

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Here we develop an approximate method for calculating the tails self consistently without any iterations. This can be done because the tails are usually small enough to justify the following approximations: (i) any terms containing products (squares) of tails can be neglected; (ii) the interaction of different fragments can be taken into account in a pairwise manner: three-fragment interactions represent higher order effects.

The analysis may be most conveniently done by turning to a bond-orbital basis, which consists of the (bonding and antibonding) self consistent SLMOs<sup>1</sup> [6, 9, 13]. Then one has to determine for each bonding MO the admixture of the antibonding orbitals of other bonds, which represents the only first order effect [13]. It was also found in [8, 14] that this type of admixture between vicinal bonds is just responsible for the rotational barriers. As a consequence of approximation (ii), the resulting MOs will not be strictly orthonormalized, so one has to perform their (Löwdin-)orthogonalization.

Let  $i$  and  $i^*$  be the appropriate bonding and antibonding SLMOs of a given fragment, and let us consider the interaction of this fragment with another one possessing orbitals  $j$  and  $j^*$ . The delocalization effects within this subproblem result in new orbitals:

$$\begin{aligned} |\psi_i\rangle &= |i\rangle + \eta|j^*\rangle & |\psi_j\rangle &= |j\rangle + \theta|i^*\rangle \\ |\psi_{i^*}\rangle &= |i^*\rangle - \theta|j\rangle & |\psi_{j^*}\rangle &= |j^*\rangle - \eta|i\rangle. \end{aligned} \quad (1)$$

Here  $\eta|i^*\rangle$  and  $\theta|j\rangle$  are the tails of the resulting bonding orbitals. (If one of the fragments describes a lone pair, the corresponding antibonding MO is absent.) If the SLMOs are orthogonal, the delocalized MOs (1) remain orthogonal but are normalized only to the first order. By Eq. (1) one can construct the  $4 \times 4$  density matrix<sup>2</sup> and the  $4 \times 4$  Fock matrix  $F$ . Because the SLMOs are solutions for the intrabond SCF problems, the condition for the self-consistency can be expressed as

$$\begin{aligned} \langle \psi_i | \hat{F} | \psi_{j^*} \rangle &= 0 \\ \langle \psi_j | \hat{F} | \psi_{i^*} \rangle &= 0. \end{aligned} \quad (2)$$

Expanding (2) for orbitals (1) and neglecting all terms of second and higher orders in  $\eta$  and  $\theta$ , one obtains a system of two linear inhomogeneous algebraic equations with the solution:

$$\eta = \frac{I_2 F_{ji^*}^0 - (J_1 + F_{i^*i^*}^0 - F_{jj}^0) F_{ij^*}^0}{(F_{i^*i^*}^0 - F_{ii}^0 + I_1)(F_{i^*i^*}^0 - F_{jj}^0 + J_1) - I_2 J_2}. \quad (3)$$

Here  $I_1 = 3(ij^*|ij^*) - (ii|j^*j^*)$ ;  $I_2 = 4(ij^*|i^*j) - (ii^*|jj^*) - (ij|i^*j^*)$ ; and the  $J$  integrals can be obtained from  $I$  by interchanging  $i$  and  $j$  everywhere.  $F^0$  is the

<sup>1</sup> They are obtained by minimizing the total molecular energy with respect to the polarities of the bonds built up of pairs of directed hybrids.

<sup>2</sup> According to (i) in the density matrix one has to conserve only terms linear in tails. Thus the density matrix will have the correct idempotency properties also up to first order, only.

zeroth order Fock matrix built up by SLMOs. (For the two-electron integrals the (11|22) convention is used.) Similarly, an analogous formula is valid for  $\theta$ .

If one uses the ZDO approximation, the terms coupling the two equations (2) are proportional to the interbond integral ( $ii^*|jj^*$ ) which can be expected very small. The neglecting of this integral permits to decouple the equations and calculate all the delocalization corrections quite independently. The relevant formula becomes:

$$\eta = \frac{h_{ij^*}}{F_{ii}^0 - F_{i^*j^*}^0 + (ii|jj^*)} \quad (4)$$

where  $h$  is the core matrix.

It is interesting to note that Eq. (4), but not the more general formula (3), is formally the same as that used in the PCILO method [14] for determining the first order delocalization contribution to the zeroth order wave function, and the corresponding second order energy term. However, in spite of this resemblance, there are some essential differences between the PCILO method and our approach. Namely, the wave function used in PCILO is a multideterminantal one, while we remain within the single determinant scheme and use formula (4) to calculate the delocalization corrections to the SLMOs. The resulting MOs are then orthonormalized and we calculate the correct *expectation value* of the energy, corresponding to the single determinant obtained. As a consequence, our energy is a strict *upper bound* to the SCF energy.

The table and the figure show the results of some CNDO/2 sample calculations. As may be seen, the calculation of tails by Eq. (4) gives energies which are significantly better than the SLMO values, and may be considered sufficiently

**Table 1.** The CNDO total energies and rotation barriers of simple molecules<sup>a</sup>

Molecule	SLMO	Total energy (a.u.)		Barrier (kcal/mol)		
		Eq. (4)	standard CNDO/2	SLMO	Eq. (4)	standard CNDO/2
CH <sub>4</sub>	-10.11219	-10.11337	-10.11359			
C <sub>2</sub> H <sub>6</sub> eclipsed	-18.75608	-18.80519	-18.80748	0.24	2.29	2.27
staggered	-18.75646	-18.80885	-18.81110			
H <sub>2</sub> O	-19.86191	-19.86271	-19.86288			
CH <sub>2</sub> O	-26.75291	-26.82912	-26.83590			
HCOOH	-45.14581	-45.29080	-45.30924			
CH <sub>3</sub> NH <sub>2</sub> eclipsed	-22.52124	-22.56153	-22.56443	0.21	1.56	1.56
staggered	-22.52157	-22.56402	-22.56691			
CH <sub>3</sub> OH eclipsed	-28.50736	-28.54741	-28.55053	0.13	0.77	0.79
staggered	-28.50756	-28.54863	-28.55179			

<sup>a</sup> Experimental bond lengths and ideal tetrahedral bond angles were used.

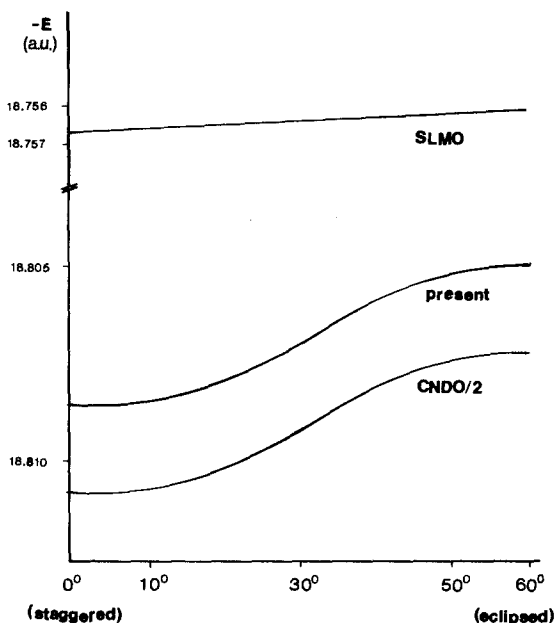


Fig. 1. The comparison of the CNDO/2 potential energy curves for ethane in different approximations

accurate. Especially important is that the energy differences (barriers of rotations) are practically equal to the exact SCF values. As Fig. 1 shows, the potential energy profile given by the present method is quite parallel to the full SCF one, while the SLMO model is unable to account for the barrier.

We hope that the present results permit to develop rather fast semiempirical (CNDO, MINDO, etc.) methods to study the conformation of very large molecules at the SCF level. The only iteration algorithm will be necessary in the calculation of the optimum SLMOs, which is very fast. An important feature of the approach is that the calculation of the tails is only an  $N^2$  procedure ( $N$  being the number of bonds and lone pairs). Work in this line is in progress.

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