Ab Initio SCF Procedure with Localized Molecular Orbitals of Fragments

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An ab initio procedure is described with a basis set of localized orbitals of the fragments. The method was tested on three molecular systems. The results are in agreement with the results of LCAO calculations.

Recently the use of molecular orbitals of fragments (φ_i) to built the orbitals of larger systems (ψ_i) has been shown to be promising [1, 2]. The method we have proposed is similar to that of Christoffersen [1]. We write

$$\psi_i = \sum_{i \neq j} C_{ij} \varphi_j \qquad (1)$$

where the coefficients C_{ij} are determined by the SCF procedure. One promise of this procedure is the fact that the distant orbitals don't interact very much and therefore can be neglected.

The proposed method (LF) was tested on butane, transbutadiene and ethylene (Table 1). The standard geometries were used [3], with the STO-3 G basis set of Pople et al. [4] and with an electron integral part of Gaussian 70 [5]. The localization on the fragments has been done with the procedure of Boys [6]. The fragments constituting the systems are CH_3 and CH_2. The localized orbitals were calculated for CH_4 and CH_3, but in forming ψ_i one of the H atoms was removed. Only interactions between localized orbitals on neighbouring C atoms have been included. This approximation is certainly valid for system with σ bonds. In fact it holds also for the π bonds. The antisymmetrization of ψ_i transfers the influence of localized orbitals throughout to whole system. The agreement between the LF and the standard LCAO method is best for butane. The differences in the eigenvalues of the molecular orbitals are 3 a. u. for the inner orbitals but small for all others (0.2 a. u.).

Table 1. Electronic energies (a.u.).

Method	Butane	Transbutadiene	Ethylene
LF	−313.551	−266.560	−109.412
LCAO	−301.449	−265.260	−110.427

In the approach we have used the localization on fragments produces a mixing between the 1 s and 2 p_y orbitals on the C atoms. This means that in the LF procedure there is no σ-π separation, though some of the calculated molecular orbitals ψ_i can easily be described as π bonds. The mixing of 1 s and 2 p_y orbitals influences the ordering of the molecular orbitals in the LF approach. The two highest occupied orbitals of transbutadiene in the LCAO procedure are π ones. In the LF procedure two σ orbitals are in between. The largest differences in the molecular eigenvalues are 3 a. u. for the inner orbitals and 0.4 a. u. for the highest ones.

A simple way to exclude the mixing between 1 s and 2 p_y orbitals is to keep the 1 s orbitals fixed in the localization procedure. This has been tested on ethylene and the molecular orbital energies are given in Table 2. The agreement with the results from the standard ab initio calculation is very good.

Table 2. Molecular orbital (occupied) energies (a.u.). Assignment of molecular orbital in brackets.

	LCAO	LF
ε_1	−11.983 (C 1s)	−11.678 (C 1s)
ε_2	−11.017 (C 1s)	−11.661 (C 1s)
ε_3	− 0.977 (CC)	− 1.309 (CC)
ε_4	− 0.743 (CH)	− 1.000 (CH)
ε_5	− 0.608 (CH)	− 0.852 (CH)
ε_6	− 0.523 (CH)	− 0.778 (CH)
ε_7	− 0.467 (CH)	− 0.560 (CH)
ε_8	− 0.322 (π)	− 0.244 (π)

For butane we have tested a variation of the LF approach. Because the localized orbitals on the fragments resemble the sp^3 hybrids and because Eq. (1) introduces enough flexibility we have taken for φ_i the ideal sp^3 hybrids on the C atom with added 1 s orbitals of the H atoms. The coefficients of the sp^3 hybrid and 1 s orbitals of the H atoms were redetermined by requirement that localized orbitals have to be orthonormal. Though the difference between the coefficients of the ab initio localized orbitals and the coefficients determined as described above is of the magnitude ±0.2 a. u. the agreement between the electronic energies is excellent. The LF approach has one computational drawback. The transformation of electronic integrals from an atomic basis to localized ones is very time consuming. This is the reason why in the calculations only integrals larger than 10^{-3} a. u. have been retained.

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