ON A POSSIBLE IMPROVEMENT OF LOCALIZED MOLECULAR ORBITALS

V.E. SAHINI
Laboratory of Physical Chemistry, Polytechnic Institute, Bucharest, Romania

and

A. SAVIN
Department of Physics, Polytechnic Institute, Bucharest, Romania

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The effect of orthogonal transformations, which maintain the equivalence restrictions, is studied on C_2H_6. It shows that, within the MINDO/2 method, it is possible to obtain C–H bond LMO's which reproduce some of the CH_4 values.

1. Introduction

Until recently it was considered that the properties of localized molecular orbitals (LMO's) show little dependence on the localization method [1]. It has lately been shown [2] that this might sometimes not be true, comparing the second moment dispersions about the centroid of the Edmiston–Ruedenberg [3] and Boys [4] LMO's. The better values for the latter are surely connected with their property of minimizing the sum of quadratic moments of each orbital about its centroid.

The aim of the present paper is to study the dependence of LMO properties upon the choice of orbitals.

2. Method

We started with MINDO/2 canonical molecular orbitals obtained for C_2H_6, in tetrahedral geometry, considering the experimental bond lengths. The molecular orbitals were localized according to the minimum resonance procedure [6]. Next, these LMO's, φ, were used to obtain other LMO's, ϕ'

$$\phi_i' = \sum_{j=1}^{n} \phi_j t_{ji}, \tag{1}$$

where n is the number of occupied molecular orbitals and t_{ji} are the elements of an orthogonal matrix which preserves the equivalence restrictions. If there are two groups of k, viz. $n-k$ equivalent LMO's the elements of the transformation matrix we used are given by:

$$\begin{aligned}
&t_{ii} = \cos^2\alpha \quad (i \leqslant k),\\
&t_{ii} = 1 - [k/(n-k)]\sin^2\alpha \quad (i > k),\\
&t_{ij} = -\sin^2\alpha \quad (i \neq j \leqslant k),\\
&t_{ij} = -[k(n-k)]\sin^2\alpha \quad (i \neq j > k),\\
&t_{ij} = -t_{ji} = (\sin\alpha)[(2 - k\sin^2\alpha)/(n-k)]^{1/2}\\
&\quad (i \leqslant k, j > k).
\end{aligned} \tag{2}$$

The overlap between the starting and the transformed LMO's is for $i \leqslant k$:

$$\langle \phi_i | \phi_i \rangle = \cos^2\alpha.$$

We further examine only those C–H bond LMO's which have an overlap larger than 0.99 with the starting LMO's, and the corresponding C–C bond LMO's.

The following bond properties are analysed:

(1) The orientation of the hybrid of the C–H bond orbital

$$\varphi = 90 + |\arctan(c_{zi}/c_{xi})|, \tag{3}$$

where c_{zi} and c_{xi} are the LCAO coefficients of the

$2p_z$ and $2p_x$ orbital of the LMO corresponding to the C–H bond contained in the xz plane, the C–C bond being oriented along the z axis.

(2) The percentage of the electronic charge included in the bond:

$$q_i = 100 \sum_{\mu}^{(i)} c_{\mu i}^2, \tag{4}$$

where the sum is performed only over the atomic orbitals which contribute to the C–H bond (LMO ϕ_i'); the maximum value of q_i corresponds to the maximum overlap of ϕ_i' with the truncated molecular orbital (obtained through the cancellation of all $c_{\mu i}$ which do not enter in the definition of q_i).

(3) The electric dipole moment of the bond:

$$M = -\sum_{\mu,\nu}^{(i)} c_{\mu i} c_{\nu i} \langle\mu|r|\nu\rangle + \sum_{A} Z_{Ai} R_A, \tag{5}$$

where $\langle\mu|r|\nu\rangle$ is calculated within the usual approximations [7], and Z_{Ai}, the part of the core charge assigned to atom A in bond i, is considered to be 1 if the LMO is localized on atom A, or else to be 0; for our choice of geometry, the dipole moment of the C–H bond is oriented along the latter if its value M is equal to three times the absolute value of its z component: $M = 3M_z$.

(4) The bond energy, chosen as:

$$E_i = \sum_{\mu,\nu}^{(i)} c_{\mu i} c_{\nu i} (H_{\mu\nu} + F_{\mu\nu}) + \frac{1}{2} \sum_{A,B(\neq A)} \mathrm{CR}_{AB} Z_{Ai}/Z_A, \tag{6}$$

where the core repulsion term CR_{AB} is defined by using the parameters given in ref. [5].

3. Results and discussion

While the overlap of the starting LMO's with the Edmiston–Ruedenberg LMO's is larger than 0.9999, it can be seen that there are equivalent orbitals, quite close to the former, as concerns overlap, but showing large differences as concerns the properties studied.

The variation of these properties, as a function of overlap, is shown in fig. 1. We analyse the closeness of the LMO properties to those based upon chemical intuition (shown with arrows in fig. 1) and the transferability of the properties of the C–H bond, from CH_4, using the valence-shell MINDO/2 LMO's, which are unique [8] (the CH_4 values are shown as dotted lines in fig. 1).

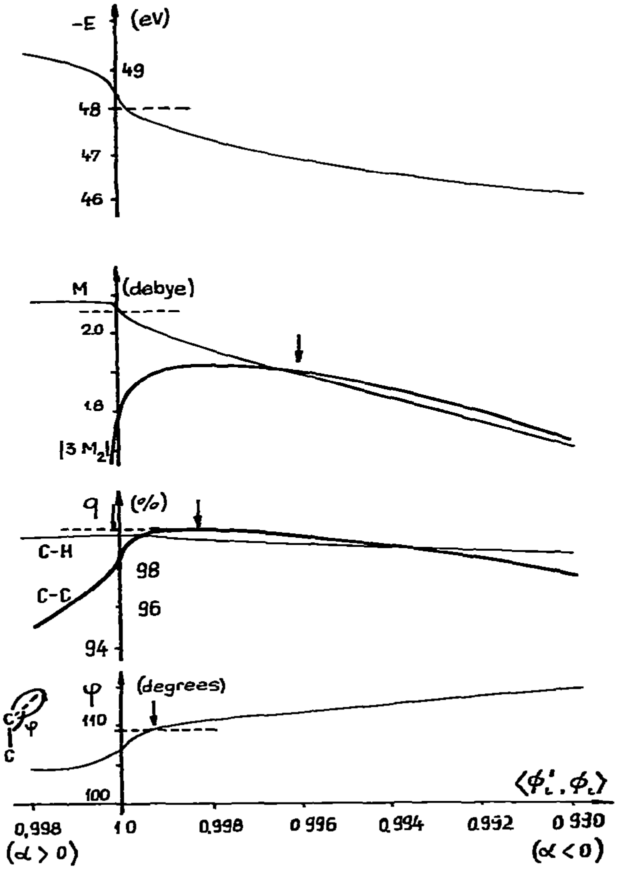

Fig. 1 Dependence of properties (——) on LMO choice and comparison with CH_4 values (– – –). For the definition of E, M, M_z, q, φ and significance of arrows see text.

In agreement with intuition, and the tetrahedral orientation of the LMO's in CH_4, it is possible to obtain C–H bond LMO's which:

- are oriented along the bonds;
- have the dipole moment vectors oriented along the bonds;
- have the same value of the dipole moment as in CH_4;
- have the whole electronic charge included in the C–C bond;
- have the same bond energy as in CH_4.

On the other hand, equivalent LMO's cannot reach the value obtained in CH_4 (100.0%) for the charge included in the bond (the maximum value for a C–H bond LMO in C_2H_6 is 99.8%). It can be observed that all the properties discussed above are obtained with different LMO's. For example, in the whole domain where the dipole moment is oriented (nearly) along the bond, the value of the former cannot reach the one obtained for the C–H bond in CH_4.

The differences between the values obtained for various conformations of the C_2H_6 molecule are too small to be shown in fig. 1. It is nevertheless worth mentioning that the curve of the C–H bond energy lies in the eclipsed conformation approximately 1/12 of the rotation barrier higher than in the intercalated conformation. It follows that there are LMO's, corresponding to very close values of the overlap, which have the same C–H bond energy in both conformations. As the molecular energy is unaltered by the orthogonal transformations (2), it is possible to conserve alternatively the C–C bond energy. Consequently, the rotation barrier in C_2H_6 could be explained entirely in terms of C–H or C–C intrabond interactions.

In conclusion, it may be pointed out that it would be useful to distinguish, when studying LMO properties, between the case in which the transfer (or the intuitive image) is obtainable and the case in which only an optimum can be obtained. However it must be stressed that the results would reflect not only the properties studied, but also the quality of the molecular orbitals (semi-empirical approximations or basis set).

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