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Short Communication

MG-FSGO Calculation of Ethane Geometry and Rotation Barrier

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MG-FSGO calculations on ethane have been performed employing a moderately large basis set with complete orbital plus geometry optimization. A nearly exact result for the rotation barrier is obtained, but the computed geometry is poor.

Key words: FSGO wave function.

The MG-FSGO (multiple Gaussian floating spherical Gaussian orbitals) method is an improvement of the simple Frost FSGO approach [1] and has been reported to be able to avoid some defects of the latter. Among these defects are [2] the too small results for valence angles in molecules containing lone pairs and the too high values obtained for barriers to internal rotation. In respect to this last point attempts have been made [3, 4] to get an accurate description of the rotation barrier in ethane through extension of the FSGO basis set. Although more or less successful, these calculations suffered of consistent limitations, namely unbalance of the basis set [3] and/or only partial optimization of nonlinear variables including geometry [4]. Therefore it is not clear (i) whether the improvement in the computed rotation barrier can be confirmed in the absence of these limitations, and (ii) how accurate the MG-FSGO geometry predictions are in such a polyatomic molecule where lone pairs are not present. To this end, two distinct calculations were performed employing the same moderately large basis set (25 FSGO's), with all local orbitals represented by linear combinations of 3 completely floating FSGO's, except for inner shells (2 FSGO's). Calculation 1 was made at fixed experimental geometry [$r_{CC} = 2.893$ a.u., $r_{CH} = 2.071$ a.u., $\sphericalangle$ CCH $= 111.1^0$ (5)] by optimizing only the 20 orbital parameters, while in Calculation 2 a full optimization of all geometry and orbital parameters was performed

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Table 1. Ethane : Molecular energy (a.u.), geometry (a.u.) and barrier (kcal/mole) from optimized MG-FSGO's

	Calculation 1[a]	Calculation 2[b]
E, eclipsed	−76.531466	−76.544352
E, staggered	−76.537543	−76.549002
Barrier	3.81	2.92
r_{CC}	...	3.073[c]
r_{CH}	...	2.142[c]
$\sphericalangle$CCH (degrees)	...	110.0[c]

[a] Experimental geometry, only orbital parameters optimized.
[b] All orbital and geometry parameters optimized.
[c] Staggered conformer.

(for a total of 23 variational parameters). All the above optimizations employed a previously described gradient method [2, 6]. The results are reported in Table 1. Whereas Calculation 1 gives a reasonable result for the rotation barrier [experimental value 2.93 kcal/mole [7]], further improvement arises from geometry optimization in Calculation 2, where a nearly exact result is obtained. Unpleasantly enough, however, this happens at the expense of the accuracy in the computed geometry, r_{CC} being in error by +6.2%, r_{CH} by +3.4%, and $\sphericalangle$ by −1.0%. The latter results are worse than the corresponding LCAO-MO results reported in the literature (STO-3G, see [8]; minimal set of optimized STO's, see [9]; Gaussian lobe functions plus bond functions, see [10]). Despite the (probably fortuitous) very good value obtained for the rotation barrier, this casts some doubts in the ability of MG-FSGO wavefunctions to give reliable structural predictions with reasonably-sized basis sets.

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