Theoret. chim. Acta (Berl.) 29, 75—83 (1973)

Local Orbitals for Bonding in Ethane

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Received August 8, 1972/November 13, 1972

An extension of the FSGO model is used to construct local bonding orbitals for ethane. These improved functions provide for a more accurate description of the internal rotational barrier in ethane, while retaining the computational simplicity and intuitive nature of the simple FSGO model.

Eine Erweiterung des FSGO-Modells wird für die Konstruktion lokalisierter Bindungsorbitale bei Äthan angewendet. Die verbesserten Funktionen vermitteln eine genauere Beschreibung der inneren Rotationsbarriere in Äthan; die einfache Berechnungsweise und die intuitive Natur des ursprünglichen einfachen FSGO-Modells bleiben jedoch erhalten.

Une extension du mode FSGO est utilisée pour construire les orbitales liantes localisées de l'éthane Ces nouvelles functions donnent une description plus exacte de la barriere de rotation interne de l'éthane, tout en retenant la simplicité de calcul et la nature intuitive du model FSGO original.

Introduction

Floating orbitals (orbitals not constrained to be centered on nuclei) have been used for many years as basis functions for quantum mechanical calculations on molecules. Early work [1, 2] and some more recent investigations [3] have utilized Slater type orbitals which were allowed to float. However, the use of floating exponential functions have the disadvantage of putting cusps in regions between nuclei. Floating gaussian functions were proposed and developed by other investigators in the form of lobe functions (as opposed to the cartesian gaussian type functions) [4, 5]. More in the spirit of the earlier calculations, an attempt was made to use floating gaussians in a valence bond calculation on H_2 [6]. Also attempts have been made to augment atomic orbital basis sets with floating gaussian functions [7–9]. These investigations found that floating functions can be very efficient for obtaining polarization effects and for building-up charge in the bonding region.

Several investigators [10–14] have developed methods where the concept of atomic orbitals is abandoned entirely in favor of floating orbitals. In particular a technique was developed [10] (the Floating Spherical Gaussian Orbitals Model – FSGO) using an absolute minimum basis set, where each orbital is doubly-occupied. As currently applied, the model has been used to predict the electronic and geometric structure of singlet ground states of molecules with local orbitals without the use of any arbitrary or semiempirical parameters. The local orbitals were constructed by using single normalized spherical Gaussian functions

$$\Phi(\vec{r}-\vec{R}_i)=\left(\frac{2}{\pi\varrho_i^2}\right)^{3/4}\exp[(\vec{r}-\vec{R}_i)^2/\varrho_i^2]$$

with orbital radius, ϱ_i, and position, $\boldsymbol{R}_i$. A single Slater determinant represents the total electronic wave function. If $\boldsymbol{S}$ is the overlap matrix of the set of non-orthogonal localized orbitals Φ_i and $\boldsymbol{T}=\boldsymbol{S}^{-1}$, then the energy expression for a molecule is

$$E=2\sum_{j,k}(j|k)\,T_{jk}+\sum_{k,l,p,q}(kl|pq)\,[2T_{kl}\,T_{pq}-T_{kp}\,T_{lq}]$$

where

$$(j|k)=\int\Phi_j\boldsymbol{h}\,\Phi_k dv\ (\boldsymbol{h}=\text{on-electron operator})$$

and

$$(kl|pq)=\int\Phi_k(1)\,\Phi_l(1)\,(1/r_{12})\,\Phi_p(2)\,\Phi_q(2)\,d\boldsymbol{v}_1\,d\boldsymbol{v}_2\,.$$

The energy is minimized by a direct search procedure with respect to all parameters: orbital radii, ϱ_1, orbital positions, $\vec{R}_i$, are nuclear positions. (Numerical difficulties have forced the inter-orbital distances for π-bonds and lone pair orbitals to be held fixed.)

In all previous work each double-occupied orbital has been constructed from a single gaussian function (SG), or at most a linear combination of two concentric gaussians (concentric double gaussian – CDG) [15]. In light of the recent renewed interest in floating orbitals, it was decided to make an extensive investigation of an extended FSGO model. The orbitals for these calculations are made up of linear combinations of up to four gaussians. (One should note here the difference between the FSGO orbitals, which are "local" orbitals, and the more commonly used "localized" orbitals, e.g., localized orbitals obtained from an Edmiston-Ruedenberg localization scheme. The localized orbital schemes start with diffuse canonical molecular orbitals, and transform them, via a unitary transformation, to localized orbitals. The FSGO orbitals are centered in a restricted region of space in their makeup, and are therefore orbitals local to that area.)

The first system to be investigated was the ethane molecule. This was done with the idea of improving upon the description given by the simple FSGO model. In particular the simple FSGO predicts a rotational barrier of 5.7 kcal/mole (concentric double gaussians give 5.0 kcal/mole), compared with an experimental value of 3.0 kcal/mole [16]. The idea was to obtain basis functions from simple systems and then transfer them to ethane. In particular methane and a "simplified" ethane molecule were used to develop the basis functions.

Other models have been developed for transferring bonding functions to "large" molecules. In particular, Christoffersen and coworkers [11] have developed a modification of the simple FSGO model to obtain a basis set for such calculations. The problem of optimizing the wave function for changes in molecular environment is handled via an SCF-MO procedure in Christoffersen's FSGO model, abandoning the concept of local orbitals. The calculations described in this paper retain the concept of non-orthogonal local orbitals, but optimize only the linear combination coefficients (a procedure borrowed from the SCF-MO method). (The effect of assuming local orbitals vs. the more general SCF-MO procedure was investigated, vide infra.)

Procedure

The orbitals necessary for ethane are: inner shells, C–H bonding orbitals, and C–C bonding orbitals.

Tests were made on methane with single (SG), double (DG), and triple (TG) gaussian inner shells. The nuclear geometry, and all orbital radii and orbital positions were optimized.

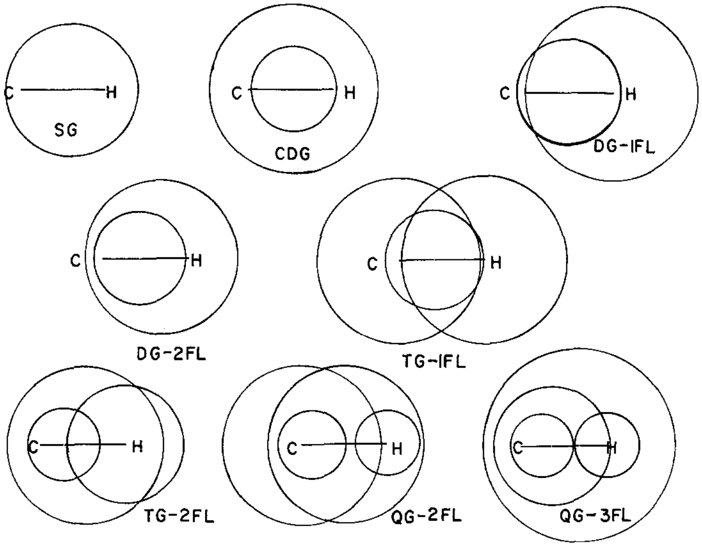

Fig. 1. C–H Bonding functions (Circle size proportional to orbital radius)

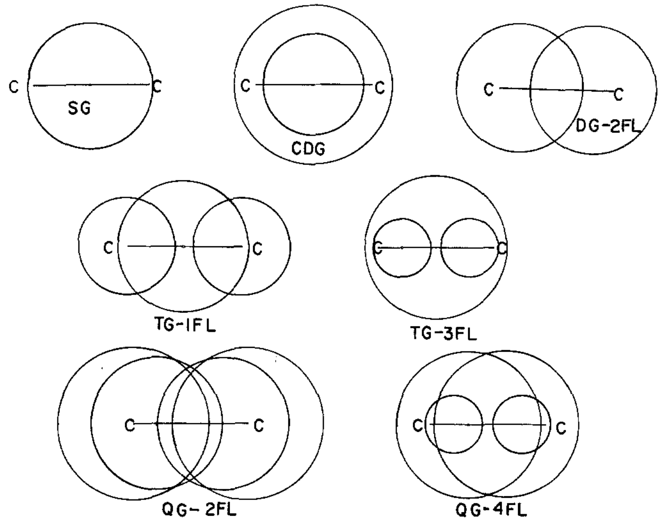

Fig. 2. C–C Bonding functions (Circle size proportional to orbital radius)

The C–H bonding orbitals were likewise constructed from calculations on methane. The various basis sets that were used are described in Fig. 1. A DG was used for the inner shell in all cases, and the orbital radii, orbital positions, and nuclear geometry were all optimized. The idea of using some floating and some fixed gaussians, either centered on the proton or on the carbon nucleus, was also investigated. [It was thought that the use of a gaussian on the proton (to help build a cusp) or on the carbon (to simulate the effect of a 2*s* atomic orbital) was reasonable from a chemical point of view.] If fixing the gaussian did not significantly affect the results of the calculation (compared to the same calculation where the constraint was removed) then using these fixed gaussians would provide increased efficiency due to the decrease in the number of parameters.

The C–C bonding orbitals (Fig. 2) were obtained from the ethane molecule, with SG everywhere except for the inner shells (DG) and for the C–C bond orbital itself. Again an attempt was made to fix some of the gaussians on the carbon nuclei.

The inner shell orbitals and the C–H and C–C bonding functions were then transferred to ethane with only linear combination coefficient optimization. Nuclear geometry was held fixed to that of Clementi and Davis [17], and orbital radii and positions fixed from the calculations on the simpler systems. (For some of the simpler orbital schemes full optimization on ethane were performed.) Both the staggered and eclipsed conformations were investigated, assuming rigid rotation [18].

Results

While the inner shell orbitals have little effect on the geometry, the energy is strongly dependent upon their form. (Table 1 shows results for methane with various inner shells.) A large decrease in energy is obtained from SG to DG inner shells. Compared to this decrease, adding a third gaussian improved the energy relatively slightly. It was also found that orbital and nuclear parameters were unchanged as the inner shell was improved. It was decided to use the DG inner shell representation in all further calculations – as it appeared that little was to be gained by using the TG representation. The lack of importance of the inner shell has been pointed out in several recent papers [19, 20]. In particular Hehre *et al.* [19] found that going to a better form for the inner shells did not affect any of the chemically important properties (geometry, relative energies).

The results for the C–H bonding orbitals appear in Table 2. The following comments are applicable to this data. (1) Fixing an orbital of the DG set on the proton (DG-1 FL, double gaussian with one floating gaussian) is too restrictive, as the elimination of this constraint (DG-2 FL) gives a much different result. (2) Fixing one gaussian on the proton with a TG set (TG-2 FL) appears to be a reasonable restriction – as it differs very little from the result when the constraint is removed. With this in mind, it was assumed that the quadruple gaussian with no gaussians fixed (QG-4 FL) would be very nearly the same as that with one orbital fixed (QG-3 FL), and this simpler set was used in place of the more complex one. (3) In all cases where an attempt was made to fix one gaussian on the carbon (TG-1 FL, QG-2 FL), results were very different from the cases without the

Table 1. Inner shell orbitals from CH_4

Orbital type				
Inner shell	SG	DG	DG	TG
C–H bond	SG	SG	CDG	CDG
Inner shell				
ϱ_1(a.u.)	0.328	0.148	0.148	0.074
C_1	1.0	0.267	0.267	0.056
ϱ_2		0.389	0.389	0.193
C_2		0.830	0.719	0.365
ϱ_3				0.441
C_3				0.707
C–H orbital				
ϱ_1	1.694	1.698	1.174	1.161
C_1	1.0	1.0	0.338	0.329
X_1 [a]	0.598	0.593	0.405	
ϱ_2			2.188	2.178
C_2			0.719	0.727
X_2 [a]			0.537	0.528
C–H bond length (Å)	1.110	1.115	1.040	1.036
$-E$ (a.u.)	33.992	38.246	38.484	39.250

[a] X is the ratio of (carbon to orbital distance)/(C–H bond length).

constraint, so these basis sets were regarded as unsatisfactory. (4) It would appear that at least a TG is necessary to give a resonable description of the electron density around the proton. Only with TG-2 FL, TG-3 FL, and QG-3 FL was a cusp-like condition developed at the proton.

The results for the C–C bonding function are given in Table 3. One can make the following observations about this data. (1) The DG-2 FL set is judged to be unsatisfactory on the grounds that it gives a very poor approximation to the C–C bond length. One should be careful about using basis sets which lead to poor geometrical predictions. To try to circumvent this problem by attempting to calculate a rotational barrier with idealized geometry, for example, is a very unrealistic procedure. (2) As with the C–H bonding functions, fixing gaussians on the carbon nuclei (TG-1 FL, and QG-2 FL) gives results very different from the cases where the constraints are removed. (3) Three to four gaussians are necessary for a reasonable description of the C–C bond. Only then does one begin to obtain a cylindrical charge distribution along the C–C bond.

Referring to Fig. 3 of the electron density along the C–H bond, only the TG-2 FL and QG-3 FL bond functions give the correct qualitative picture of a relative minimum near the midpoint of the bond and a "cusp" on the proton. (Densities for the CDG, DG-2 FL, and TG-1 FL resemble those of the SG and DG-1 FL.) Likewise in Fig. 4 (the total electron density along the C–C bond in ethane), only the TG-3 FL and QG-4 FL bond functions approach the correct picture of a relative minimum at the midpoint of the C–C bond. (CDG, TG-1 FL, and QG-2 FL resemble SG and DG-2 FL plots.)

Table 2. C–H Bonding orbitals from CH_4 [a]

	SG	CDG	DG-1 FL	DG-2 FL	TG-1 FL	TG-2 FL	TG-3 FL	QG-2 FL	QG-3 FL
ϱ_1(a.u.)	1.694	1.174	1.339	0.811	1.924	0.941	0.938	2.104	0.709
C_1	1.000	0.332	0.617	0.167	0.010	0.234	0.234	0.900	0.109
X_1 [b]	0.598	0.525	0.494	0.244	0.000	0.262	0.260	0.000	0.216
ϱ_2		2.192	2.264	1.870	1.335	2.097	2.096	0.899	1.551
C_2		0.724	0.465	0.901	0.605	0.793	0.794	0.051	0.489
X_2		0.525	1.000	0.612	0.492	0.524	0.526	0.111	0.355
ϱ_3					2.247	0.730	0.731	2.068	2.521
C_3					0.469	0.109	0.110	0.075	0.454
X_3					1.000	1.000	0.994	0.525	0.665
ϱ_4								0.756	0.752
C_4								0.011	0.104
X_4								1.000	1.000
R(C–H) (Å)	1.115	1.040	1.077	1.083	1.078	1.129	1.130	1.114	1.132
$-E$(a.u.)	38.24689	38.48489	38.48004	38.52158	38.47995 [c]	38.84232	38.84250	38.87572	38.88746

[a] All calculations with DG inner shell.

[b] Ratio of (carbon to orbital distance)/(C–H distance).

[c] Apparently a local minimum.

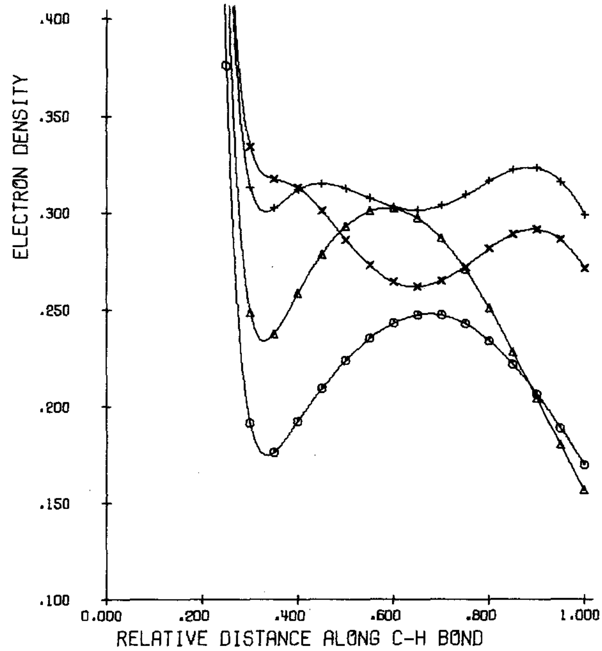

Fig. 3. Total electron density along C–H bond in methane for SG (○), DG-1 FL (△), TG-2 FL (+), and QG-3 FL (×)

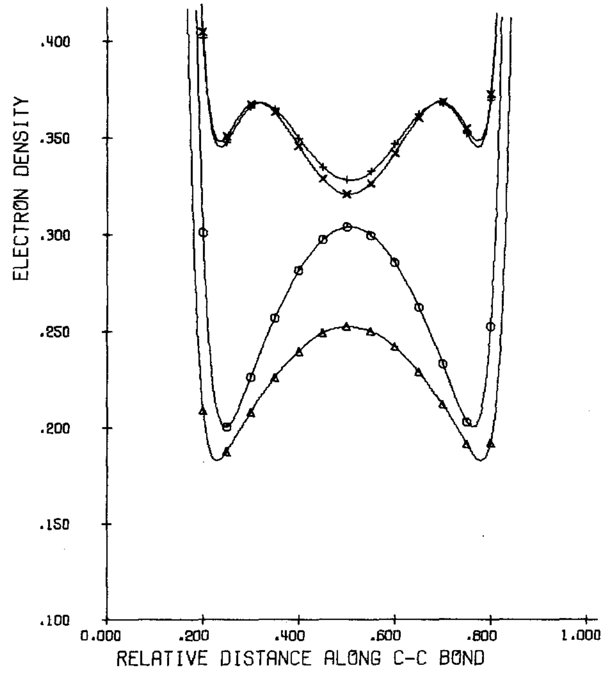

Fig. 4. Total electron density along C–C bond in ethane for SG (○), DG-2 FL (△), TG-3 FL (+), and QG-4 FL (×)

Table 3. C–C Bonding orbitals from C_2H_6 [a]

	SG	CGD	DG-2 FL	TG-1 FL	TG-3 FL	QG-2 FL	QG-4 FL
ϱ_1(a.u.)	1.646	1.300	1.639	1.745	1.844	1.725	1.846
C_1	1.000	0.316	0.587	0.779	0.886	0.568	0.452
X_1 [b]	0.000	0.000	0.655	0.000	0.000	0.600	0.304
ϱ_2		2.020		1.382	0.741	1.959	0.740
C_2		0.740		0.169	0.110	$<10^{-8}$	0.116
X_2		0.000		1.000	0.562	1.000	0.561
R(C–C) (Å)	1.504	1.487	1.669	1.553	1.581	1.660	1.552

[a] SG C–H orbitals, and DG inner shells, except for CDG calculations where CDG everywhere. All calculations had only C–C geometry optimization, except for SG and CDG, where a full optimization was performed.

[b] X is relative distance from center of C–C bond. X = 0 at midpoint, X = 1 at carbon nucleus.

Table 4. Barrier to internal rotation in C_2H_6 from FSGO basis sets

Bonding type		Orbital C–H	-Energy (staggered) (a.u.)	Rotational barrier (kcal/mole)
I.S.	C–C			
DG [a]	SG	SG	75.5134	6.3
DG [a]	CDG	CDG	75.8620	5.0
DG	TG-3 FL	TG-2 FL	76.5070	3.7
DG	QG-4 FL	QG-3 FL	76.5633	4.0
DG	TG-3 FL	TG-2 FL (SCF)	76.8762	3.8
STO-3 G [b]			78.8623	3.3
Experimental [c]				

[a] Optimized geometry.

[b] Pople, J. A., Radom, L.: J. Amer. chem. Soc. **92**, 4786 (1970).

[c] Lide, D. R.: J. chem. Physics **29**, 1426 (1958).

The results for the rotational barrier calculations appear in Table 4. These results show that acceptable values for the rotational barrier in ethane are obtained with the extended FSGO functions. Values of 3.7–4.0 kcal/mole are given by the three and four gaussian extended FSGO basis sets.

To test the effect of the restriction of local orbitals, SCF–MO calculations (using POLYATOM II) [21] were performed on the staggered and eclipsed forms of ethane, using the DG (inner shell), TG-2 FL (C–H), and TG-3 FL (C–C) basis set. (All gaussians were treated as uncontracted orbitals, except for the DG inner shell gaussians which were contracted to a single orbital, with relative coefficients as found in the local orbital FSGO calculation.) The results (Table 4) show that while there is a considerable decrease in the total energy (0.37 a.u.), the rotational barrier is only very slightly affected (0.1 Kcal/mole).

Discussion

The results of these calculations indicate that an extended FSGO model can be used to obtain local bonding functions. The main advantages in using this type of function are that they are transferable, and that polarization effects can be accounted for with them. Other bond function approaches [22, 23] have been built upon an LCAO framework. The LCAO framework has the advantage of being less arbitrary in choosing basis functions (for example where the extended FSGO method assumed fixed orbital positions). However the extended FSGO basis set is much more adaptable for including polarization effects. It is also encouraging to note that the restriction to local orbitals does not seem to invalidate the results.

Work is continuing on developing computational procedures for handling the extended FSGO model and in the development of "bonding functions" for pi bonds and lone-pair orbitals.

Acknowledgements. Many helpful discussions were held with Klaus Mueller. We would also like to thank the referee for several helpful suggestions. This research was supported by a grant from the National Science Foundation. O. H. Crawford suggested the expression "local orbital" in order to differentiate from "localized orbital".

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