Theoret. chim. Acta (Berl.) 22, 337 – 352 (1971)

Ab Initio Calculations on Large Molecules Using Molecular Fragments. First Order Electronic Properties for Hydrocarbons*

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Received May 2, 1971

A number of first order electronic properties for the hydrocarbons C_2H_6, C_3H_8, C_2H_4, C_6H_6, and $C_{10}H_8$ are investigated. The wavefunctions employed here result from SCF calculations, using basis orbitals that have been optimized in molecular fragment studies. Comparisons are made with experimental values as well as with other calculated values, and the suitability of various molecular fragment bases is discussed.

Eine Reihe von Elektroneneigenschaften 1. Ordnung für die Kohlenwasserstoffe C_2H_6, C_3H_8, C_2H_4, C_6H_6, $C_{10}H_8$ wurden mittels SCF-Funktionen aus Basisfunktionen, die für Molekül-Fragmente optimalisiert worden waren, berechnet. Auf Grund der Vergleiche mit anderen Rechnungen und experimentellen Ergebnissen wird die Qualität verschiedener Fragmente diskutiert.

Etude d'un certain nombre de propriétés électroniques du premier ordre pour les hydrocarbures C_2H_6, C_3H_8, C_2H_4, C_6H_6 et $C_{10}H_8$. Les fonctions d'onde utilisées ici sont obtenues dans des calculs SCF en utilisant des orbitales de base optimisées dans des études sur des fragments moléculaires. Des comparaisons sont faites avec les valeurs expérimentales et avec d'autres valeurs calculées, et l'on discute l'adaptation des différents fragments moléculaires.

1. Introduction

Historically, the central role that the total energy has played in the determination of wavefunctions for molecular systems has served to justify its use as the primary measure of overall wavefunction utility and accuracy. However, as pointed out by Mulliken [1], the overall balance of the basis set and total wavefunction, which may not coincide with the minimum energy criterion, is a more appropriate measure of utility. Furthermore, as molecules become larger, the total energy becomes more and more burdened with large (and often uninteresting) contributions from the inner shells. The introduction of Gaussian basis orbitals [2] has allowed the extension of *ab initio* techniques to reasonably large molecules [3], where the inner shell energy is a significant part of the total energy. For these

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* This work was supported in part by grants from the University of Kansas and The Upjohn Company, Kalamazoo, Michigan.

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cases in particular, the need for accuracy criteria other than the total energy is emphasized. Consequently, several recent efforts [4] have been directed toward providing other measures of wavefunction accuracy, usually involving evaluation of first order molecular properties. These studies provide particularly appropriate probes into the adequacy of a trial wavefunction, since a first-order change in the wavefunction is accompanied by a first order change in one-electron properties, while affecting the total energy only in the second order.

In previous studies [5–7] an *ab initio* method for the determination of wavefunctions of large molecules has been described and applied to a set of hydrocarbons, both saturated and unsaturated. This method, based on the study of molecular fragments as a means of obtaining a basis set suitably balanced for use in large molecule calculations, has been shown to provide a reliable procedure for answering questions concerning conformational analysis as well as electronic structure. The current study is designed to reveal the adequacy of wavefunctions determined in this manner for the calculation of properties other than the total energy.

In the following sections a variety of first order properties are calculated for ethane, propane, ethylene, benzene, and naphthalene, and an evaluation of the effectiveness and balance of the initial choice of molecular fragment bases is given.

2. Mathematical Formulation

The wavefunctions employed in these studies have been obtained by means of the usual Hartree-Fock-Roothaan [8] procedure. The resulting molecular orbitals can be written as

$$\varphi_i(1) = \sum_{t=1}^{N} c_{ti} G_t(1). \tag{1}$$

The G_t are basis orbitals chosen to be floating spherical Gaussian orbitals (FSGO), and the summation is taken over all fragments and FSGO within each fragment. The FSGO are defined as

$$G_t(1) = [2/\pi\varrho_t^2]^{\frac{3}{4}} \exp\left\{-\frac{(\boldsymbol{r}_1 - \boldsymbol{R}_t)^2}{\varrho_t^2}\right\}, \tag{2}$$

where ϱ_t is referred to as the orbital radius, and $\boldsymbol{R}_t$ represents the position of the FSGO relative to some arbitrary origin. The determination of optimum values of the non-linear parameters is accomplished by examination of molecular fragments, and the choice of parameters for the particular fragments of interest in these studies has been described earlier [6].

The expectation value of any one-electron operator, Ω, can be written as

$$\langle\Omega\rangle = \langle\Omega^{\mathrm{nuc}}\rangle + \sum_{t=1}^{N} \sum_{u=1}^{N} P_{tu} \Omega_{tu}^{\mathrm{el}}, \tag{3}$$

Table 1. *One-electron operators (atomic units)*[a]

Operator	Mathematical Form
Molecular Dipole Moment (at center of mass)	$\mu_\alpha = \sum_K Z_K(\boldsymbol{R}_K - \boldsymbol{R}_C)_\alpha - \sum_i (\boldsymbol{r}_i - \boldsymbol{R}_C)_\alpha$
Molecular Second Moment (at center of mass)	$Q_{\alpha\beta} = \sum_K Z_K(\boldsymbol{R}_K - \boldsymbol{R}_C)_\alpha (\boldsymbol{R}_K - \boldsymbol{R}_C)_\beta - \sum_i (\boldsymbol{r}_i - \boldsymbol{R}_C)_\alpha (\boldsymbol{r}_i - \boldsymbol{R}_C)_\beta$
Molecular Quadrupole Moment (at center of mass)	$\Theta_{\alpha\beta} = \frac{1}{2}(3Q_{\alpha\beta} - \delta_{\alpha\beta} \sum_\gamma Q_{\gamma\gamma})$
Potential at a point (A)	$\Phi(A) = \sum_{K(\neq A)} \frac{Z_K}{\lvert\boldsymbol{R}_K - \boldsymbol{R}_A\rvert} - \sum_i \frac{1}{\lvert\boldsymbol{r}_i - \boldsymbol{R}_A\rvert}$
Electric Field (Hellmann-Feyman) at a point (A)	$\varepsilon_\alpha(A) = -\sum_{K(\neq A)} \frac{Z_K(\boldsymbol{R}_K - \boldsymbol{R}_A)_\alpha}{\lvert\boldsymbol{R}_K - \boldsymbol{R}_A\rvert^3} + \sum_i \frac{(\boldsymbol{r}_i - \boldsymbol{R}_A)_\alpha}{\lvert\boldsymbol{r}_i - \boldsymbol{R}_A\rvert^3}$
Electric Field Gradient at at point (A)	$q_{\alpha\beta}(A) = -\sum_{K(\neq A)} Z_K \left\{ \frac{3(\boldsymbol{R}_K - \boldsymbol{R}_A)_\alpha (\boldsymbol{R}_K - \boldsymbol{R}_A)_\beta - \delta_{\alpha\beta}\lvert\boldsymbol{R}_K - \boldsymbol{R}_A\rvert^2}{\lvert\boldsymbol{R}_K - \boldsymbol{R}_A\rvert^5} \right\} + \sum_i \left\{ \frac{3(\boldsymbol{r}_i - \boldsymbol{R}_A)_\alpha (\boldsymbol{r}_i - \boldsymbol{R}_A)_\beta - \delta_{\alpha\beta}\lvert\boldsymbol{r}_i - \boldsymbol{R}_A\rvert^2}{\lvert\boldsymbol{r}_i - \boldsymbol{R}_A\rvert^5} \right\}$
One-Electron Delta Function	$\delta(\boldsymbol{r} - \boldsymbol{R}_A)$
Nuclear Quadrupole Coupling Constant	$eQ \frac{\partial^2 \Phi}{\partial r_{\alpha'}^2} = eQ(-q_{\alpha'\alpha'})$

[a] See Ref. [9].

where Ω^{nuc} represents the contribution to the property from the nuclei, P_{tu} is an element of the charge and bond order matrix:

$$P_{tu} = 2 \sum_{j=1}^{\text{occ}} c_{tj} c_{uj}\,, \tag{4}$$

and

$$\Omega_{tu}^{\text{el}} = \langle G_t \lvert \Omega^{\text{el}} \rvert G_u \rangle\,.$$

The forms of the various operators employed in this study are summarized in Table 1. For each operator, the nuclear contribution is tabulated first, followed by the electronic contribution. Also, nuclear coordinates are represented by upper case letters and electronic coordinates by lower case letters. Greek letter subscripts refer to Cartesian coordinates, and the particular point (C) is taken to be the center of mass of the molecule of interest. Finally, the primed coordinates in the definition of the nuclear quadrupole coupling constant indicate that the calculation is made relative to the principal axis system, with the convention that α' is the largest component, i.e.,

$$\lvert q_{\alpha'\alpha'}\rvert \geqq \lvert q_{\beta'\beta'}\rvert \geqq \lvert q_{\gamma'\gamma'}\rvert \tag{6}$$

The asymmetry parameter for the principal axis components is given by

$$\eta = \frac{q_{\gamma'\gamma'} - q_{\beta'\beta'}}{q_{\alpha'\alpha'}} \tag{7}$$

so that $0 \geqq \eta \geqq 1$. The explicit form for all of the integrals needed in the calculations using FSGO basis orbitals are summarized in the Appendix. The particularly convenient forms for computation that result when FSGO are employed is worth noting. All calculations were carried out in double precision arithmetic, using a Honeywell 635 computer.

3. Results and Discussion

Since experimental data for comparisons to the hydrocarbons studied here is not available for many properties, it is appropriate that the discussion begin with a property that can be compared precisely in each case. Such a property is the Hellmann-Feynman electric field [10], since each component will be identically zero for the exact wavefunction. Consequently, the closeness to zero of the various components provides a measure of the accuracy of an approximate wavefunction. Table 2 presents the relevant data for saturated hydrocarbons, and Table 3

Table 2. *Electric field data*[a] *at nuclei for saturated hydrocarbons*

Ethane:	Staggered		Eclipsed	
Description[b]	C	H	C	H
Exptl. distances and angles	0.061	0.023	0.059	0.023
Exptl. distances, tetrahedral angles	0.066	0.023	0.064	0.023
Exptl. distances, tetrahedral angles, FSGO on nuclei	0.169	0.644	0.169	0.645
Exptl. distances, tetrahedral angles, split inner shell	0.020	0.016	0.018	0.016
Pitzer-Lipscomb[c]	0.017	0.096	0.016	0.094

Propane:[b] (Exptl. distances, tetrahedral angles)

Atom[d]	Staggered-Staggered	Staggered-Eclipsed	Eclipsed-Eclipsed
C_1	0.076	0.076	0.073
C_2	0.063	0.061	0.060
C_3	0.076	0.073	0.073
H_1	0.043	0.043	0.042
H_2	0.041	0.041	0.042
H_3	0.041	0.041	0.040
H_4	0.043	0.042	0.042
H_5	0.041	0.041	0.040
H_6	0.041	0.042	0.042
H_7	0.030	0.030	0.030
H_8	0.030	0.030	0.030

[a] Each entry corresponds to $|\varepsilon|$, calculated by the use of Eq. (8), and is reported in Hartree atomic units. See Ref. [9].

[b] See Ref. [6] for details.

[c] See Ref. [12, 13].

[d] See Fig. 1 for details of atom numbering.

Table 3. *Electric field data*[a] *at nuclei for unsaturated hydrocarbons*

Ethylene: Description[b]	C	H
$R_\pi = 0.1$, ϱ_{1s} from CH_4	0.146	0.097
$R_\pi = \langle \lvert z \rvert \rangle$, ϱ_{1s} varied	0.147	0.097
$R_\pi = 0.1$, ϱ_{1s} varied	0.149	0.094
$R_\pi = 0.1$, split inner shell	0.080	0.086

Benzene: Description[b]	C	H
$R_\pi = 0.1$, ϱ_{1s} varied	0.096	0.066
$R_\pi = \langle \lvert z \rvert \rangle$, ϱ_{1s} varied	0.094	0.070
$R_\pi = \langle \lvert z \rvert \rangle$, ϱ_{1s} varied, FSGO on nuclei	0.106	0.593
$R_\pi = 0.1$, split inner shell	0.066	0.056

Naphthalene:	Atoms[d]				
Description[c]	C_1	C_2	C_9	H_1	H_2
$R_\pi = 0.1$, ϱ_{1s} varied	0.102	0.097	0.001	0.065	0.066

[a] Each entry corresponds to $|\varepsilon|$, calculated by the use of Eq. (8) and is reported in Hartree atomic units. See Ref. [9].

[b] See Ref. [6] for details.

[c] See Ref. [7] for details.

[d] See Fig. 1 for details of atom numbering.

contains the analogous data for unsaturated hydrocarbons. The entries in the table correspond to the overall magnitude of the electric field at the various atoms, defined as

$$|\varepsilon(A)| = [\varepsilon_x^2(A) + \varepsilon_y^2(A) + \varepsilon_z^2(A)]^{\frac{1}{2}} \tag{8}$$

As Tables 2 and 3 indicate, the calculated fields are generally quite small. For the specific case of ethane, the calculated fields agree well with the Pitzer-Lipscomb wavefunction [12, 13] obtained from considerably more extensive calculations. In all cases, the split inner shell description gives the lowest values, and the FSGO-on-nuclei give the poorest (highest) values. Also, the use of idealized instead of experimental geometry does not affect the results significantly, as illustrated for the case of ethane [11].

Several calculations of the delta function were also performed. Again direct comparisons with experimental or other theoretically calculated values are difficult, due to a lack of other data. Only for the case of the ethane hydrogens is a direct comparison possible. In this case, Buenker, *et al.* [24], found a value of 0.493 a.u. for staggered ethane. This is to be compared with values ranging from 0.180 or 0.220 a.u. using wavefunctions obtained in the current study, the latter value arising from the use of the FSGO-on-nuclei basis. The values obtained for hydrogen atoms of the other molecules studied are also too low, when compared with an "average" value for a number of different molecular environments [33]. The value obtained for this "average" charge density lies approximately between

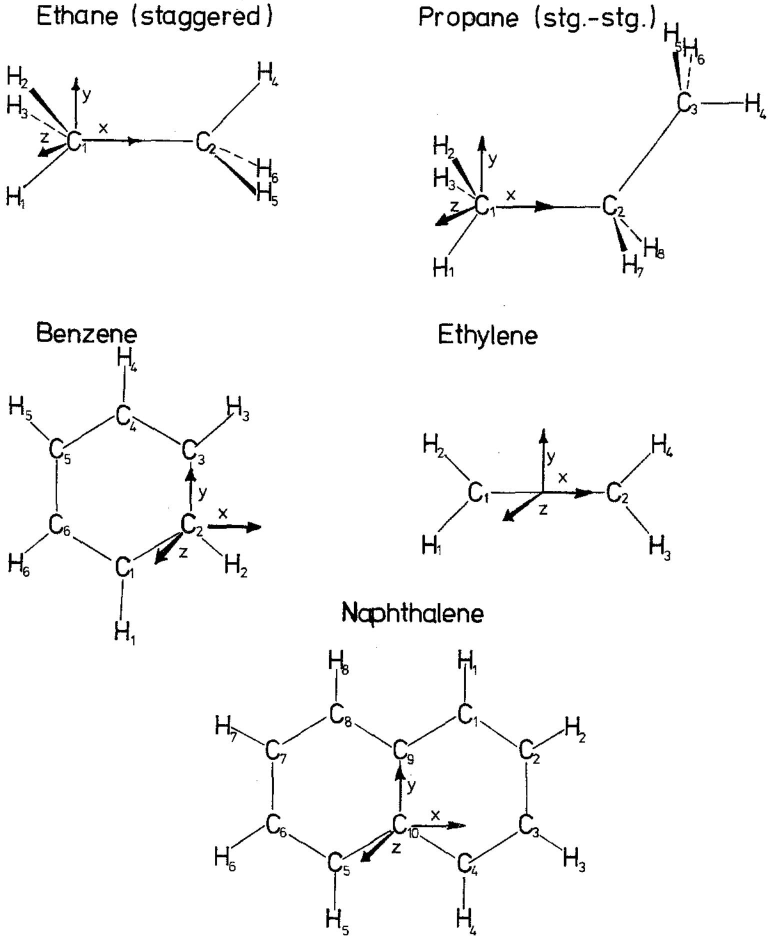

Fig. 1

0.35 and 0.42 a.u. Since most emphasis in the current method is placed on the description of the carbon atoms and C–C bonds, it is not unexpected that the results for hydrogen are some distance from other calculated results. In the case of the carbon atoms, the "average" value [33] is also about a factor of two greater than the values obtained in this study. The split inner shell basis again provides the best value, as might be expected.

For the other operators listed in Table 1, the results are summarized in Tables 4–9. Also included are experimental results, as well as results obtained from other calculations. As for the case of Hellmann-Feynmann fields and the one-electron delta function, it is clear that the split inner shell representation nearly always produced values in closer agreement with both the experimental and theoretical results obtained by others. The FSGO-on-nuclei representation, on the other hand, produced values which are generally in much poorer agreement.

Table 4. *Molecular second and quadrupole moments*[a] *for saturated hydrocarbons*

		Q_{xx}	Q_{yy}	Q_{zz}	$\langle r^2 \rangle^b$	Θ_{xx}	Θ_{yy}	Θ_{zz}
Ethane:								
Experimental angles and distances.	Stg.	−15.645	−13.070	−13.070	30.192	−2.575	1.287	1.287
	Ecl.	−15.737	−13.063	−13.063	30.209	−2.674	1.337	1.337
Experimental distances and tetrahedral angles	Stg.	−15.677	−13.031	−13.031	30.078	−2.646	1.323	1.323
	Ecl.	−15.776	−13.025	−13.025	30.095	−2.751	1.376	1.376
Experimental distances and tetrahedral angles FSGO on nuclei	Stg.	−25.739	−28.007	−28.007	38.408	+2.268	−1.133	−1.133
	Ecl.	−25.694	−28.011	−28.011	38.401	+2.317	−1.157	−1.157
Experimental distances and tetrahedral angles Split inner shell	Stg.	−15.151	−13.118	−13.118	30.004	−2.033	0.890	0.890
	Ecl.	−15.256	−13.112	−13.112	30.024	−2.132	1.066	1.066
Hoyland-(5, 2, 2) basis[c]	Stg.				30.481	−0.6672		
	Ecl.				30.480	−0.7365		
Hoyland-(5, 3, 3) basis[c]	Stg.				30.137	−0.5343		
	Ecl.				30.140	−0.5902		
Pitzer-Lipscomb[d]	Stg.	−17.713	−16.820	−16.820	43.196	−0.893	0.447	0.447
	Ecl.	−17.810	−16.743	−16.743	43.180	−1.066	0.562	0.562
Ditchfield, *et al.*[e] STO-2G basis	Stg.					−0.870		
	Ecl.					−1.079		
Ditchfield, *et al.*[e] STO-6G basis	Stg.					−0.894		
	Ecl.					−1.066		
Bond Moments[f]	Stg.					0.90	0.45	0.45
Experiment[g]						−0.8 ± 0.1		
Propane:								
Stg.-Stg.		−22.635	−20.961	−19.340	61.560	−2.485	−0.027	2.458
Stg.-Ecl.		−22.727	−20.971	−19.348	61.583	−2.568	0.067	2.501
Ecl.-Ecl.		−22.863	−20.970	−19.360	61.614	−2.698	0.142	2.557

[a] All second and quadrupole moments are in units of 10^{-28} esu cm^2.

[b] Electronic component, in units of 10^{-16} cm^2.

[c] See Ref. [14].

[d] See Refs. [12, 13].

[e] See Ref. [31].

[f] See Ref. [16].

[g] See Ref. [15].

The properties calculated with poorest accuracy are the one-electron delta function and the electric field gradient (Tables 8, 9). This is not unexpected since, in all representations, the nuclear cusp and electronic behavior very near the nucleus are not adequately described. While a large amount of energy can be recovered by a simple improvement of the description of the inner-shell electrons, almost independently of the valence electrons, the field gradient and delta function are much more sensitive to the detailed wavefunction behavior near the nucleus. In particular, the electric field gradient is of $O(r^{-3})$, and the delta function depends on the value of the wavefunction at the nucleus only. Thus, these operators are extremely sensitive to the electronic description at distances very close to the nucleus. Another example of the sensitivity of the field gradient to the basis set

Table 5. *Molecular second and quadrupole moments*[a] *for unsaturated hydrocarbons*

	Q_{xx}	Q_{yy}	Q_{zz}	$\langle r^2\rangle^c$	Θ_{xx}	Θ_{yy}	Θ_{zz}
Ethylene:							
$R_\pi = \langle\lvert z\rvert\rangle$, ϱ_{1s} from CH_4	−12.381	−11.399	−16.440	−8.395	1.439	3.062	−4.500
$R_\pi = \langle\lvert z\rvert\rangle$, ϱ_{1s} varied	−12.485	−11.403	−16.452	−8.399	1.442	3.066	−4.508
$R_\pi = 0.1$, ϱ_{1s} varied	−12.511	−11.407	−15.989	−8.309	1.187	2.844	−4.030
$R_\pi = 0.1$, split inner shell	−11.400	−10.860	−15.553	−7.506	1.807	2.617	−4.423
Bond Moment (Kern)[d]					0.85	1.48	−2.33
Conjugated Systems (Schweig)[e]					1.53	1.53	−3.06
Schulman, *et al.*[f]							
Extended				−8.424	2.150	1.740	−3.890
Best-Atom				−9.419	1.315	1.791	−3.105
Ethylene Optimized				−8.577	1.738	1.763	−3.501
"Averaged" exptl. results[g]					1.5		
Experimental (Buckingham)[h]					2.0±0.15		
Benzene:				$\langle z^2\rangle^b$			
$R_\pi = \langle\lvert z\rvert\rangle$, ϱ_{1s} varied	−31.734	−31.734	−42.661	8.882	5.464	5.464	−10.927
$R_\pi = 0.1$ Bohr, ϱ_{1s} varied, FSGO on nuclei	−68.997	−68.997	−40.834	8.502	−14.082	−14.082	28.164
$R_\pi = 0.1$ Bohr, ϱ_{1s} varied	−31.806	−31.806	−41.288	8.597	4.741	4.741	−9.482
$R_\pi = 0.1$ Bohr, split inner shell	−29.813	−29.813	−40.901	8.516	5.545	5.545	−11.087
Conjugated systems (Schweig)[e]					4.59	4.59	−9.18
Schulman, *et al.*[f]							
Extended					5.225	5.225	10.451
Ethylene Optimized					4.916	4.916	−9.833
Experimental (Disch and Golub)[i]							−12.7±1.3
Experimental (Flygare)[k]				7.7±1.5	2.8±1.4	2.8±1.4	−5.6±2.8
Experimental (Hill and Smith)[l]							3.6
Experimental (Spurling and DeRocco)[m]							15.7
Naphthalene:				$\langle r^2\rangle$			
ϱ_{1s} varied, $R_\pi = 0.1$ Bohr	−52.379	−50.608	−66.542	355.21	6.196	8.853	−15.049
Conjugated Systems (Schweig)[e]					7.65	7.65	−15.29

[a] All second and quadrupole moments are in units of 10^{-26} esu cm^2.

[b] Electronic component, in units of 10^{-16} cm^2.

[c] This represents the total of both nuclear and electronic components, in units of 10^{-16} cm^2.

[d] See Ref. [16].

[e] See Ref. [17].

[f] See Ref. [32].

[g] See Ref. [18].

[h] See Ref. [15].

[i] See Ref. [34].

[k] See Ref. [19].

[l] See Ref. [20].

[m] See Ref. [21].

Table 6. *Electric potential*[a] *at nuclei for saturated hydrocarbons*

Ethane		Staggered		Eclipsed	
Description[b]	Atom	Electronic	Total	Electronic	Total
Exptl. distances and angles	C	−16.639	−12.411	−16.639	−12.411
	H	− 6.551	− 1.043	− 6.541	− 1.044
Exptl. distances, tetrahedral angles	C	−16.643	−12.413	−16.643	−12.413
	H	− 6.547	− 1.041	− 6.551	− 1.043
Exptl. distances, tetrahedral angles, FSGO – on nuclei	C	−15.877	−11.647	−15.877	−11.648
	H	− 6.417	− 0.911	− 6.422	− 0.914
Exptl. distances, tetrahedral angles, split inner shell	C	−18.000	−13.769	−17.999	−13.769
	H	− 6.550	− 1.044	− 6.554	− 1.046
Other calculations[d]	C	−18.873		−18.873	
	H	− 6.672		− 6.675	

Propane[b] (Exptl. distances, tetrahedral angles)

Atom[c]	Staggered-Staggered		Staggered-Eclipsed		Eclipsed-Eclipsed	
	Electronic	Total	Electronic	Total	Electronic	Total
C_1	18.212	−12.368	18.216	−12.369	18.216	−12.369
C_2	18.912	−12.310	18.911	−12.308	18.910	−12.308
C_3	18.212	−12.368	18.212	−12.368	18.216	−12.369
H_1	7.775	− 1.037	7.776	− 1.037	7.863	− 1.039
H_2	8.093	− 1.032	8.094	− 1.030	7.863	− 1.039
H_3	8.093	− 1.032	8.094	− 1.030	8.219	− 1.027
H_4	7.775	− 1.037	7.863	− 1.039	7.863	− 1.039
H_5	8.093	− 1.032	8.273	− 1.030	8.291	− 1.027
H_6	8.093	− 1.032	7.863	− 1.039	7.863	− 1.039
H_7	8.383	− 1.044	8.387	− 1.045	8.391	− 1.046
H_8	8.383	− 1.044	8.387	− 1.045	8.391	− 1.046

[a] In Hartree atomic units. See Ref. [9].

[b] See Ref. [6].

[c] See Fig. 1 for details of atom numbering.

[d] See Ref. [14].

is found in the calculations of Schulman, *et al.* [32]. From their results it is clear that the degree of optimization of the basis set is extremely important, since some of their values differed by an order of magnitude, depending upon which basis set was employed. This is especially true of the field gradients at carbon atoms, since their environment is much more polarized than that of the protons.

It should also be noted that several properties can be calculated with reasonable reliability using these small basis sets. In addition to the Hellmann-Feynman electric field, relative values of the electric potential and the molecular quadrupole moment (for unsaturated molecules) appear to be satisfactorily calculated. Apparently, the ability of these basis orbitals to provide "balanced" basis sets for electronic structure determinations [6, 7] also allows for an appropriate cancellation of errors in the computation of, e.g., molecular quadrupole moments of unsaturated hydrocarbons.

Due to symmetry, only the propane molecule in this study possesses a dipole moment. Using tetrahedral angles and experimentally determined distances,

Table 7. *Electric potential*[a] *at nuclei for unsaturated hydrocarbons*

	Atom	Electronic	Total
Ethylene:			
Description[b]			
$R_\pi = \langle\lvert z\rvert\rangle$, ϱ_{1s} from CH_4	C	−16.134	−12.295
	H	− 6.125	− 0.471
$R_\pi = \langle\lvert z\rvert\rangle$, ϱ_{1s} varied	C	−16.162	−12.323
	H	− 6.125	− 0.971
$R_\pi = 0.1$, ϱ_{1s} varied	C	−16.175	−12.336
	H	− 6.131	− 0.977
$R_\pi = 0.1$, split inner shell	C	−17.560	−13.721
	H	− 6.105	− 0.951
Schulman, *et al.*[c]			
Extended	C		−14.725
	H		− 1.107
Best-Atom	C		−14.520
	H		− 0.981
Ethylene-Optimized	C		−14.675
	H		− 1.091
Benzene:			
Description[b]			
$R_\pi = 0.1$, ϱ_{1s} varied	C	−22.033	−12.271
	H	−10.354	− 0.981
$R_\pi = \langle\lvert z\rvert\rangle$, ϱ_{1s} varied	C	−22.015	−12.253
	H	−10.346	− 0.973
$R_\pi = 0.1$, ϱ_{1s} varied; FSGO on nuclei	C	−21.696	−11.934
	H	−10.362	− 0.989
$R_\pi = 0.1$, split inner shell	C	−23.504	−13.743
	H	−10.347	− 0.974
Schulman, *et al.*[c]			
Extended	C		−14.676
	H		− 1.044
Ethylene Optimized	C		−14.640
	H		− 1.077
Naphthalene:			
Description[b]			
$R_\pi = 0.1$, ϱ_{1s} varied	C_1	−25.946	−12.255
	C_2	−25.070	−12.270
	C_9	−28.042	−12.270
	H_1	−13.871	− 0.973
	H_2	−12.850	− 0.981

[a] In Hartree atomic units. See Ref. [9].
[b] See Ref. [6].
[c] See Ref. [32].

it was found that

$$\begin{aligned} \mu_{\text{stg-stg}} &= 0.002\,D \\ \mu_{\text{stg-ecl}} &= 0.029\,D \\ \mu_{\text{ecl-ecl}} &= 0.024\,D \end{aligned} \tag{9}$$

This is to be compared with $\mu_{\text{stg-stg}} = 0.083 \pm 0.001D$,obtained from the microwave studies of Lide [22]. Although the value given in Eq. (9) for $\mu_{\text{stg-stg}}$ is too low, it

Table 8. *Electric field gradients and deuteron quadrupole coupling constants for saturated hydrocarbons*

Case[b]	Conformer		Carbon				Atom numbers	Hydrogen				
			$q_{\alpha'\alpha'}$	$q_{\beta'\beta'}$	$q_{\gamma'\gamma'}$	η		$q_{\alpha'\alpha'}$	$q_{\beta'\beta'}$	$q_{\gamma'\gamma'}$	η	$eQ_D(-q_{\alpha'\alpha'})$[a]
Ethane												
Experimental distances and angles	stg		0.0646	−0.0323	−0.0323	0.000		−0.5108	0.2559	0.2549	0.002	335.7
	ecl		0.0635	−0.0318	−0.0318	0.000		−0.5110	0.2555	0.2555	0.000	335.8
Experimental distances and tetrahedral angles	stg		0.0653	−0.0326	−0.0326	0.000		−0.5107	0.2556	0.2551	0.001	335.6
	ecl		0.0642	−0.0321	−0.0321	0.000		−0.5109	0.2556	0.2552	0.001	335.7
Split inner shell, expt. distances and tetrahedral angles	stg		0.0576	−0.0288	−0.0288	0.000		−0.5074	0.2549	0.2525	0.005	333.4
	ecl		0.0565	−0.0282	−0.0282	0.000		−0.5076	0.2544	0.2532	0.002	333.5
Expt. distances, tetrahedral <'s, FSGO on nuclei	stg		0.0263	−0.0131	−0.0131	0.000		−0.7145	0.3669	0.3476	0.027	469.5
	ecl		0.0253	−0.0127	−0.0127	0.000		−0.7150	0.3624	0.3527	0.014	469.8
Hoyland[c] (5, 2, 2) basis	stg							−0.3158	0.1599	0.1558	0.013	235.9
	ecl							−0.3158	0.1601	0.1552	0.015	235.7
Hoyland[c] (5, 3, 3) basis	stg							−0.3590	0.1813	0.1778	0.010	207.5
	ecl							−0.3587	0.1813	0.1774	0.011	207.2
Harrison[d], Gaussian Lobe Functions	stg							−0.3317				218
	ecl							−0.3310				218
Propane												
Experimental distances and tetrahedral angles	stg-stg	C_1	0.0741	−0.0386	−0.0355	0.041	H_1	−0.5779	0.2903	0.2876	0.005	379.7
		C_2	0.0643	−0.0643	−0.0000	1.000	H_2	−0.5720	0.2879	0.2850	0.004	375.9
							H_7	−0.5593	0.2809	0.2784	0.005	367.5
	stg-ecl	C_1	0.0744	−0.0386	−0.0358	0.039	H_1	−0.5780	0.2903	0.2877	0.005	379.8
		C_2	0.0640	−0.0638	−0.0002	0.994	H_2	−0.5711	0.2862	0.2849	0.002	375.3
		C_3	0.0725	−0.0363	−0.0362	0.001	H_4	−0.5757	0.2893	0.2864	0.005	378.3
							H_5	−0.5695	0.2859	0.2836	0.004	374.2
							H_7	−0.5596	0.2808	0.2787	0.004	367.7
	ecl-ecl	C_1	0.0724	−0.0368	−0.0356	0.017	H_1	−0.5758	0.2893	0.2865	0.005	378.4
		C_2	0.0636	−0.0632	−0.0005	0.985	H_3	−0.5698	0.2868	0.2830	0.007	374.4
							H_7	−0.5598	0.2805	0.2794	0.002	367.9

[a] In units of kc/sec. [b] See Ref. [6] for details. [c] See Ref. [14]. [d] See Ref. [26].

Table 9. *Electric field gradients*[c] *and deuteron quadrupole coupling constants for unsaturated hydrocarbons*

Molecule	Case[b]	Carbon				Hydrogen				
		$q_{\alpha'\alpha'}$	$q_{\beta'\beta'}$	$q_{\gamma'\gamma'}$	η	$q_{\alpha'\alpha'}$	$q_{\beta'\beta'}$	$q_{\gamma'\gamma'}$	η	$eQ_D(-q_{\alpha'\alpha'})$[a]
Ethylene	ϱ_{1s} CH_4 frag. $R_\pi = \langle\lvert Z\rvert\rangle$	0.0986	−0.0510	−0.0476	0.035	−0.6510	0.3503	0.3007	0.076	427.8
	ϱ_{1s} varied $R_\pi = \langle\lvert Z\rvert\rangle$	0.0987	−0.0506	−0.0481	0.025	−0.6512	0.3504	0.3008	0.076	427.9
	ϱ_{1s} varied $R_\pi = 0.1$ Bohr	0.0935	−0.0574	−0.036	0.228	−0.6490	0.34941	0.2995	0.076	426.5
	Split Inner Shell $R_\pi = 0.1$ Bohr	0.0801	−0.0718	−0.0083	0.793	−0.6323	0.3421	0.2902	0.082	415.4
	Gaussian[d] Lobe Functions					−0.3780				248
	Single Gaussian[e] FSGO					−0.5648				370.84
	Double Gaussian[e] FSGO					−0.2777				182.33
	Extended Gaussian[f]	−0.3785	0.2858	0.09274		−0.3188	0.1680	0.1509	0.054	209.5
	Best-Atom Gaussian[f]	0.08778	−0.08736	−0.00242		−0.4034	0.2047	0.1987	0.015	265.1
	Ethylene-Optimized Gaussian[f]	−0.4187	0.2743	0.1443		−0.3454	0.1773	0.1680	0.027	227.0
Benzene	ϱ_{1s} varied $R_\pi = \langle\lvert Z\rvert\rangle$	0.1875	−0.1207	−0.0668	0.288	−0.6171	0.3316	0.2854	0.074	405.5

	ϱ_{1s} varied $R_\pi=0.1$ Bohr		0.1819	−0.1098	−0.0721	0.207		−0.6147	0.3302	0.2845	0.074	403.9
	Split Inner Shell $R_\pi=0.1$ Bohr		0.1537	−0.1021	0.1515	0.329		−0.5975	0.3242	0.2733	0.085	392.6
	ϱ_{1s} varied $R_\pi=0.1$ Bohr FSGO on Nuclei		−0.2918	0.2708	0.0211	0.855		−0.7451	0.3892	0.3559	0.045	−489.6
	Bonera and Rigamonti[g]							−0.2371				154
	Extended Gaussian[f]		−0.3124	0.1616	0.1508			−0.3638	0.1949	0.1689	0.072	239.1
	Ethylene-Optimized Gaussian[f]		−0.4138	0.3132	0.1006			−0.3449	0.1800	0.1649	0.044	226.6
	Expt.[h]							−0.294				193
Naphthalene	ϱ_{1s} varied $R_\pi=0.1$ Bohr	C_1	0.1759	−0.1065	−0.0694	0.211	H_1	−0.6132	.3312	− .2820	0.080	402.9
		C_9	−0.1793	0.0904	0.0889	0.008	H_2	−0.6148	0.3307	− .2841	0.076	404.0
		C_2	0.1784	−0.1076	−0.0708	0.206						

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[a] In units of kc/sec. See Ref. [25] for value of deuteron quadrupole moment.

[b] See Ref. [6] and [7] for details.

[c] *Efg* in Hartree atomic units. See Ref. [9].

[d] See Ref. [26].

[e] See Ref. [27].

[f] See Ref. [32].

[g] See Ref. [29].

[h] See Ref. [28, 30].

should be pointed out that other *ab initio* calculations employing considerably larger basis sets have experienced similar difficulties. For example, Hoyland [14] obtained $\mu_{\text{stg-stg}} = 0.0017 D$ using a (5, 2, 2) basis, and $\mu_{\text{stg-stg}} = 0.0019 D$ for a (5, 3, 3) basis. Also, use of a slightly different basis set for CH_4 as suggested by Frost [23], with tetrahedral angles and experimental distances, results in $\mu_{\text{stg-stg}} = 0.067 D$.

It should also be noted that, in the cases tested, several properties seem to be reasonably insensitive to the use of idealized geometries. This applies mainly to those operators whose origin is on an atomic center, and is not true for operators such as the dipole and quadrupole moment, which depend strongly on overall nuclear geometry.

As to the question of which representation provides the best basis for overall wavefunction accuracy and utility, it appears from the above analysis that the split inner shell basis is preferable. Also, it is clear that FSGO-on-nuclei basis provides the poorest representation in terms of all properties considered (except in the case of the delta function on the hydrogen nuclei). At this point, however, definitive recommendations as to which basis is optimum await the completion of similar studies, now in progress, on nitrogen and oxygen containing molecules. These studies will provide a more complete analysis of basis suitability, due to the large amount of experimental and theoretical data available for comparison. However, it should be remembered that, in order to be able to treat large molecules, the basis must be kept reasonably simple. Therefore, merely adding FSGO (i.e., approaching the Gaussian lobe function or other techniques [24]) will ultimately place severe restrictions on the size of molecule amenable to calculation. Consequently, it is encouraging that several first order electronic properties, as well as overall geometric and electronic structure, can be adequately predicted for hydrocarbons using small basis sets.

Finally, the ease with which the various integrals can be evaluated over FSGO bases, even for quite complicated operators, should also be noted. This observation is in contradistinction to the usual situation arising in semiempirical and some *ab initio* studies, where evaluation of integrals over Slater-type orbitals causes major difficulties.

Acknowledgment. The authors would like to express their gratitude to the University of Kansas for support of the computer time required for this work.

Appendix

Integrals Needed for Molecular Property Calculations

Overlap:

$$\langle G_t | G_u \rangle = S_{tu} = \left(\frac{\pi}{a_t + a_u} \right)^{\frac{3}{2}} \exp \left\{ - \left(\frac{a_t a_u}{a_t + a_u} \right) |\boldsymbol{R}_t - \boldsymbol{R}_u|^2 \right\}$$

Dipole Moment:

$$\langle G_t | (r - \boldsymbol{R}_C)_\alpha | G_u \rangle = (\boldsymbol{R}_p - \boldsymbol{R}_C)_\alpha S_{tu} .$$

Second Moment:

$$\langle G_t|(\boldsymbol{r}-\boldsymbol{R}_C)_\alpha(\boldsymbol{r}-\boldsymbol{R}_C)_\beta|G_u\rangle=\left\{(\boldsymbol{R}_p-\boldsymbol{R}_C)_\alpha(\boldsymbol{R}_p-\boldsymbol{R}_C)_\beta+\frac{\delta_{\alpha\beta}}{2a_{tu}}\right\}S_{tu}.$$

Electric Potential at a point (A):

$$\langle G_t||\boldsymbol{r}-\boldsymbol{R}_A|^{-1}|G_u\rangle=2\left(\frac{a_{tu}}{\pi}\right)^{\frac{1}{2}}F_0[a_{tu}|\boldsymbol{R}_p-\boldsymbol{R}_A|^2]\,S_{tu}.$$

Electric Field at a point (A): (Hellmann-Feynman)

$$\left\langle G_t\left|\frac{(\boldsymbol{r}-\boldsymbol{R}_A)_\alpha}{|\boldsymbol{r}-\boldsymbol{R}_A|^3}\right|G_u\right\rangle=4a_{tu}^{\frac{3}{2}}\pi^{-\frac{1}{2}}(\boldsymbol{R}_p-\boldsymbol{R}_A)_\alpha\cdot F_1\,[a_{tu}|\boldsymbol{R}_p-\boldsymbol{R}_A|^2]\,S_{tu}.$$

Electric Field Gradient at a point (A):

$$\left\langle G_t\left|\frac{3(\boldsymbol{r}-\boldsymbol{R}_A)_\alpha(\boldsymbol{r}-\boldsymbol{R}_A)_\beta-\delta_{\alpha\beta}|\boldsymbol{r}-\boldsymbol{R}_A|^2}{|\boldsymbol{r}-\boldsymbol{R}_A|^5}\right|G_u\right\rangle$$
$$=8a_{tu}^{\frac{5}{2}}\pi^{-\frac{1}{2}}\{(\boldsymbol{R}_p-\boldsymbol{R}_A)_\alpha(\boldsymbol{r}-\boldsymbol{R}_A)_\beta-\tfrac{1}{3}\delta_{\alpha\beta}|\boldsymbol{R}_p-\boldsymbol{R}_A|^2\}\,F_2[a_{tu}|\boldsymbol{R}_p-\boldsymbol{R}_A|^2]\,S_{tu}.$$

One-electron Delta Function at a point (A):

$$\langle G_t|\delta(\boldsymbol{r}-\boldsymbol{R}_A)|G_u\rangle=\left(\frac{a_{tu}}{\pi}\right)^{\frac{3}{2}}\exp\{-a_{tu}|\boldsymbol{R}_p-\boldsymbol{R}_A|^2\}\,S_{tu}.$$

In the above equations,

$$\boldsymbol{R}_p=X_p\boldsymbol{i}+Y_p\boldsymbol{j}+Z_p\boldsymbol{k}$$
$$X_p=\frac{a_sX_s+a_tX_t}{a_s+a_t},\quad\text{etc.},$$
$$a_s=1/\varrho_s^2,$$
$$a_{tu}=a_t+a_u,$$

and

$$F_n(\zeta)=\int_0^1 u^{2n}\exp(-\zeta u^2)\,du,\qquad\zeta>0;\qquad n=0,1,2\ldots.$$

References

1. Mulliken, R. S.: J. chem. Physics **36**, 3428 (1962).
2. Boys, S. F.: Proc. Roy. Soc. (London) A **200**, 542 (1950).
3. See, for example: Buenker, R. J. Peyerimhoff, S. D.: Chem. Physics Letters **3**, 37 (1969).
4. For a recent review, see: Allen, L. C.: Annu. Rev. physic. Chem. **20**, 315 (1969).
5. Christoffersen, R. E., Maggiora, G. M.: Chem. Physics Letters **3**, 419 (1969).
6. — Genson, D. W., Maggiora, G. M.: J. chem. Physics **54**, 239 (1971).
7. — JACS (in press).
8. Roothaan, C. C. J.: Rev. mod. Physics **23**, 69 (1951).
9. Shull, H., Hall, G. G.: Nature **184**, 1559 (1959).
10. Hellmann, H. H.: Einführung in die Quantenchemie. Leipzig: Franz Deuticke 1937; Feynmann, R. P.: Physic. Rev. **56**, 340 (1939).
11. Other data supporting this observation includes the scale factors, which are nearly identical for each conformer. See Ref. [6] for details.
12. Pitzer, R. M., Lipscomb, W. N.: J. chem. Physics **39**, 1995 (1963).

13. Sovers, O. J., Kern, C. W., Pitzer, R. M., Karplus, M.: J. chem. Physics **49**, 2592 (1968).
14. Hoyland, J. R.: J. Amer. chem. Soc. **90**, 2227 (1968).
15. Buckingham, A. D., Disch, R. L., Dunmur, D. A.: J. Amer. chem. Soc. **90**, 3104 (1968).
16. Pritchard, R. H., Kern, C. W.: J. Amer. chem. Soc. **91**, 1631 (1969).
17. Schweig, A.: Molecular Physics **14**, 533 (1968).
18. Stogryn, D. E., Stogryn, A. P.: Molecular Physics **11**, 371 (1966).
19. Shoemaker, R. L., Flygare, W. H.: J. chem. Physics **51**, 2988 (1969).
20. Hill, R. M., Smith, W. V.: Physic. Rev. **82**, 451 (1951).
21. Spurling, T. H., DeRocco, A. G.: J. chem. Physics **49**, 2867 (1968).
22. Lide, D. R.: J. chem. Physics **33**, 1514 (1960).
23. Frost, A. A.: J. physic. Chem. **72**, 1289 (1968).
24. Buenker, R. J., Peyerimhoff, S. D., Allen, L. C., Whitten, J. L.: J. chem. Physics **45**, 2835 (1966).
25. The value of the deuteron quadrupole moment that has been used in these calculations is $Q_D = 2.7965 \times 10^{-27}\,\mathrm{cm}^2$, as determined by: Narumi, H., Watanabe, J.: Prog. theoret. Physics (Kyoto) **35**, 1154 (1966).
26. Harrison, J. F.: J. chem. Physics **48**, 2379 (1968).
27. Ray, N. K.: Chem. Physics Letters **6**, 225 (1970).
28. Olympia, Jr., P. L., Wei, I. Y., Fung, B. M.: J. chem. Physics **51**, 1610 (1969).
29. Bonera, G., Rigamonti, A.: J. chem. Physics **42**, 175 (1965).
30. Caspary, W. J., Millett, F., Reichbach, M., Dailey, B. P.: J. chem. Physics **51**, 623 (1969).
31. Ditchfield, R., Miller, D. P., Pople, J. A.: J. chem. Physics **53**, 613 (1970).
32. Schulman, J. M., Hornback, C. J., Moskowitz, J. W.: Chem. Physics Letters **8**, 4 (1971).
33. For examples of this observation, see: Unland, M. L., Van Wazer, J. R., Letcher, J. H.: J. Amer. chem. Soc. **91**, 1045 (1969); Letcher, J. H., Unland, M. L., Van Wazer, J. R.: J. chem. Physics **50**, 2185 (1969); Neumann, D. B., Moskowitz, J. W.: J. chem. Physics **49**, 2056 (1968); **50**, 2216 (1969).
34. Golub, S.: Thesis, Columbia University (1968); Disch, R. L., Golub, S.; to be published.

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