Less than 10% of the carbon suboxide was decomposed in any one experiment. For the most reactive olefins, the amount of suboxide decomposed was sometimes a significant fraction of the olefin pressure. For these cases, the pressure of added olefin given in Table I is an average value, calculated by assuming that every C_2O which did not form C_3H_4 in cell 2 removed one molecule of olefin x. These corrections, being important only at the lowest ratio of (olefin x)/(ethylene), had little effect on the relative reactivities.

The carbon suboxide was generated as described previously.[4] After several trap-to-trap distillations under vacuum, the only impurity detected by gas chromatography was a fraction of a per cent of CO_2. All hydrocarbons were degassed under vacuum before using. The olefins were Phillips Research Grade, with the exception of the following: 1,3-butadiene, Matheson Instrumental Grade; isobutylene and *trans*-2-butene, Matheson CP Grade; 2,3-dimethyl-2-butene, 2,4-dimethyl-2,3-pentadiene, and 2-butyne, Columbia Organic Chemicals, 99.5%; acetylene, Matheson, 99.66%, passed through a cold trap. The following gases were used directly from the tanks: oxygen, Gordon Duff, 99.8%; nitrogen, Matheson, 99.997%; helium, Matheson, 99.99%.

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A Floating Spherical Gaussian Orbital Model of Molecular Structure. IV. Hydrocarbons[1]

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Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois. Received October 19, 1967

Abstract: The FSGO model is applied to a series of hydrocarbons: methane, ethane, ethylene, acetylene, and cyclopropane. Bond lengths and bond angles are obtained with an average absolute deviation of 1.7 and 1.0%, respectively, from observed values. The barrier to internal rotation of ethane is calculated.

The floating spherical Gaussian orbital (FSGO) model is discussed in detail in paper I[2a] of this series. As currently applied, the model predicts the electronic and geometric structure of singlet ground states of molecules with localized orbitals without the use of any arbitrary or semiempirical parameters. The localized orbitals are constructed by using single normalized spherical Gaussian functions

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

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

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

where $(j|k) = \int\phi_j h\varphi_k \, dv$ (h = one-electron operator) and $(kl|pq) = \int\phi_k(1)\phi_l(1)(1/r_{12})\phi_p(2)\phi_q(2) \, dv_1dv_2$. The energy is minimized by a direct search procedure with respect to all parameters: orbital radii, ρ_i, orbital positions, $\vec{R}_i$, and nuclear positions.

Previous work with the FSGO model[2b,3] indicated that the model works best for elements in the middle of the second row of the periodic table. So in choosing larger and more complicated molecules to which to apply the model, the hydrocarbons were a natural selection. Simple hydrocarbons present a variety of molecular structure, double and triple bonds, ring compounds, and several interesting energetic quantities.

Results

Methane provides a simple example for detailed consideration of the application of the FSGO model to the hydrocarbons. In order to make the calculation most efficient, tetrahedral symmetry is imposed, thus allowing identification of symmetrically related integrals which are calculated only once. This in effect places a symmetry constraint on the minimization; *i.e.*, while the orbital positions and radii are varied, they are varied in such a way that the symmetry is maintained. Parameters were defined so that the four C–H orbital radii are varied together; the twelve orbital positions (x, y, and z for four C–H bonding orbitals) formed another parameter. The carbon 1s orbital radius was another parameter, but the orbital was held at the origin to maintain symmetry. The 12 hydrogen positions were defined by the fourth and final parameter with the carbon being held at the origin.

This symmetry constraint is not as serious as one might suspect. Several calculations were made with relaxed symmetry with LiH and BH_3, and the results were essentially the same as corresponding symmetry-constrained calculations. The remainder of the results reported here have the indicated symmetry imposed and presumably no error is introduced by such tactics.

The results for methane were presented in paper III[3] along with other first-row hydrides but are reproduced here for comparison with the other hydrocarbons. As-

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(1) Portions of this paper were presented at the Computers in Chemistry Symposium, San Diego, Calif., June 1967, and at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

(2) (a) A. A. Frost, *J. Chem. Phys.*, 47, 3707 (1967) (paper I); (b) 47, 3714 (1967) (paper II).

(3) Paper III: A. A. Frost, *J. Phys. Chem.*, 72, 1289 (1968); also see the preliminary communication: A. A. Frost, B. H. Prentice, III, and R. A. Rouse, *J. Am. Chem. Soc.*, 89, 3064 (1967).

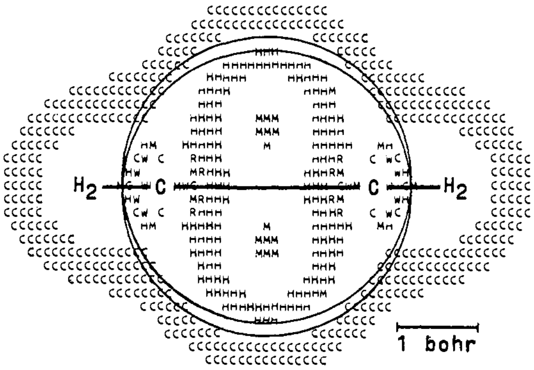

Figure 1. Electron density diagram for ethylene in a plane perpendicular to plane of the molecule. Contours, if drawn, would increase successively at outside and inside edges of the lettered regions of the computer output. Outside edge of C's, 0.05 au; inside of C's, 0.10 au; outside of H's, 0.15 au, etc. The circles represent the double-bond orbitals drawn with radii equal to the "orbital radii," ρ. The centers of these orbitals are only 0.2 bohr apart, but the maxima of the electron density lie in regions M which are about 1.5 bohrs apart because of the orbital overlap effect in the electron density.

suming a tetrahedral structure, the bond length was calculated to be 2.107 bohrs. The bonding orbitals had an orbital radius of 1.694 bohrs and were located 1.256 bohrs from the carbon nucleus. The orbital radius of the carbon inner shell was 0.328 bohr. The total energy for methane was −33.992 hartrees.

Both staggered and eclipsed conformations of ethane were investigated and Tables I and II present the results.

Table I. Ethane (Staggered, D_{3d}, Atomic Units)

Nuclear positions		x	y	z
C_a		0.0	0.0	1.418
C_b		0.0	0.0	−1.418
H_{a1}		0.0	1.979	2.166
H_{a2}		1.714	−0.990	2.166
H_{a3}		−1.714	−0.990	2.166
		(three other H's at z = −2.166 with x and y interchanged)		

Orbitals	Radii	x	y	z
C_a 1s	0.328	0.0	0.0	1.418
C_b 1s	0.328	0.0	0.0	−1.418
C_a–C_b	1.646	0.0	0.0	0.0
C_a–H_{a1}	1.695	0.0	1.201	1.869
C_a–H_{a2}	1.695	1.040	−0.601	1.869
C_a–H_{a3}	1.695	−1.040	−0.601	1.869
		(three other orbitals at z = −1.869 with x and y interchanged)		

Bond lengths, bohrs	Bond angles, deg	Energy, hartrees
C–C, 2.837 C–H, 2.116	C–C–H, 110.7 H–C–H, 108.2	−67.005

In ethylene the double bond is encountered for the first time. It is constructed by placing two identical spherical Gaussian functions at equal distances above and below the plane of the molecule at the midpoint of the C–C axis as shown in Figure 1. When the minimization procedure is applied to ethylene, the bonding orbitals tend to coalesce similarly to the cases mentioned previously in connection with lone pairs in paper III[3] in this series. So the positions of these orbitals were fixed and the other parameters varied to attain a minimum. The results for ethylene are presented in Table III. Figure 2 shows the electron density in the plane of the nuclei.

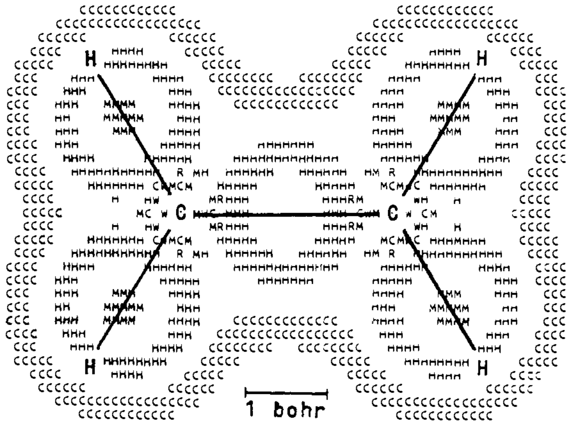

Figure 2. Electron density diagram of ethylene in the plane of the nuclei: contour intervals, 0.05 au.

Table II. Ethane (Eclipsed, D_{3h}, Atomic Units)

Nuclear positions		x	y	z
C_a		0.0	0.0	1.430
C_b		0.0	0.0	−1.430
H_{a1}		0.0	1.9071	2.195
H_{a2}		1.707	−0.985	2.195
H_{a3}		−1.707	−0.985	2.195
		(three other H's at z = −2.195)		

Orbitals	Radii	x	y	z
C_a 1s	0.328	0.0	0.0	1.430
C_b 1s	0.328	0.0	0.0	1.430
C_a–C_b	1.651	0.0	0.0	0.0
C_a–H_{a1}	1.695	0.0	1.193	1.892
C_a–H_{a2}	1.695	1.033	−0.597	1.892
C_a–H_{a3}	1.695	−1.033	−0.597	1.892
		(three other orbitals at z = −1.892)		

Bond lengths, bohrs	Bond angles, deg	Energy, hartrees
C–C, 2.859 C–H, 2.114	C–C–H, 111.2 H–C–H, 107.7	−66.996

Table III. Ethylene (D_{2h}, Atomic Units)

Nuclear positions		x	y	z
C_a		0.0	0.0	1.277
C_b		0.0	0.0	−1.277
H_{a1}		1.791	0.0	2.338
H_{a2}		−1.791	0.0	2.338
		(two other H's at z = 2.338)		

Orbitals	Radii	x	y	z
C_a 1s	0.328	0.0	0.0	1.277
C_b 1s	0.328	0.0	0.0	−1.277
C_a=C_b	1.794	0.0	(0.100)	0.0
	1.794	0.0	(−0.100)	0.0
C_a–H_{a1}	1.642	1.084	0.0	1.937
C_a–H_{a2}	1.642	−1.084	0.0	1.937
		(two other orbitals at z = −1.937)		

Bond lengths, bohrs	Bond angles, deg	Energy, hartrees
C=C, 2.554 C–H, 2.081	C–C–H, 120.7 H–C–H, 118.7	−65.835

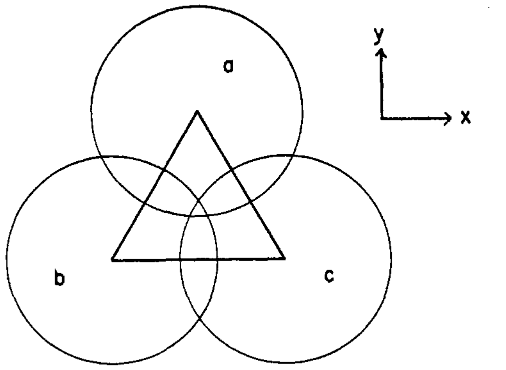

Figure 3. Schematic diagram of construction of the triple bond in acetylene.

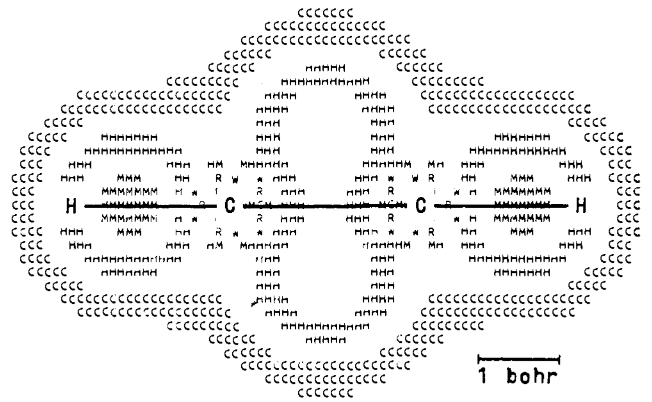

Figure 4. Electron density diagram of acetylene in the *xz* plane. The density in the triple bond is not quite exactly symmetrical with respect to reflection across the internuclear axis due to the finite separation of the orbital centers. Results for the *yz* plane are essentially the same: contour interval, 0.05 au.

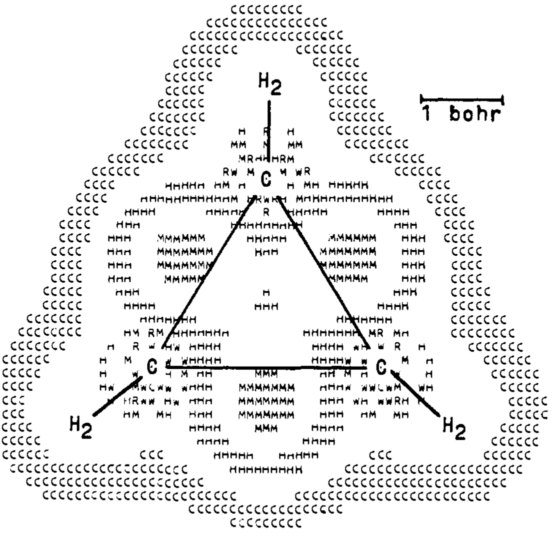

Figure 5. Electron density diagram of cyclopropane in the plane of the carbons: contour interval, 0.05 au.

The triple bond in acetylene is represented by three identical orbitals placed at the corners of an equilateral triangle located at the midpoint of the C–C axis; this is shown schematically in Figure 3. Coalescence of the bonding orbitals again occurs and their positions are fixed and the minimization carried forth. Table IV and Figure 4 show the acetylene results.

Table IV. Acetylene (Nuclei Linear; Orbitals D_{3h}, Atomic Units)

Nuclear positions		*x*	*y*	*z*
C_a		0.0	0.0	1.148
C_b		0.0	0.0	−1.148
H_a		0.0	0.0	3.187
H_b		0.0	0.0	−3.187
Orbitals	Radii	*x*	*y*	*z*
C_a 1s	0.328	0.0	0.0	1.147
C_b 1s	0.328	0.0	0.0	−1.147
C≡C	1.781	0.0	(0.200)	0.0
	1.781	(0.173)	(−0.100)	0.0
	1.781	(−0.173)	(−0.100)	0.0
C_a–H_a	1.581	0.0	0.0	2.360
C_b–H_b	1.581	0.0	0.0	−2.360
Bond lengths, bohrs				Energy, hartrees
C≡C, 2.295 C–H, 2.039				−64.678

Table V. Cyclopropane (D_{3h})

Nuclear positions		*x*	*y*	*z*
C_a		0.0	1.672	0.0
C_b		1.448	−0.836	0.0
C_c		−1.448	−0.836	0.0
H_{a1}		0.0	2.814	1.771
H_{a2}		0.0	2.814	−1.771
Orbitals	Radii, bohrs	*x*	*y*	*z*
C_a 1s	0.3278	0.0	1.672	0.0
C_b 1s	0.3278	1.448	−0.836	0.0
C_c 1s	0.3278	−1.448	−0.836	0.0
C_a–C_b	1.770	0.781	0.451	0.0
C_b–C_c	1.770	0.0	−0.901	0.0
C_c–C_a	1.770	−0.781	0.451	0.0
C_a–H_{a1}	1.683	0.0	2.367	1.076
C_a–H_{a2}	1.683	0.0	2.367	−1.076
Bond length	Calcd, bohrs	Calcd, Å	Exptl nmr[a]	Exptl electron density
C–C	2.897	1.533	(1.510)	1.510[b]
C–H	2.108	1.115	1.123	1.089[b]
Bond angle, H–C–H		114.4°	114.4°	115.1°
Energy	−98.895 hartrees			

[a] L. C. Snyder and S. Meiboom, *J. Chem. Phys.*, **47**, 1480 (1967).
[b] J. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Cryst.*, **17**, 538 (1964).

The simplest ring hydrocarbon is cyclopropane and its predicted geometry, compared to observed geometry, is shown in Table V. Figure 5 shows the electron density map found for cyclopropane.

Discussion

Table VI compares the calculated bond lengths with experimental values. Examination of the results shows excellent agreement between experimental and calculated bond lengths and bond angles. Bond-length errors range from 0.7 to 2.5% with an average absolute error of 1.7%. Bond angle errors are found between 0.58 and 1.2% with an average absolute error of 1.0%. While little can be added to the discussion of methane, several points should be emphasized in the ethane investigation. The FSGO model yields an H–C–H angle of 108.2° within each methyl group in the staggered form that is smaller than the tetrahedral angle, in qualitative agreement with experiment. Also in the

Table VI. Comparison of FSGO Structural Results with Other Calculations and Experiment (Å)

	This calcn	SCF	Extended Hückel[b]	Observed[c]
Methane				
C–H	1.115	1.09[a]	1.02	1.093
Ethane				
C—C	1.501	...	1.92	1.534
C—H	1.120	...	1.0	1.093
∠H–C–H	108.2°	...	(109.45°)	109.1°
Ethylene				
C═C	1.351	1.333[d]	1.47	1.337
C—H	1.101	1.056[d]	0.95	1.086
∠H–C–H	118.7°	...	125°	117.3°
Acetylene				
C≡C	1.214	1.215[e]	0.85	1.205
C—H	1.079	1.085[e]	1.0	1.059
Cyclopropane				
C—C	1.533	1.54[f]		1.510[g]

[a] M. Krauss, *J. Res. Natl. Bur. Std., A*, **68**, 635 (1964). [b] R. Hoffmann, *J. Chem. Phys.*, 39, 1397 (1963). [c] L. E. Sutton, Ed., "Interatomic Distances," Special Publication No. 18, The Chemical Society, London, 1965. [d] J. W. Moscowitz and M. C. Harrison, *J. Chem. Phys.*, **42**, 1726 (1965). [e] H. Preuss, *et al.*, "Arbeitsbericht der Gruppe Quanten Chemie," No. 5, Max-Planck-Institut, Munich, 1967, p 68. [f] H. Preuss and H. Diercksen, *Intern. J. Quantum Chem.*, **1**, 361 (1967). [g] Reference *b*, Table V.

eclipsed form the angle is still smaller, and in addition the C–C bond length is greater. All of these effects as well as the energy barrier can be interpreted by assuming repulsions between the two methyl groups. It would be tempting to interpret these effects in terms of repulsions between filled orbitals, but this does not seem to be possible in this model where the orbitals are definitely nonorthogonal. Although in paper III the bond angles for H_2O and NH_3 as calculated were too small by 17%, more faith can be put in calculations of hydrocarbons where lone-pair electrons are absent.

The energy of the eclipsed conformation is higher by 5.7 kcal/mole, yielding a barrier to internal rotation about twice the observed value, 3.03 ± 0.30 kcal/mole.[4] This energy is very poor compared to most other calculations.[5]

Ethylene serves as an example for the double bond. As was previously discussed, a "banana bond" approach was taken in constructing the double bond, and, upon minimizing, the bonding orbitals coalesced and the calculation became impossible as the off-diagonal elements of the overlap matrix converged toward unity, making the inverse matrix results void. It should be pointed out that the failure lies ultimately in an inherent violation of the Pauli exclusion principle manifested through the Slater determinant: with coalescence two electrons in the same molecule have the same set of quantum numbers, hence two rows in the Slater determinant are identical and the wave function is nonexistent. Following the appendix of paper III,[3] the orbitals in the limit of coalescence for ethylene are

$$\lim_{R \to 0}(a + b) = \text{s-type Gaussian}$$

$$\lim_{R \to 0}(a - b) = \text{p}_y\text{-type Gaussian}$$

where R = the distance between the two Gaussians. So the model gives the simple molecular orbital picture of a double bond (a σ bond and a π bond), which is equivalent to the banana bond through a transformation of the Slater determinantal wave function. It should also be noted that the H–C–H angle is less than 120°, possibly due to interaction of the C–H bonding orbitals with the double-bond orbitals as predicted by Gillespie.[6]

The triple bond of acetylene is interpreted in a similar manner. In the limit of $R \to 0$ (the distance from the center of the equilateral triangle to a vertex), two p- and one s-type orbital are obtained (see Figure 3).

$$\lim_{R \to 0}(a + b + c) = \text{s-type Gaussian}$$

$$\lim_{R \to 0}(b - c) = \text{p}_x\text{-type Gaussian}$$

$$\lim_{R \to 0}(2a - b - c) = \text{p}_y\text{-type Gaussian}$$

Again the simple molecular orbital picture of a triple bond is found, a σ bond and two π bonds. To check how close to the limit of $R = 0$ are the calculations for ethylene and acetylene, the POLYATOM program[7] was employed to calculate the energy using actual p orbitals. These orbitals were centered on the C–C axis, perpendicular to it, and had the identical exponential parameter as the spherical Gaussians. The results are (in hartrees)

	This calcn	POLYATOM
Ethylene	−65.835	−65.836
Acetylene	−64.678	−64.682

The energies are within 0.2% of each other and indicate that, in holding the bonding orbitals fixed at a small separation, no large error was introduced in the minimization process.

Cyclopropane exhibits several interesting features. Careful examination of the positions of the C–C bonding orbitals discloses that they lie outside of the C–C axis, essentially forming a bent bond. When cyclopropane was first synthesized, the existence of a three-membered ring was rationalized by saying the C–C bond must be bent in order to make the compound stable. The FSGO model reinforces this initial view. The H–C–H angle is greater than tetrahedral and is in excellent agreement with the experimental results shown in Table V.

Table VI also sets forth a comparison of the FSGO structural predictions with other calculated results. The FSGO findings are much better than the extended Hückel results as one expects and are comparable with accurate SCF results. In comparison to the extended Hückel method, the FSGO model is strictly quantum mechanical and involves no approximations or semiempirical parameters.

Figure 6 shows a comparison of calculated and experimental bond lengths, the FSGO predictions falling very close to the theoretical 45° line. In addition the C–C bond lengths decrease with increasing unsaturation,

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(4) D. R. Lide, *J. Chem. Phys.*, **29**, 1426 (1958).

(5) R. M. Pitzer, *ibid.*, **47**, 965 (1967). This author summarized other calculations in addition to his own.

(6) R. T. Gillespie and R. S. Nyholm, *Quart. Rev.* (London), **11**, 339 (1957); R. T. Gillespie, *Can. J. Chem.*, **38**, 818 (1960); R. A. Rouse and A. A. Frost, paper presented at 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

(7) I. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, and B. T. Sutcliffe, *Theoret. Chim. Acta*, **6**, 191 (1966).

ethane the longest and acetylene the shortest. The C–H bond lengths also follow the correct trend with the C–H bond in ethane being the longest, then ethylene, and finally acetylene. This result comes automatically from the calculation without any necessary reference to changing hybridization of orbitals. The hybridization concept has no particular significance in the present model. Inspection of the carbon 1s orbital positions and radii discloses that these orbitals are always found very close to the carbon nuclei and with the same orbital radii. This indicates the inert behavior of this pair of electrons in the hydrocarbons.

Comparisons of FSGO and SCF energies are shown in Table VII. As pointed out previously[8] the FSGO energies are typically about 85% of the SCF values. This deviation is principally due to the lack of cusps in the inner-shell orbitals at the nuclei.

Table VII. Comparison of FSGO Energy Results (in Hartrees) to Hartree–Fock SCF Calculations

	This calcn	SCF
Methane	−33.992	−40.198[a]
Ethane		
Staggered	−67.005	−79.09797[b]
Eclipsed	−66.996	−79.09233[b]
Ethylene	−65.835	−78.0012[c]
Acetylene	−64.678	−76.7916[c]
Cyclopropane	−98.895	−116.02[d]

[a] C. D. Ritchie and H. F. King, *J. Chem. Phys.*, **47**, 564 (1967). [b] R. M. Pitzer, *ibid.*, **47**, 965 (1967). [c] R. J. Buenker, S. D. Peyerimhoff, and J. L. Whitten, *ibid.*, **46**, 2029 (1967). [d] Reference *f*, Table VI.

The time required on the CDC3400 for computing each of these molecules varied from about 1 min for methane to 4 min for two-carbon species to 8 min for cyclopropane. These times include the search for the energy minimum for various nuclear configurations.

In a typical run the internuclear distances and bond angles not determined by symmetry are set at initial values which are within only about 10–20% of values that are known experimentally or just guessed from previous experience. Starting positions and radii of orbitals are estimated from experience with simpler molecules. The pattern search minimization procedure is then begun with 10% changes in the various parameters and allowed to proceed with decreasing step sizes until final parameter changes are of the order of only 0.001% of the original values. The cyclopropane calculation was accomplished with a variation of nine parameters in which the energy was computed 268 times requiring about 1.7 sec for each fixed set of parameters.

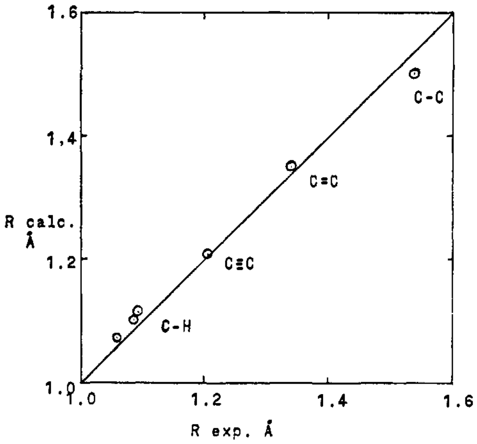

Figure 6. Plot comparing calculated and experimental CC and CH bond lengths.

Conclusion

The hydrocarbon results presented here have enlarged the range of applicability of the floating spherical Gaussian orbital model. Structural predictions are very good and encourage the expansion of the investigation to systems with a larger number of electrons.

The basis set in the FSGO model contains the fewest number of orbitals and yet in a sense contains an infinite variety. With all orbital parameters being varied, the very best orbitals are found while still keeping the number of orbitals low. We have chosen to call this optimized basis set a Lewis basis set in deference to G. N. Lewis, who suggested the electron dot model to have pairs of electrons representing bonds. It is important to notice the difference between a Lewis basis set and a minimal basis set in SCF jargon. For example, in a methane calculation, the SCF minimal basis set consists of five carbon orbitals: 1s, 2s, $2p_x$, $2p_y$, and $2p_z$, and four 1s H orbitals for a total of nine. The Lewis basis set would have just five orbitals: a 1s on carbon and four C–H bonding orbitals. Only in such cases as the He and Ne atoms would the basis sets be the same. The Lewis basis set through application of the FSGO model allows manageable programming and yields good results in reasonable times.

Finally we wish to emphasize that calculations with the FSGO model are strictly *ab initio* involving no arbitrary or semiempirical parameters.[8]

Acknowledgments. The National Science Foundation supported this research with a grant to Northwestern University.

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(8) The present model is equivalent to the variation of a single "constellation" as defined by H. Preuss, *Mol. Phys.*, **8**, 157 (1964). For earlier history see paper I and ref 24 therein.