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## Limited Expansion Gaussian Lobe Orbitals in Ab Initio Studies of Atoms and Molecules

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# Limited Expansion Gaussian Lobe Orbitals in *Ab Initio* Studies of Atoms and Molecules

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Results of *ab initio* calculations for first-row atoms and ions and LCAO-MO calculations for methane, fluoromethane, difluoromethane, trifluoromethane, and ethylene are presented for basis sets consisting of groups of limited numbers of *s*-type Gaussians and simple Gaussian lobe *p* orbital representations. Parameters are presented for atoms and ions of elements beryllium through fluorine using a three-Gaussian *1s*-core group, an additional Gaussian for the *2s* orbital and a two-Gaussian lobe *p* orbital. When used in LCAO-MO calculations this atomic orbital representation appears to provide results for charge distributions, molecular geometries, valence shell MO energies, calculated HF dissociation energies, and excitation energies (for ethylene) comparable to results obtained using minimum STO basis sets. A method for isolating the core orbitals from the LCAO variation process is applied and discussed for the molecular calculations.

## I. INTRODUCTION

Gaussian functions have been frequently employed in SCF-LCAO-MO calculations simply in large basis sets,<sup>1</sup> used in groups with more limited parameter variation,<sup>2</sup> and used as a basis for expansion of STO functions to facilitate integral evaluation over a "pseudo-STO" basis.<sup>3</sup>

It is well known that a minimum STO basis, with carefully selected exponents, can yield molecular geometries to 1% or 2%, and can provide at least semiquantitative information regarding energy levels and charge distributions. This has lead us in this work to explore the use of simplified Gaussian lobe pair representations within the framework of the minimum basis SCF-LCAO-MO treatments. Preuss<sup>4</sup> and Whitten<sup>5</sup> initiated the use of Gaussian lobe pairs to supplant spherical harmonics with radial functions; however, the speed of integral evaluation with such Gaussian lobe *p* representations is partly countered by the number of such lobe pairs which were employed to provide atomic functions of near hf quality. Ease of integral evaluation using Gaussian functions has led to recent efforts to examine the effects of using limited numbers of Gaussians in ways which would allow cancellation of errors due to poor core functions. A previous paper<sup>6</sup> has reviewed efforts along these lines and reported calculations for two-, three-, and four-electron atomic and molecular species. Good values were obtained for calculations of ionization potentials, dissociation energies, and bond lengths, even though imperfect core functions lead to inaccurate total system energy values. Frost<sup>7</sup> has used single spherical Gaussian functions with adjustable center locations as bond and inner-shell orbitals for atoms and molecules. With complete parameter optimization, he is able to come to within 5%–20% of the experimental values for bond lengths and angles although energies and energy differences are very poor.

This paper continues the search for useful ways to use relatively small numbers of Gaussian functions in

atomic and molecular calculations. It was hoped to be able to retain the convenience of integral evaluation using *s*-type Gaussian functions without having to employ the large representations of Whitten *et al.* It was thought that the lobe representations offered unexplored opportunities for use in calculations where rough energy differences, molecular geometries, and charge distributions are desired. It was a question of prime importance to determine conditions for cancellation of energy errors when using poor core functions. Sachs, Geller, and Kaufman<sup>8</sup> have also noted, when using rather high quality SCF functions, that energy differences and population analyses converged much more rapidly than the total energy as the expansion basis set size is increased; this has been observed for both large Gaussian and STO basis sets. Whitten<sup>9</sup> earlier considered lobe functions representations of varying size for excited states of atomic hydrogen. However, these comparisons were not continued to systems of more than one electron. The later lobe functions published for first-row atoms used 10 Gaussians for the *1s* and *2s* orbitals and five-Gaussian lobe pairs for each *p* orbital representation. In this work we report results utilizing chiefly two-Gaussian lobe pairs for each *p* orbital in atomic and molecular calculations.

## II. ATOMIC SYSTEMS

Previous work on beryllium using uncorrelated closed-shell wavefunctions was extended to the other first-row four-electron ions through  $F^{+5}$ , using a two-Gaussian *1s* core representation with an additional Gaussian as a *2s* orbital. The difference in calculated energies for the two- and four-electron species, e.g., for the pair  $C^{+2}$  and  $C^{+4}$ , was then compared with the sum of the experimental ionization potentials<sup>10,11</sup> after correction for the correlation energies<sup>12</sup> of the ions. This gives a comparison between calculated and experimental Hartree-Fock energies. The calculated and experimental energy difference for the configura-

TABLE I. Effects of representation on energy and energy differences. Energies in atomic units.

	Gaussian lobe representation			STO <sup>b</sup>	Hartree-Fock <sup>c</sup>
	(2, 1, 1)	(2, 1, 2)	(3, 1, 2) <sup>a</sup>		
C <sup>2+</sup>	-35.3808	-35.3808	-36.1247		
C <sup>+</sup>	-36.0529	-36.2140	-36.9827	-37.266	-37.284
C( <sup>3</sup> P)	-36.2575	-36.5574	-37.3285 <sup>d</sup>	-37.6285	-37.6886
$E(C^+) - E(C^3P)$	0.2046	0.3434	0.3458	0.363	0.405
$E(C, ^1S) - E(C, ^1D)$	0.0961	0.0806	0.0860	0.096	0.0818
$E(C, ^1D) - E(C, ^3P)$	0.0666	0.0603	0.0578	0.065	0.0573
F	...	-96.3868	-98.1305	-98.9545	-99.4093
$E(F) - E(F^-)$	...	-0.185	-0.159	-0.252	+0.050

<sup>a</sup> This work, (3, 1, 2) denotes three Gaussian in core group; 1 independent Gaussian added for 2s orbital; and two-Gaussian functions *per* lobe in *p* orbital.

<sup>b</sup> Tubis, optimized minimum STO basis, Ref. 14.

<sup>c</sup> Hartree-Fock limit, Refs. 12, 13.

<sup>d</sup> After completion of all molecular calculations with the (3, 1, 2) carbon

atom representation, it was discovered that further adjustment in the individual 1s core group exponents reduced the <sup>3</sup>P state energy by 0.0120 a.u. Appropriate carbon atom energy to be used in dissociation energy calculations with the (3, 1, 2) representation is -37.3166 a.u. The small change in the core function is not expected to alter any calculated energy differences or conclusions.

tion change  $(1s)^2(2s)^2 \rightarrow (1s)^2 + 2e$  was found to vary from 0.19 to 0.34 eV for the series Be through F<sup>+</sup>. The energy differences for the two- and four-electron systems are computed fairly accurately with this small basis set even though the *total* energy values are, to say the least, poor. Since work with the *p* orbital lobe functions suggested that two-Gaussian lobe, or four-spherical Gaussians for a complete *p*

orbital representation, would be required, it seemed that the use of three, rather than two, Gaussians in the core group would not cause a large relative increase in computing time for a molecular system. Appendix A summarizes comments on numerical precision requirements in integral calculation.

Table I summarizes some of the work for atomic systems examining the effects of core and *p* orbital expansion size on the energy and energy differences for representative first-row elements, carbon and fluorine. The notation (3, 1, 2) refers to a three-Gaussian core function, a single-Gaussian 2s function which is combined with the core group function for an orthogonal 2s function, and a two-Gaussian lobe, or two lobe pair 2*p* orbital representation. For comparison, values are given for the ultimate energies obtainable with independent particle model wavefunctions, i.e., hf energy values.<sup>12,13</sup> A more realistic set of numbers for comparison in all calculations described here are the energy values obtained by Tubis<sup>14</sup> for a minimum Slater basis with optimized exponents.

It is seen that the two-Gaussian lobe *p* functions, (2, 1, 2) and (3, 1, 3) give carbon state splittings which lie between the optimized minimum basis STO values and the HF values. Even the (2, 1, 1) function gives acceptable carbon state splittings. The results for the (2, 1, 2) and (3, 1, 2) functions show that the carbon ionization potential and the electron affinity for fluorine depend only slightly on the quality of the 1s core function employed, but that the use of the simpler *p* function, (2, 1, 1), leads to an error of 0.46 a.u. in the sum of the first two carbon ionization potentials, or at least 0.2 a.u. error in the ionization potential for one electron. We may therefore expect to employ at least the (2, 1, 2) representations if meaningful energy differences are to be computed

TABLE II. Energies and energy differences for states of first-row atoms and ions. Energy is for ground state unless otherwise noted. Orbital parameters for (3, 1, 2) basis are in Appendix B.

Species	(3, 1, 2) basis	STO <sup>b</sup>
Li	-7.3720 <sup>a</sup>	
$E(\text{Li}^+) - E(\text{Li})$	0.1923 <sup>a</sup>	
Be	-14.4567	
$E(\text{Be}^+) - E(\text{Be})$	0.2888	
B	-24.3189	-24.502
$E(\text{B}^+) - E(\text{B})$	0.2643	
C, <sup>3</sup> P	-37.3166	-37.6285
$E(C, ^1D) - E(C, ^3P)$	0.0610	0.065
$E(C, ^1S) - E(C, ^1D)$	0.0890	0.096
$E(C^+) - E(C, ^3P)$	0.3501	0.363
N, <sup>4</sup> S	-53.8352	-54.2765
$E(N, ^2D) - E(N, ^4S)$	0.1112	0.120
$E(N, ^2P) - E(N, ^2D)$	0.0722	0.080
$E(N^+, ^3P) - E(N, ^4S)$	0.4357	0.448
O, <sup>3</sup> P	-73.9376	-74.5505
$E(O, ^1D) - E(O, ^3P)$	0.0849	0.0935
$E(O, ^1S) - E(O, ^1D)$	0.1266	0.140
$E(O^+, ^4S) - E(O, ^3P)$	0.3110	0.300
F	-98.1305	-98.9545
$E(F) - E(F^-)$	-0.1585	-0.252

<sup>a</sup> Reference 6.

<sup>b</sup> Tubis, optimized minimum STO basis, Ref. 14.

with these functions. The calculated carbon ionization potential is within 0.013 a.u. of the STO value for the (3, 1, 2) representation. A minimum STO set is also insufficient to calculate a stable  $F^-$  ion; the functions used here give values for the electron affinity ranging between the STO value of  $-0.252$  a.u. and the HF value of  $0.050$  a.u. We therefore conclude that both the (2, 1, 2) and the (3, 1, 2) optimized representations for first-row atomic states permit calculations of quantities such as ionization potentials and multiplet splittings with errors comparable to those seen with the use of optimized minimum STO orbital sets.

Table II summarizes results obtained for (3, 1, 2) basis sets for the ground states, or lowest multiplets in the cases of carbon, nitrogen, and oxygen, as well as the lowest state of the singly charged ion for the species lithium through fluoride. Parameters have been optimized for each state of each species shown. Appendix B gives the orbital parameters for each of these species. Parameters for the hydrogen atom have been published elsewhere.

### III. CONSTRAINED LCAO-MO-SCF METHOD

Taylor<sup>15</sup> has presented a simple way of solving the Roothaan SCF equations for a closed-shell system subject to the constraint that core electrons occupy molecular orbitals which are purely linear combinations of a subset of the basis set used. His method is summarized here. This core subset is taken to be the set of  $1s$  core atomic orbitals for the elements heavier than hydrogen. The core orbitals used have small overlap integrals, less than  $10^{-7}$  for the carbon cores used in ethylene and  $10^{-9}$  for carbon-fluorine cores in  $CH_3F$ , and thus become, in this method, an orthogonal set of core molecular orbitals. They may be orthogonalized if the core orbital overlap integrals are not sufficiently small. The partitioning of a  $\nu$  term atomic orbital basis into  $m$  core orbitals and  $\nu-m$  noncore basis functions serves to partition the Fock and basis overlap matrices into corresponding blocks, or

$$F = \begin{pmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{pmatrix}; \quad S = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}.$$

The  $S_{11}$  overlap matrix for the core orbitals is practically diagonal for nonhydrogen  $1s$  core functions. The problem is then to find the MO coefficient matrix constrained to be of the form

$$C = \begin{pmatrix} C_{11} & C_{12} \\ O & C_{22} \end{pmatrix}.$$

Here the  $m \times m$  core orbital matrix block  $C_{11}$  is diagonal for the  $m$  core functions. The  $C_{22}$  block contains the

coefficients which are to be varied, and the  $m \times (\nu-m)$  block  $C_{12}$  is fixed by  $C_{22}$  and the orthogonality requirement.  $C_{22}$  is obtained as a solution of the  $(\nu-m)$  th order secular equation:

$$|F_{22}^1 - \epsilon S_{22}^1| = 0,$$

where

$$S_{22}^1 = S_{22} - S_{21} S_{11}^{-1} S_{12},$$

$$F_{22}^1 = F_{22} - S_{21} S_{11}^{-1} F_{12} - F_{21} S_{11}^{-1} S_{12} + S_{21} S_{11}^{-1} F_{11} S_{11}^{-1} S_{12}.$$

The  $C_{22}$  matrix obtained from this secular equation, and the orthogonality requirement  $C_{12} = -S_{11}^{-1} S_{12} C_{22}$  then determine the  $(\nu-m)$  valence-shell molecular orbitals for the  $2(\nu-m)$  electrons moving in the field provided by the  $2m$  core electrons placed in the simple core orbital functions.

The complete molecular orbital coefficient matrix obtained as a solution of this  $(\nu-m)$  order variation problem then does not diagonalize the original full Fock matrix. Although a reduced secular equation is solved, the  $F_{22}^1$  matrix involves all the two-electron exchange and Coulomb integrals computed over the whole basis set. If all integrals are calculated (as in the work reported here), no time is saved in the integral evaluation stage of the SCF procedure. However, the isolation of the core orbitals in the variation problem will be seen to permit the utilization of poorer core representations, since combinations of ligand orbitals cannot effectively "improve" the core function, relative to that possible for the free atoms. Energy differences (e.g., calculated dissociation energies) might then be more reliably independent of basis size, particularly of the number of  $s$ -type Gaussians used in a core orbital representation. The Taylor method might also prove useful in larger calculations using approximations for Coulomb and exchange integrals (e.g., the various CNDO methods) where the dimensions of the matrix diagonalization problem are more significant in computation time than are the demands of integral evaluation and assembly.

### IV. MOLECULAR CALCULATIONS

#### A. $CH_4$

Results are presented in Table III for both the complete coefficient variation (Roothaan)<sup>16</sup> method and the constrained variation (Taylor)<sup>15</sup> method using different orbital representations. The notation (2, 1, 2, 2) refers to a (2, 1, 2) carbon atomic orbital representation combined with a two-Gaussian representation of a hydrogen atom  $1s$  function. The four-exponent scale factors are then the adjustable orbital parameters; linear coefficients and relative values of the Gaussian exponent constants *within* the orbital groups are left

TABLE III. CH<sub>4</sub>.

Basis	Full variation		Constrained variation		Min. STO <sup>a</sup>	Large GTO <sup>b</sup>	Large STO <sup>c</sup>
	(2, 1, 2, 2)	(3, 1, 2, 2)	(2, 1, 2, 2)	(3, 1, 2, 2)			
R <sub>C-H</sub>	2.067	2.067	2.10	2.10	2.059	2.12	2.067
C <sub>1s</sub> <sup>d</sup>	1.03	1.01	0.997	0.997			
C <sub>2s</sub>	1.5	1.30	1.20	1.20			
C <sub>2p</sub>	1.34	1.34	1.34	1.34			
H <sub>1s</sub>	1.24	1.30	1.24	1.24			
E	-39.0872	-39.7956	-39.0076	-39.7802	-40.1283	-40.1983	-40.2045
T	38.9516	39.8292	39.0396	39.7130			
a <sub>1</sub>	-10.8205	-11.1326	-10.7323	-11.1298	-11.2049	-11.2216	-11.2148
a <sub>2</sub>	-0.9212	-0.9245	-0.9448	-0.9302	-0.9252	-0.9295	-0.9343
l	-0.5306	-0.5202	-0.5178	-0.5198	-0.5384	-0.5348	-0.5363
Calc HF dissoc. energy	0.5894	0.5386	0.5088	0.5232			0.54 <sup>e</sup>
Atomic charge H	-0.062	-0.027	-0.013	-0.016	-0.019		
C	+0.248	+0.106	+0.052	+0.066	-0.075		

<sup>a</sup> Reference 19.<sup>b</sup> Reference 2.<sup>c</sup> Reference 18.<sup>d</sup> Exponent scale factors for free atom orbital groups.<sup>e</sup> Calculated using -40.22 as nonrelativistic HF limit.<sup>2,18</sup>

unchanged at the free-atom values. Exponent scale factors were varied in addition to variation in the bond length. The  $R_{CH}$  values presented are estimated to be within 2% of optimum values for the basis sets employed, and all  $R_{CH}$  values given are at least within 4% of the experimental  $R_C$  value. It has been noted by Allen and Russel,<sup>17</sup> using functions of improved quality, that equilibrium bond lengths and molecular geometries are readily calculated from approximate HF functions if optimized orbital exponents are used.

The calculated dissociation energy in the work described here is not strongly dependent on the size of the hydrogen representation, as seen by comparing the results obtained with the (2, 1, 2, 3) and (2, 1, 2, 2) basis sets using the same scale factors, bond length, and the Taylor variation method. The calculated dissociation energy changes by 0.0018 a.u. on increasing the size of the hydrogen 1s orbital representation. Use of only *one* Gaussian for the hydrogen orbital is not worth the saving in computation time, given the size of the *p* orbital representation. The calculated dissociation energies for the (2, 1, 2, 2) and (3, 1, 2, 2) basis sets are both much closer together for the Taylor method than for the free variation (Roothaan) method, and the values slightly under the HF limit obtained with the Taylor method are more plausible than the values [e.g., 0.589 for (2, 1, 2, 2) basis] calculated using the standard Roothaan method. Core isolation in the Taylor method makes the calculated dissociation energy more meaningful when a very limited (poor) core representation is used. Molecular orbital energies for all but the lowest core orbital are seen to be close (within about 0.02 a.u.) to those obtained in more

complete treatments. The (2, 1, 1, 2) basis set is seen to provide rather poorer results. The one-Gaussian lobe 2*p* orbital is inadequate for use in quantitative studies involving the energy or orbital energies, as was suggested by consideration of calculated ionization energy of atomic carbon when using the (2, 1, 1) basis set.

The different basis sets and procedures give essentially the same gross atomic populations, using the Mulliken definition, with the constrained (Taylor) variation method and with the standard Roothaan method. The poorest core representation gives the most discrepant charge when used in the full variation method, just as the calculated HF dissociation energy was too large. Hydrogen is seen to be negative by the amount of about 0.015*e*, whereas the SCF calculation by Pitzer<sup>18</sup> shows a slight (0.019*e*) positive charge on hydrogen. The charge is small in magnitude, and the two values are in relatively good agreement. Arrighini *et al.*,<sup>19</sup> with the best published SCF energy for CH<sub>4</sub>, do not include a population analysis but conclude that the negative end of the CH bond moment lies towards the proton. Orbital energies are satisfactorily close to those reported for the functions of nearly HF quality, except for the 1*a*<sub>1</sub> value, which is expected to deviate for an incomplete core function.

### B. CH<sub>3</sub>F

The orbital exponent scale factors for 2*s*, 2*p*, and hydrogen 1*s* orbitals were varied using the (3, 1, 2) basis sets for the carbon and fluorine atoms, the two-Gaussian expansion for the hydrogen 1*s* orbital, and the experimental bond lengths and angles. Variations

TABLE IV. CH<sub>3</sub>F.

Basis	(2, 1, 2) atom <sup>a</sup>		(3, 1, 2) atom <sup>a</sup>		(3, 1, 2) atom <sup>b</sup>		Minimum <sup>c</sup> STO	Large <sup>d</sup> STO
	Full var.	Constrained var.	Full var.	Constrained var.	Full var.	Constrained var.		
<i>E</i>	-134.971	-134.888	-137.424	-137.407	-137.426	-137.407		-139.061
<i>T</i>	133.992	135.239	136.553	137.124	136.828	137.414		140.178
1 <i>a</i> <sub>1</sub>	-25.323	-25.211	-26.169	-26.142	-26.172	-26.145		-26.280
2 <i>a</i> <sub>1</sub>	-10.886	-10.773	-11.208	-11.174	-11.207	-11.171		-11.305
3 <i>a</i> <sub>1</sub>	-1.487	-1.576	-1.503	-1.524	-1.1508	-1.530		-1.600
4 <i>a</i> <sub>1</sub>	-0.899	-0.931	-0.907	-0.916	-0.907	-0.916		-0.940
1 <i>e</i>	-0.606	-0.600	-0.604	-0.603	-0.603	-0.602		-0.692
5 <i>a</i> <sub>1</sub>	-0.553	-0.549	-0.553	-0.552	-0.560	-0.558		-0.668
2 <i>e</i>	-0.430	-0.428	-0.431	-0.432	-0.433	-0.433		-0.524
C <sup>e</sup>	+0.38	+0.37	+0.37	+0.38	+0.38	+0.38	+0.17	
H	-0.06	-0.05	-0.05	-0.05	-0.06	-0.06	-0.00	
F	-0.21	-0.21	-0.22	-0.22	-0.21	-0.21	-0.16	
Δ <i>E</i> <sup>f</sup>	0.582	0.489	0.523	0.505	0.526	0.505	0.474	0.463
μ <sup>g</sup>	1.41	1.37	1.45	1.44	1.41	1.40	0.96	2.40

<sup>a</sup> *R*<sub>C-H</sub> = 2.095 a.u., *R*<sub>C-F</sub> = 2.628 a.u., HCF angle = 109.5°; C<sub>1s</sub>, C<sub>2s</sub>, C<sub>2p</sub>, H<sub>1s</sub> Gaussian exponent scale factors 1.00, 1.35, 1.40, 1.3; all fluorine orbital scale factors 1.00.

<sup>b</sup> *R*<sub>C-H</sub> = 2.10, *R*<sub>C-F</sub> = 2.62, HCF angle = 111°, C<sub>1s</sub> and F<sub>1s</sub> exponent scale factors = 1.003. Other orbital exponent scale factors are same as in (a).

<sup>c</sup> Reference 3.

<sup>d</sup> Reference 21.

<sup>e</sup> Atomic populations.

<sup>f</sup> Calculated HF dissociation energy.

<sup>g</sup> Dipole moment (debyes).

in the two unique bond lengths and the unique bond angle (assuming C<sub>3v</sub> symmetry) indicate that the calculated bond lengths are 1% to 2% larger than the experimental values,<sup>20</sup> and that the calculated FCH angle is likewise about 2% (or 2°) larger than the experimental value. Calculations were made by both the standard Roothaan method and by the Taylor method in which the 1s core orbitals for the heavy atoms were isolated from the variation problem. The carbon-fluorine core overlap integral value was typically 10<sup>-10</sup> for the three-Gaussian core representations, so the core functions are orthogonal through spatial separation as required for simple application of the Taylor method. Core representations with only two-Gaussian terms give smaller overlap integrals. Both Roothaan and Taylor methods gave the same bonding orbital exponent scale factors to within the precision of the optimization process. Small adjustments in the core exponents changed the kinetic to potential energy ratio without significant (less than 0.001 a.u.) changes in total energy or bonding orbital energies in studies with CH<sub>4</sub>. This was also found in calculations for CHF<sub>3</sub>.

Table IV shows the effect of changing the core basis size for both the Roothaan and Taylor methods, using the experimental molecular structure parameters and the same set of atomic orbital exponent scale factors for both basis sets. All calculated dissociation energies are computed using the best atom energies for comparable basis sets. The computed dipole moments are

relatively independent of basis set or method of calculation. The calculated dissociation energies for the Taylor method changes by only 0.016 a.u., when changing from the (2, 1, 2) to (3, 1, 2) heavy atom representations, although the improvement in the core function changes the *total* system energy by 2.5 a.u., as seen in Columns 2 and 4. The Roothaan full variation method shows an appreciably larger change, 0.06 a.u. (Columns 1 and 3), in the calculated dissociation energy. This reinforces the view that meaningful energy differences can be computed using incomplete core representations *if* the core orbital functions are isolated in the molecule. It is also seen that the upper occupied valence-shell orbital energies and gross atomic populations are insensitive both to the core representations used and to the variation method employed. The best all-electron SCF-MO calculation reported to date for CH<sub>3</sub>F is that of Arrighini *et al.*<sup>21</sup>; they used a basis of 47 STO's and a geometry close to the experimental one. Some of their results are also included in Table IV. Difficulties in *ab initio* calculation of reliable dipole moments are well known, and little should be said except to note that all values listed in Table IV are "reasonably" close to the experimental value of 1.847 D.<sup>22</sup> Correct Hartree-Fock atomic energies were used in calculating the HF dissociation energy from the molecular energy obtained by Arrighini. Their estimate of the correlation energy of CH<sub>3</sub>F seems to provide the best current by available route to a value for the nonrelativistic

HF energy of  $\text{CH}_3\text{F}$ . The value they obtained,  $-139.149$  a.u., is used with atomic nonrelativistic HF energies to obtain the "experimental" HF dissociation energy of  $0.551$  a.u. for comparison with the calculated values in Table IV. Only the value computed using the two Gaussian core functions with the full variation (Roothaan) method gives a poor result. The computed dissociation energy and dipole moment are as good or better than the values obtained by Hehre *et al.*<sup>3</sup> using a minimum STO basis expanded into Gaussian functions. The fluorine atom charge,  $-0.21 e$ , agrees well with the value of  $-0.19$  obtained by Hush and Segal<sup>23</sup> using the CNDO/2 method and with the value of  $-0.16$  obtained by Hehre, Stewart, and Pople using an optimized minimum STO basis. The atomic charge values, defined for each atom as the difference between the Mulliken gross atomic population and the nuclear charge, obtained using unscaled, free atom orbitals, differ significantly from the values obtained using scaled or optimized atomic orbital representations in these minimum basis calculations. However, these values seemed to be insensitive to moderate changes in the orbital exponent scale factors; parameter optimization was not highly critical in determining the gross atomic populations.

### C. $\text{CH}_2\text{F}_2$ and $\text{CHF}_3$

Calculations were performed for the molecules  $\text{CH}_2\text{F}_2$  and  $\text{CHF}_3$  using the (3, 1, 2) basis sets for C and F atoms, and the two-Gaussian 1s function for hydrogen. The valence atomic orbitals of the functions were scaled using the same scale factors obtained in the more detailed  $\text{CH}_3\text{F}$  work. Experimental values were taken for the unique molecular coordinates.<sup>20</sup> and  $C_{2v}$  and  $C_{3v}$  symmetries were assumed for the two molecules. Both the complete Roothaan variation was carried out as well as the restricted (Taylor) variation in which the 1s atomic orbitals on carbon and fluorine were used unchanged as the lowest energy molecular orbitals, with the upper occupied molecular orbitals being determined by solution of the reduced secular equation as described previously. The carbon-fluorine and fluorine-fluorine core orbital overlap integrals were  $10^{-10}$ , and  $10^{-40}$ , respectively, although the hydrogen 1s-fluorine core overlap integrals were about  $10^{-3}$ . This suggests that variable precision or variable assumption routines should be employed in *ab initio* calculations such as these to extend the molecular size for practical calculations with polyatomic systems. The *magnitude* of the overlap integral could be used to provide a criterion for the neglect of certain exchange integrals or for simplifications to be used in evaluating Coulomb integrals for widely spaced centers. Such a GNDO (gradual neglect of differential overlap) scheme might lead to an amalgamation, for large systems, of the more useful aspects of the INDO

TABLE V.  $\text{CH}_2\text{F}_2$  and  $\text{CHF}_3$ .<sup>a</sup>

	$\text{CH}_2\text{F}_2^b$		$\text{CHF}_3^c$	
	Full var.	Constrained var.	Full var.	Constrained var.
<i>E</i>	-235.077	-235.054	-332.742	-332.715
<i>T</i>	233.462	234.145	330.276	331.093
Ca	+0.51	+0.51	+0.68	+0.68
H	-0.04	-0.04	-0.04	-0.04
F	-0.21	-0.21	+0.21	+0.22
$\Delta E^e$	0.507	0.485	0.540	0.513
f	-1.581	-1.601	-1.663	-1.683
	-1.517	-1.538	-1.561*	-1.582
	-0.905	-0.914	-0.898	-0.906
	-0.685	-0.684	-0.743	-0.742
	-0.656	-0.655	-0.695*	-0.695
	-0.618	-0.617	-0.556*	-0.555
	-0.518	-0.517	-0.520	-0.520
	-0.486	-0.485	-0.513*	-0.512
	-0.481	-0.480	-0.463	-0.462
	-0.429			

<sup>a</sup> (3, 1, 2) representations used for carbon and fluorine, two-term hydrogen orbital. All fluorine atom Gaussian exponent scale factors at 1.0; carbon 1s, 2s, and 2p orbital exponent scale factors at 1.0, 1.34, 1.40; and hydrogen 1s scale factor at 1.30.

<sup>b</sup>  $R_{\text{CH}} = 2.065$  a.u.,  $R_{\text{C-F}} = 2.57$  a.u., HCH angle =  $109.5^\circ$ , FCF angle =  $108.5^\circ$ .

<sup>c</sup>  $R_{\text{CH}} = 2.075$  a.u.,  $R_{\text{C-F}} = 2.517$  a.u., HCF angle =  $110.0^\circ$ .

<sup>d</sup> Atomic populations.

<sup>e</sup> Calculated HF association energy.

<sup>f</sup> Orbital energies, starting with first levels above core functions.

\* Doubly degenerate.

and CNDO schemes and the complete calculations. Table V gives orbital and total energies, total atomic populations, and computed binding energies for the two molecules, using exponent scale factors suggested by the  $\text{CH}_3\text{F}$  calculations. It is seen that the fluorine and hydrogen atomic populations are virtually the same for  $\text{CH}_3\text{F}$ ,  $\text{CH}_2\text{F}_2$ , and  $\text{CHF}_3$ . Hydrogen becomes slightly less negative in the series of molecules. Carbon becomes significantly more positive with fluorine substitution, supplying most of the charge taken by the fluorines. The agreement of the calculated  $\text{CH}_3\text{F}$  atomic populations with the calculations of Hehre, Stewart, and Pople adds some credence to the populations computed here for  $\text{CH}_2\text{F}_2$  and  $\text{CHF}_3$ . Arrighini *et al.* unfortunately did not report a population analysis. The increase in positive charge on carbon with fluorination corresponds to an increase in ionic character of bonding and in this context is consistent with the shortening of the CF bond observed experimentally as one goes from  $\text{CH}_3\text{F}$  to  $\text{CF}_4$ . The constancy of the charge on fluorine in the series suggests that carbon in  $\text{CF}_4$  may well have a charge of  $+0.75$ – $0.85$ . The large CF bond strength in  $\text{CF}_4$  is also qualitatively more interpretable in terms of the large positive charge



TABLE VI. C<sub>2</sub>H<sub>4</sub>.

	This work full var.	(3, 1, 2, 2) basis <sup>a</sup> constrained <sup>b</sup> var.	Minimum STO <sup>c</sup>	Large basis <sup>d</sup>
$E(^1A_g)$	-77.2272	-77.2001	-77.8355	-78.0062
$T$	-77.0366	-77.8911		
$1a_g$	-11.1371	-11.1034	-11.2794	-11.2395
$1b_{3u}$	-11.1369	-11.1034	-11.2787	-11.2379
$2a_g$	-1.0020	-1.0131	-1.0130	-1.0397
$2b_{3u}$	-0.7607	-0.7667	-0.7815	-0.7959
$1b_{2u}$	-0.6096	-0.6080	-0.6431	-0.6549
$3a_g$	-0.5254	-0.5231	-0.5605	-0.5812
$1b_{1g}$	-0.4722	-0.4710	-0.5054	-0.5145
$1b_{1u}$	-0.3294	-0.3270	-0.3691	-0.3736
$1b_{2g}$	+0.2865	+0.2895	+0.2452	+0.1436
$E-E(1A_g)$ for:				
$3B(3u)(T)^e$	0.1273	0.1279	0.1268	0.1540
$1B_{2u}(V)^e$	0.4468	0.4474	0.4447	0.3419
$3B_{3g}(\sigma \rightarrow \pi^*)$	0.3838	0.3858	0.3688	0.3408
$1B_{3g}(\sigma \rightarrow \pi^*)$	0.4067	0.4086	0.3928	0.3599
Calculated HF	0.6536	0.6265	0.5785	>0.6290
Binding energy				

<sup>a</sup>  $R_{C-C}=2.022$  a.u.,  $R_{CH}=2.551$  a.u., HCH angle =  $120^\circ$ . Gaussian exponent scale factors for carbon 1s, 2s, 2p, and hydrogen 1s orbital groups are 1.002, 1.30, 1.20, and 1.36 starting with free atom exponents.

<sup>b</sup> Taylor method with carbon 1s core orbitals as lowest two MO.

<sup>c</sup> Reference 27, using same geometry as this work, minimum Slater basis

using Slater rule exponents.

<sup>d</sup> Reference 29; SCF calculation using a large (*sp*) Gaussian basis.

<sup>e</sup> Energies are computed relative to the ground state using the ground state geometry and virtual orbitals.

on carbon and large ionic character in the carbon-fluorine bond. Dipole moments of 1.61 and 1.32 D were calculated for CH<sub>2</sub>F<sub>2</sub> and CHF<sub>3</sub>, in satisfactory agreement with the reported experimental values of 1.96<sup>24</sup> and 1.646 D.<sup>25</sup>

#### D. C<sub>2</sub>H<sub>4</sub>

Calculations were performed for ethylene using the (3, 1, 2, 2) basis set, i.e., the (3, 1, 2) atomic carbon representation with the two-Gaussian hydrogen orbital representation. The near equilibrium geometry of  $R_{CC}=2.022$  a.u.,  $R_{CH}=2.551$  au, HCH angle =  $120^\circ$  was used to facilitate comparisons with previous calculations using the same geometry. After varying the free carbon atom 2s exponent scale factor, optimum values were found in succession for the carbon 2p and the hydrogen 1s orbital scale factors. A final small adjustment of the carbon 1s core function scale factor improved the kinetic/potential energy ratio for the Roothaan calculation without significant changes in the total or noncore orbital energy values. Final results for the best exponent scale factor set are shown in Table VI. The calculation was also carried out using the Taylor constrained variation method holding the two-carbon 1s core orbitals as the lowest two orthogonal molecular orbitals in the ethylene molecule. Coulomb and exchange integrals were computed between the two highest occupied and the two lowest virtual

molecular orbitals, and vertical excitation energies were calculated for the transitions from the ground state to singlet and triplet states resulting from both  $\sigma$  and  $\pi$  orbital excitations. The excitation energies for single-electron excitations from either the  $1b_{1u}$  or the  $1b_{1g}$  molecular orbital to the  $\pi^*$  ( $1b_{2g}$ ) molecular orbital are also given in Table VI.

References and summaries of a variety of experimental and theoretical work on the states of ethylene are found in the recent review by Merer and Mulliken,<sup>26</sup> and in recent calculations presented by Kaldor and Shavitt,<sup>27</sup> Switkes, Stevens, and Lipscomb,<sup>28</sup> and by Schulman, Moskowitz, and Hollister.<sup>29</sup> Some of the results of Schulman *et al.* are given in Table VI as providing the best single-determinant ground state calculation to date. Their publication provides one of the few published sources for excitation energies obtained from the ground state wavefunction. Some results of the calculation of Kaldor and Shavitt using a minimum Slater basis set with selected exponent values are also included for comparison in Table VI. Their work includes the calculations of Palke and Lipscomb<sup>30</sup> as a special case in the more extensive set of calculations. Switkes, Stevens, and Lipscomb fully optimized the exponents of a minimum Slater basis set and obtained an energy of -77.8558 a.u., calculated HF dissociation energy 0.599 a.u., with net charges on carbon and hydrogen of -0.16 and

+0.08. The net charges on carbon and hydrogen in our work were found to be  $-0.04$  and  $+0.02$ , in reasonable agreement with Switkes *et al.* They did not report any values for orbital or excitation energies for comparison with the values obtained with selected Slater exponents. Optimization of orbital exponents improved the total energy by only  $0.02$  a.u. over the value obtained by Kaldor and Shavitt, Column 3 of Table VI, so we presume that orbital energies and transition energies for fully optimized exponents using a minimum Slater basis would be similar to the values reported by Kaldor and Shavitt. It is seen that the limited lobe Gaussian basis used in our work provides excitation energies and calculated HF dissociation energy which are close to the values for the minimum STO basis; the calculated HF dissociation energy for the full Roothaan variation shown in Column 1 of Table VI is too large as explained in connection with the methane and fluoromethane calculations. The Taylor constrained variation method, holding the carbon core orbitals and pure molecular orbitals, without core improvement through use of other basis orbital combinations, probably provides a better calculation when the limited core representation is used. Neither this work nor the work with the limited STO basis produces the same ordering of excitation energies for the transition to  $^1B_{3g}$  and  $^1B_{3u}$  states as is obtained by Schulman *et al.* using a greatly expanded basis set.

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### APPENDIX A: INTEGRAL PRECISION

Use of Gaussian lobe functions as  $p$  orbital representations introduces two types of errors: The first is the failure of the lobe functions with limited numbers of terms to reproduce the spherical harmonic functions. Neon, for example, will have a spherically symmetrical charge distribution when using spherical harmonics and the usual STO's, whereas the charge distribution will be slightly "lumpy" when using the limited lobe functions.<sup>31</sup> The significance of these effects in molecular calculations, with the simple lobe representations used here, is to be evaluated in terms of the quality of results for molecular properties. For spherical harmonic atomic  $p$  functions, the following identity is valid:

$$(p_x p_y | p_x p_y) = [(p_x p_x | p_x p_x) - (p_x p_x | p_y p_y)]/2.$$

Using the two-Gaussian lobe carbon  $p$  function, for example, we find the values of the left and right sides of the above expression differ by only  $0.000186$  a.u. Whitten and Allen<sup>32</sup> also comment on the precision requirements for integral calculations using lobe functions; care must be taken in intermediate stages

since the lobe function integrals are really obtained as differences of integrals using the spherical-type Gaussians with slightly different centers.

While most of the atomic and early  $\text{CH}_4$  calculations were performed on an IBM System 360/65, the remaining calculations were performed on an IBM S360/44 which provided variable precision arithmetic. For most of the  $\text{CH}_4$  calculations, full double precision (56 binary digit representation of mantissa, of  $\log_{16}$ , approximately 10 decimal digits) was used. The energy calculated for methane using single precision (24 binary digit representation of mantissa of  $\log_{16}$ , approximately 8 decimal digits) differed from the energy calculated using full double precision by less than  $0.0001$  a.u. The calculated energy for  $\text{CH}_3\text{F}$  using 36 bit arithmetic was also found to be within  $0.0001$  a.u. of the value obtained using full double precision.

The carbon and fluorine atomic energy values were found to be relatively insensitive to the spacing between the centers of the  $s$ -type Gaussians which comprise a  $p$  lobe pair. This value was fixed at  $0.20$  a.u. for the two-Gaussian lobe pairs in the  $(2, 1, 2)$  and  $(3, 1, 2)$  basis sets. Variation in this parameter for each of the two-lobe pairs used was thought not worth while, and reduction in the lobe spacing below the value given leads to increasing imprecision in integral calculations.

Electron-nuclear attraction and electron-electron repulsion integrals using  $s$ -type Gaussian functions require evaluation of the factor<sup>33,34</sup>:

$$F_0(z^2) = z^{-1} \int_0^z e^{-v^2} dv = \pi^{1/2} \text{erf}(z)/(2z).$$

Some care should be used in using standard computer library routines for the calculation of  $\text{erf}(z)$  to avoid loss of accuracy in  $\text{erf}(z)/z$  for certain values of  $z$ . We have slightly modified the procedure of Larcher,<sup>35</sup> used previously,<sup>6</sup> by taking

$$\pi^{1/2} \text{erf}(z)/(2z) = \pi^{1/2}/(2z); \quad z > 4.3,$$

$$\text{IBM S360 Fortran IV library erf}(z) \quad 4.3 > z > 0.7, \\ \text{routine};$$

$$\pi^{1/2} \text{erf}(z)/(2z) = \sum_{n=0}^{\infty} (-1)^n z^{2n} / [n!(2n+1)]; \\ 0.7 > z > 10^{-4},$$

(sum is continued until term value is  $10^{-8}$ ),

$$\pi^{1/2} \text{erf}(z)/(2z) = 1.0; \quad 10^{-4} > z.$$

This insures values of  $F_0(z^2)$  accurate to seven digits in single precision and to nine or more digits when using double precision arithmetic. Tighter precision limits seemed unnecessary on comparing results for individual integrals and for complete calculations. Similar methods have been used independently by Schaad.<sup>36</sup>

## APPENDIX B: ORBITAL PARAMETERS FOR (3,1,2) ATOMIC REPRESENTATIONS

The following table provides the exponents and linear coefficients for each of the Gaussian functions in the normalized 1s, 2s, and (for more than four electrons) the unique pair of Gaussians in the 2p orbital groups for first-row atoms and ions for the (3, 1, 2) representations. The spacing between the centers of the lobe pairs is 0.2 a.u. for all of the 2p orbitals. Hydrogen atom parameters have been published elsewhere.<sup>37</sup> All energies are in atomic units.

Li	$E = -7.3720$			Be	$E = -14.4567$			Be <sup>+</sup>	$E = -14.1680$		
0.10191231E	01	0.47340614E	00	0.19510822E	01	0.75741661E	00	0.19487934E	01	0.75675017E	00
0.50308475E	01	0.97561610E	00	0.91328354E	01	0.15472097E	01	0.91221228E	01	0.15458488E	01
0.33950943E	02	0.76447266E	00	0.61372192E	02	0.12044792E	01	0.61300201E	02	0.12034197E	01
0.43925200E	-01	0.68382502E	-01	0.98863482E	-01	0.12565708E	00	0.13080984E	00	0.15502095E	00
B	$E = -24.3189$			B <sup>+</sup>	$E = -24.0546$			C, <sup>3</sup> P	$E = -37.3285$		
0.32148190E	01	0.10995684E	01	0.32417021E	01	0.11124306E	01	0.47338161E	01	0.14462013E	01
0.14651364E	02	0.21957941E	01	0.14826364E	02	0.22032089E	01	0.20819046E	02	0.28917131E	01
0.97183777E	02	0.16989937E	01	0.99217316E	02	0.16866198E	01	0.13527962E	03	0.22813101E	01
0.18128240E	00	0.19800532E	00	0.21514511E	00	0.22514313E	00	0.28394508E	00	0.27722722E	00
0.93314898E	00	0.11633511E	01					0.15731277E	01	0.13591061E	01
0.16966462E	00	0.18505716E	01					0.28117353E	00	0.20913801E	01
C, <sup>1</sup> D	$E = -37.2707$			C	<sup>1</sup> S $E = -37.1857$			C <sup>+</sup>	$E = -36.9827$		
0.47512169E	01	0.14659643E	01	0.47772608E	01	0.14826460E	01	0.47626553E	01	0.14663734E	01
0.21364380E	02	0.29287443E	01	0.21699951E	02	0.29435720E	01	0.21296417E	02	0.29249220E	01
0.14129504E	03	0.22525816E	01	0.14460762E	03	0.22354345E	01	0.14117766E	03	0.22534275E	01
0.28614342E	00	0.27883542E	00	0.28972566E	00	0.28144938E	00	0.32357055E	00	0.30576432E	00
0.15225906E	01	0.13671436E	01	0.14389420E	01	0.13841200E	01	0.19421329E	01	0.13907328E	01
0.26480788E	00	0.20587149E	01	0.23973936E	00	0.20028572E	01	0.37684488E	00	0.22474270E	01
N	<sup>4</sup> S $E = -53.8352$			N	<sup>2</sup> D $E = -53.7240$			N	<sup>2</sup> P $E = -53.6519$		
0.67462177E	01	0.19521132E	01	0.67769203E	01	0.19643641E	01	0.67759752E	01	0.19625692E	01
0.30894424E	02	0.37553959E	01	0.31059158E	02	0.37556610E	01	0.31015366E	02	0.37556887E	01
0.20575064E	03	0.27810631E	01	0.20740379E	03	0.27745209E	01	0.20740971E	03	0.27771954E	01
0.40750223E	00	0.36350262E	00	0.41089636E	00	0.36577106E	00	0.41305971E	00	0.36721438E	00
0.23628540E	01	0.15318670E	01	0.23007555E	01	0.15415354E	01	0.22608156E	01	0.15484514E	01
0.41697305E	00	0.23026991E	01	0.39719814E	00	0.22721386E	01	0.38449639E	00	0.22518368E	01

## APPENDIX B—(Continued)

N <sup>+</sup> <sup>3</sup> P <i>E</i> = −53.3995				O <sup>3</sup> P <i>E</i> = −73.9376				O <sup>1</sup> D <i>E</i> = −73.8528			
0.67891865 <i>E</i>	01	0.19659805 <i>E</i>	01	0.88502159 <i>E</i>	01	0.23683062 <i>E</i>	01	0.88954258 <i>E</i>	01	0.23876209 <i>E</i>	01
0.31016312 <i>E</i>	02	0.37523670 <i>E</i>	01	0.40092209 <i>E</i>	02	0.46288576 <i>E</i>	01	0.40384674 <i>E</i>	02	0.46250858 <i>E</i>	01
0.20731412 <i>E</i>	03	0.27732267 <i>E</i>	01	0.26754932 <i>E</i>	03	0.34368925 <i>E</i>	01	0.26861670 <i>E</i>	03	0.34232216 <i>E</i>	01
0.45344245 <i>E</i>	00	0.39382356 <i>E</i>	00	0.55651075 <i>E</i>	00	0.45921415 <i>E</i>	00	0.55879700 <i>E</i>	00	0.46062833 <i>E</i>	00
0.27923031 <i>E</i>	01	0.15560408 <i>E</i>	01	0.32189264 <i>E</i>	01	0.17025785 <i>E</i>	01	0.31840448 <i>E</i>	01	0.17073059 <i>E</i>	01
0.52841538 <i>E</i>	00	0.24420366 <i>E</i>	01	0.54960883 <i>E</i>	00	0.24604330 <i>E</i>	01	0.53850204 <i>E</i>	00	0.24465828 <i>E</i>	01
O <sup>1</sup> S <i>E</i> = −73.7261				O <sup>+</sup> <sup>4</sup> S <i>E</i> = −73.6267				F <i>E</i> = −98.1305			
0.88984413 <i>E</i>	01	0.23879843 <i>E</i>	01	0.89039879 <i>E</i>	01	0.23879061 <i>E</i>	01	0.11191292 <i>E</i>	02	0.27867489 <i>E</i>	01
0.40383835 <i>E</i>	02	0.46255713 <i>E</i>	01	0.40330887 <i>E</i>	02	0.46241713 <i>E</i>	01	0.49943817 <i>E</i>	02	0.55420732 <i>E</i>	01
0.26873071 <i>E</i>	03	0.34235687 <i>E</i>	01	0.26932520 <i>E</i>	03	0.34225283 <i>E</i>	01	0.33131250 <i>E</i>	03	0.41587858 <i>E</i>	01
0.56197101 <i>E</i>	00	0.46258920 <i>E</i>	00	0.60357368 <i>E</i>	00	0.48804271 <i>E</i>	00	0.72610593 <i>E</i>	00	0.56060904 <i>E</i>	00
0.31325722 <i>E</i>	01	0.17147255 <i>E</i>	01	0.37949409 <i>E</i>	01	0.17109842 <i>E</i>	01	0.42470932 <i>E</i>	01	0.18582163 <i>E</i>	01
0.52221906 <i>E</i>	00	0.24257870 <i>E</i>	01	0.70481533 <i>E</i>	00	0.26215401 <i>E</i>	01	0.71248019 <i>E</i>	00	0.26216221 <i>E</i>	01
F <sup>−</sup> <i>E</i> = −97.9720											
0.11466538 <i>E</i>	02	0.29032316 <i>E</i>	01								
0.52071838 <i>E</i>	02	0.55568810 <i>E</i>	01								
0.34696582 <i>E</i>	03	0.40750551 <i>E</i>	01								
0.68912792 <i>E</i>	00	0.53905737 <i>E</i>	00								
0.56574249 <i>E</i>	00	0.24693813 <i>E</i>	01								
0.36510134 <i>E</i>	01	0.18542471 <i>E</i>	01								

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## Dimerization of Methylene by Their Least Motion, Coplanar Approach: A Multiconfiguration Self-Consistent Field Study

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The one-dimensional path of reaction in the least motion, coplanar approach of two methylenes to form ethylene has been calculated using the nonempirical multiconfiguration self-consistent field (SCF) method in a large Gaussian basis. Orthogonality between open- and closed-shell molecular orbitals of the same symmetry is constrained by a "partitioned basis set" technique which is found to give rapid and uniform convergence to the proper SCF solution. The results obtained for the reaction path suggest that the ground state of bent ( $\sim 120^\circ$ ) methylene is the triplet. Therefore, in this study, it is the triplet states (and not closed-shell singlet states) of two appropriately oriented bent methylenes that correlate with the normal (ground) state of ethylene. For two closed-shell singlet-state methylenes the reaction path is found to be purely repulsive.

The orbital correlation diagram for the least motion, coplanar (LMC) approach of two methylenes ( $\text{CH}_2$ ), in their lowest energy singlet electronic states, to form normal ethylene exhibits a level crossing, i.e., a doubly occupied level (orbital) on one side of the diagram connects with an empty orbital on the other side, and *vice versa*. By the orbital conservation rule of Woodward and Hoffmann<sup>1,2</sup> a level crossing in the orbital correlation diagram, for a given reaction path in a concerted reaction, is sufficient evidence that the particular approach geometry under consideration is forbidden; there should then exist an alternate route to the reaction products along which path the reaction actually

proceeds. Hoffmann *et al.*<sup>3</sup> have actually carried out orbital correlation and numerical analyses of the titled reaction and arrive at the above-stated conclusions.

The justification, or basis, for the orbital conservation rule in nonempirical electronic structure theory, as specifically applied to the dimerization reaction, is as follows. A level crossing in the *orbital* correlation diagram should lead to an avoided crossing in the *state* level diagram at intermediate carbon-carbon bond distances, as the direct result of an attempted crossing of two electronic states of the same symmetry species. The avoided crossing, in turn, is expected to give rise to a hump in the lower energy branch of the potential