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TRANSFERABLE LOCALIZED ORBITALS FOR ACYCLIC HYDROCARBONS.

Iowa State University, Ph.D., 1973
Physics, molecular

Transferable localized orbitals for acyclic hydrocarbons

by

Walter Bernard England

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
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Department: Chemistry
Major: Physical Chemistry

Approved:

In Charge of Major Work

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For the Graduate College

Iowa State University
Ames, Iowa

1973

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INTRODUCTION

Some of man's most powerful learning tools are his ability to organize, compare and draw upon experience. With them, he understands by understanding relatively, by first understanding what is easily understood, and is able to use today what he learned, with whatever means, yesterday.

This thesis combines two powerful techniques: rigorous molecular quantum mechanics and classical valence theory. The former provides a firm theoretical basis for investigation and counteracts one's own prejudices and inconsistencies, while the latter furnishes the concepts, suggestiveness and subjective intuition so successfully employed even in the years before quantum mechanics (1-4), and certainly before very complete theoretical investigations were available.

The combination is performed with the energy localized representation (5-8) of closed-shell INDO (9-13) molecular orbital theory (14). It - like all others - is a subjective representation, as has been known for many years (15), but is nonetheless rigorous and has proved exceedingly useful for studying phenomena which don't involve electronic excitations (6,7,16-25). The applications at present will be to the electron distributions in acyclic hydrocarbons, with emphasis on the transferability and <u>inherent</u> delocalization of the localized orbitals which describe the electronic motion. By using INDO, it overcomes the economic and technical problems (computer storage and time, multicenter integrals, etc.) encountered in <u>ab initio</u> methods, which would restrict the study to just a few molecules (7,16,17,24,25), at the expense of having a more phenomenological description. However, experience has shown this to create a problem only insofar as absolute energies are concerned, which are not at issue here. In fact, recent ab initio results (25-28) indicate that trends in INDO and minimal basis theory differ from those of near Hartree-Fock results in similar ways (29).

Unlike some studies which concern themselves with the examination of properties (16,17,20,24), the present philosophy is that wave functions are more fundamental, and therefore more useful and interesting than any of the expectation or pseudo-expectation (22) values they provide. Also unlike some other studies, it does not consider localized orbitals perfectly confined to one or two centers (30-33), and examines transferability in much greater detail (6,7,16,17,24). The former obtains because of the rigorous approach (5) used, and differs from others (30-33) which are closer to classical valence theory, while the latter makes transferability as quantitative as is reasonably possible, illustrating its use and theoretical meaningfulness, confirming what has long been appreciated (or suspected) by chemists (34-38).

Dirac's bra and ket notation (39) will be used throughout. Since closed-shell molecular orbital theory is well documented (14) and appears in many texts (34,40-46) it will not be discussed in very great detail in this work. The INDO approximations (9-13) will be presented descriptively, with attention to the basic reasoning, which leads to some interesting features.

Very little discussion will be given the model geometries employed (47), which are closely related to the hybrid atomic orbitals defined on each atom. The former were obtained with the 'Model-Builder' program (47) automatically, thereby rendering an unpleasant technical problem trivial. The latter serve as a consistent set of atomic basis functions which form perfectly localized first approximations to the localized orbitals, and hence display their behavior very effectively.

Energy localization is also well documented (5,6,8) and beginning to find its way into quantum chemistry books (45,48). The important features and needed equations will be given, as will some new contributions of the present work to the computation of the localized orbitals.

The major effort will be the analysis of the localized orbitals for the thirty-three molecules studied. The orbitals will be partitioned into fragments that are independent of the molecules, and each group will be classified and discussed separately, revealing their behavior and the ways in which each transfers. Following this, discussions will be given of some bond properties and important chemical topics, including the direct observation and physical significance of transferrable localized bonding. Methods for obtaining the unoccupied and canonical symmetry molecular orbitals will also be given.

Finally, the programs which made this project possible are the works of many hands. The energy localization methods were built from the originals of Professor Clyde Edmiston (Wyoming University). The INDO self-consistent-field and integrals packages originated in Professor John Pople's research group at Carnegie-Mellon University, and the 'Model-Builder' was written at the same place by Professor Mark Gordon of North Dakota State University. Together, these are around 20,000 cards, or about ten IBM boxes!

MOLECULAR ORBITAL THEORY

Introduction

Molecular orbital (MO) theory was introduced more than forty years ago by Hund (49-51) and Mulliken (52,53), and now forms a major portion of every modern theoretical chemistry text and plays an active role in chemical, physical and biological research of all kinds (54). There are perhaps two developments which led to this state of affairs more than any others:

1. The introduction of the MO method to organic chemistry by Hückel (55).
2. The appearance of the Roothaan Equations (14) and the rise of computers.

The former stimulated virtually all of recent pi electron organic chemistry, while the latter's rigorous reduction of the MO problem to iterative solution of matrix equations fits perfectly with machine calculation. Along with the less appreciated free-electron MO theory (38,56-58) it is thus fair to say that these contributed greatly, and will continue to do so, each in their way, to the mathematical tractability of MO theory and its ability to reproduce, predict and interpret experimental results.

CNDO and INDO

These are all-valence-electron linear-combination-of-atomic-orbitals (LCAO)-MO self-consistent-field (SCF) theories developed by Pople and co-workers (9-13) in which the approaches and approximations used so fruitfully in pi electron theory (41,59) are suitably introduced into the Roothaan

Equations. The most novel and far-reaching feature is their use of unitary invariance, i.e. the Roothaan Equations are invariant both to unitary transformations among the occupied MO's (14) and the basis functions (9). The former obtains because any single determinant wave function is so invariant (15), and has lately been widely appreciated because of the interest in energy localization. The latter was the one used by Pople et al. to guide the development of their approximate LCAO-MO-SCF theories.

The discussion was first restricted to atomic bases, eliminating from consideration all unitary transformations that mix atomic orbitals (AO's) on one center with those on another. Subsequent approximations were then required to be invariant to the remaining possibilities: rotations of the local coordinate axes; and hybridization changes. To this was added the 'neglect of differential overlap'

$$f(\underline{x}) \cdot g(\underline{x})dV = 0, \text{ if } f \neq g \qquad (1)$$

where f and g are AO's, thus leading to the formulation of CNDO:

1. The Slater AO basis (9,10,59) is assumed orthogonal (thus neither admits a truly extensional basis, only a means of approximating expectation values).

2. All integrals are reduced to one- or two-centers (hence the total energy reduces to a sum of one- and two-atom terms (9,60).

3. One-center, one-electron matrix elements are obtained empirically by equating the average of the AO ionization potentials and electron affinities to the theoretical energy of the valence electron in the corresponding atomic state.

4. After some experience (11) with the earliest versions (9,10), the two-center, one-electron Coulomb integrals (the analogous integrals which involve two different AO's on the same center are zero because of Eq. 1) were assigned values which neglect 'penetration' effects (those leading to attraction even when the bond order between the two atoms is zero, i.e. electrons in an orbital on one atom 'penetrate' the shell of another).

5. Two-center, one-electron resonance integrals were parameterized to give the best overall fit with minimal basis *ab initio* LCAO-SCF-MO diatomic molecule calculations. (Strictly, this violates the neglect of differential overlap, but these integrals are the one-electron interference density contributions (19) and hence must be included in any theory hoping to describe chemical bonds (61)).

6. All two-electron integrals are reduced to one- or two-center Coulomb integrals over the valence s functions.

Notice that - because of 3 and 5 - valence AO's are distinguished only in the one-electron integrals. INDO (12) also distinguishes them in the two-electron integrals by retaining all one-center, two-electron Coulomb and exchange integrals (which affects the one-electron matrix elements via 3), and in keeping with the guidelines, they are given values quoted by Slater (62) as representing the best fit with atomic experimental data. Again this violates the neglect of differential overlap, but the absence of spherical averaging is crucial for energy localization (63).

The differences mentioned in the last paragraph are the only ones separating CNDO from INDO. There are, however, some interesting features that follow from 1 which have not been mentioned yet: the very simple and unambiguous definitions of the atomic quasiclassical (19,61) densities

$$Q(\underline{x},A) = \sum_{L}\sum_{i}^{A}(C_{Li}\chi_i(\underline{x}))^2 \qquad (2)$$

and diatomic interference (19,61) densities

$$I(\underline{x},AB) = \sum_{L}\sum_{M}\sum_{i}^{A}\sum_{j}^{B} C_{Li}C_{Mj}\chi_i(\underline{x})\chi_j(\underline{x}). \qquad (3)$$

The sums on i and j are over all AO's χ on atoms A and B, respectively, while L and M are sums over the occupied MO's u

$$u_L(\underline{x}) = \sum_{A}\sum_{i} C_{Li}\chi_i(\underline{x}) \qquad (4)$$

with expansion coefficients C_{Li}. The former yields the usual definition of Mulliken's gross atomic populations (64,65), likewise not troubled with overlap partitioning

$$Q(A) = \langle Q(\underline{x},A)\rangle, \qquad (5)$$

and both satisfy the conservation equations (61)

$$\sum_{A} Q(A) = 2N \qquad (6)$$

$$\langle I(AB)\rangle = 0 \qquad (7)$$

where N is the number of occupied MO's. Not only are these definitions straightforward and precise, but it may even be that the concepts they represent cannot be established with total precision unless overlap is neglected.

Both theories are fast and manageable for polyatomic calculations involving first row atoms, as manifest by their wide application to topics such as electric moments (20,66-68), rotation barriers (18,19,29,60,69,70), equilibrium geometries (11,60,71), isomerization energies (72), bond energies (29,73), hydrogen bonding (74,75), spectra[1] (76) and spin densities (11,12). Except for the last two,[1] where INDO does better (12), they generally give similar results in good agreement with experiment. However, both give very poor absolute energies (10).

---

[1] M. S. Gordon, Fargo, North Dakota. Configuration interaction using INDO. Private communication. 1972.

GEOMETRY AND HYBRIDIZATION

Introduction

Directed valence theory (77,78) is used to take advantage of the intimate connection between geometry and hybridization in organic chemistry (79). Thus, there are tetrahedral (alkyl), trigonal (vinyl) and linear (ethynyl) carbons, the nomenclature specifying both the geometry and - partially - hybridization. The latter is only partially specified for several reasons:

1. The relative status of the sigma and pi orbitals is not fixed.

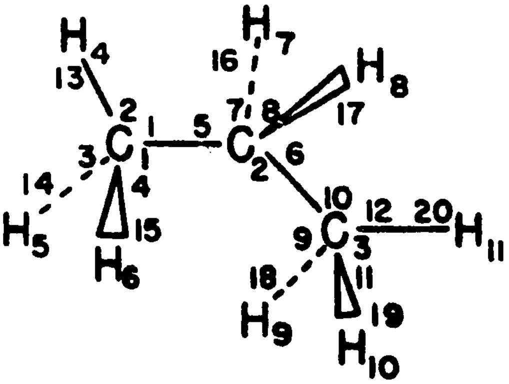
2. The s-character (80) of the linear hybrids is arbitrary, i.e. it corresponds to a free parameter.

3. The absolute orientation of the triple bond is not defined, i.e. they may be rotated freely about the bond axis. A dividend resulting from the present analysis is that these hybridization ambiguities can be settled by reference to the localized orbitals that will be presented later. In case 1, the LMO's mix the sigma and pi, producing bent 'banana' bonds (6, 7), so when there is unsaturation banana hybrids are used. In case 2, best fit with localized orbitals obtains if the s-character (80) is assigned the value .4779 (it is .5 for pure sp hybrids). In case 3, the absolute orientation in non-symmetric situations is defined by maximizing overlaps between hybrids and localized MO's.

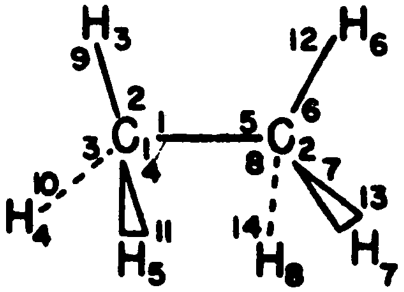
Geometries and Numberings of Atoms and Hybrid Basis Functions

Figure 1 depects for each molecule the geometrical arrangement of the atoms, carbon hybrid AO's and hydrogen AO's. The atoms are labeled

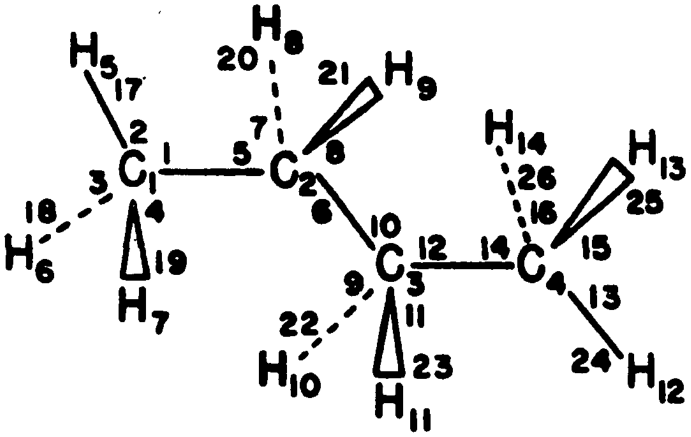
Figure 1. Geometries and numberings of atoms and hybrid basis functions



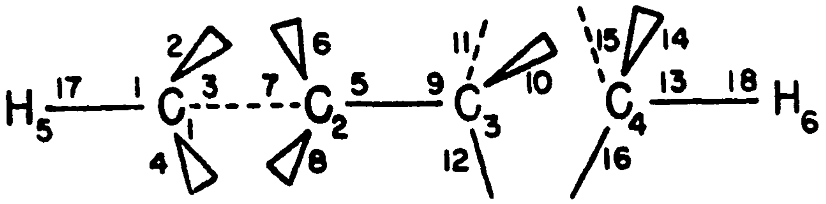
PROPANE



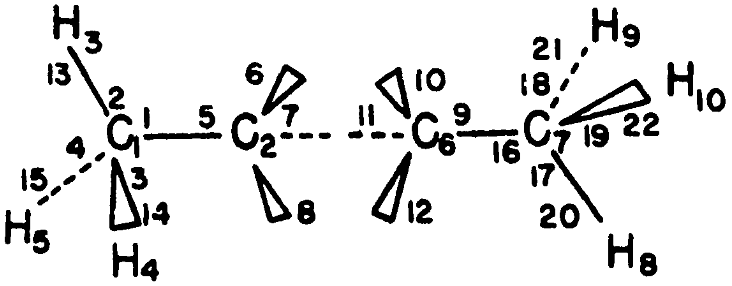
ECLIPSED
ETHANE



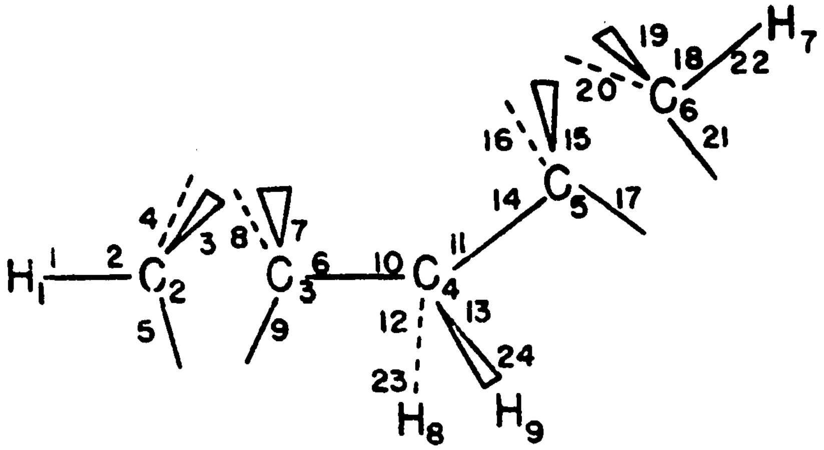
BUTANE



BUTADIYNE

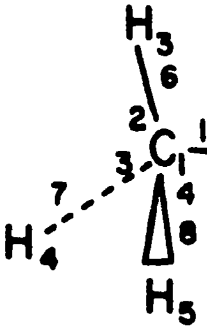


2-BUTYNE

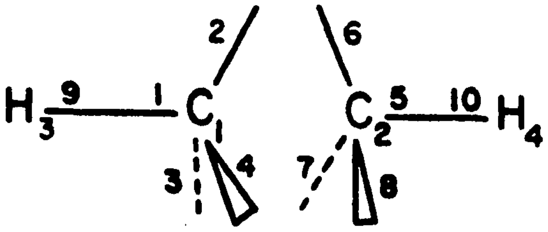


1,4-PENTADIYNE

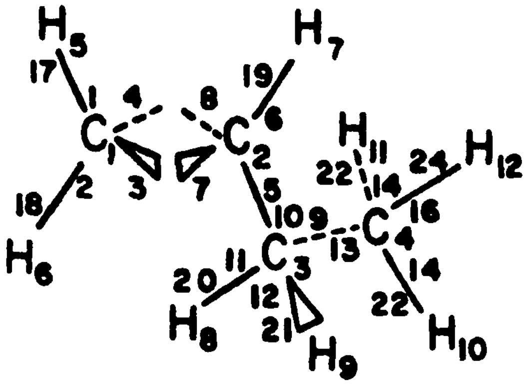
Figure 1 (Continued)



METHANE

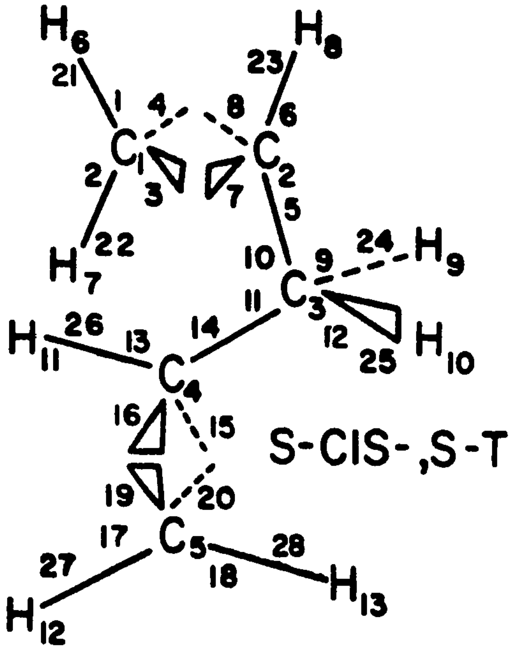


ACETYLENE



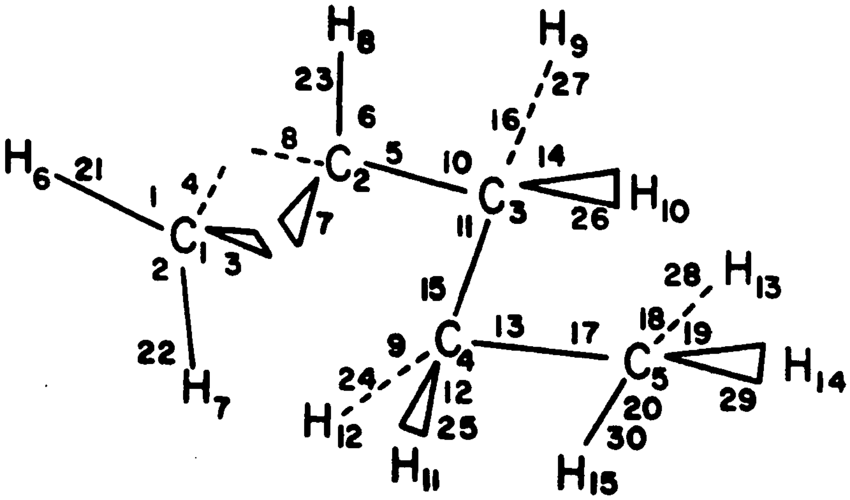
S-GAUCHE-1-BUTENE

Figure 1 (Continued)



S-CIS-,S-TRANS-1,4-PENTADIENE

PENTENE



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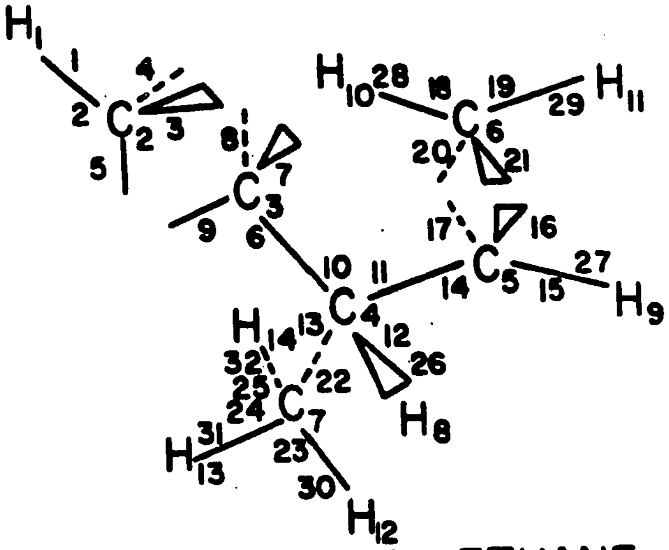
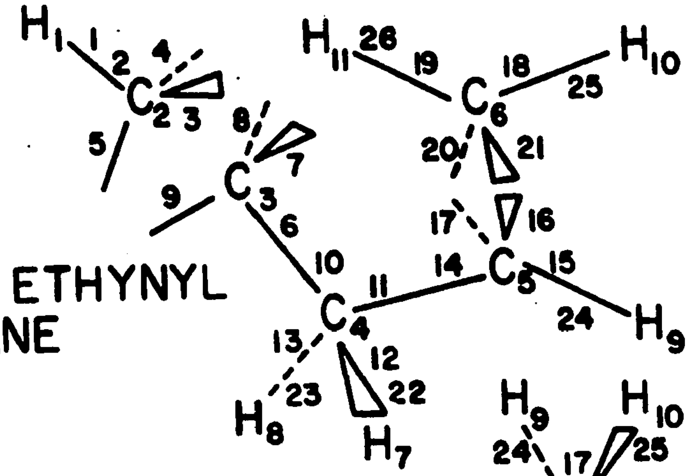
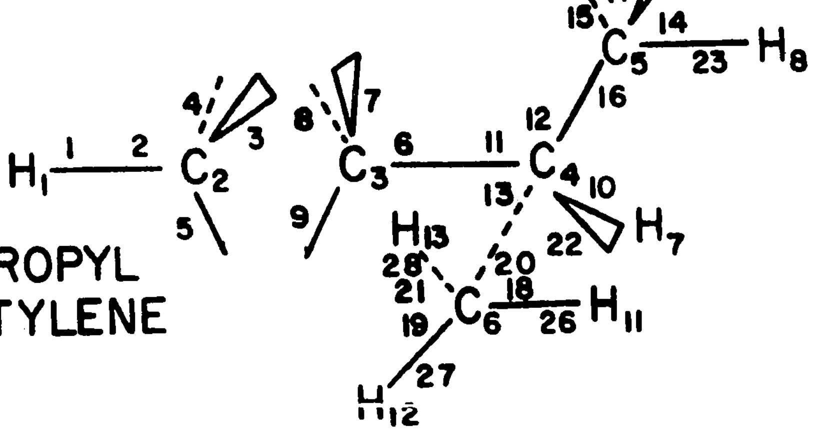


VINYL ETHYNYL ETHANE

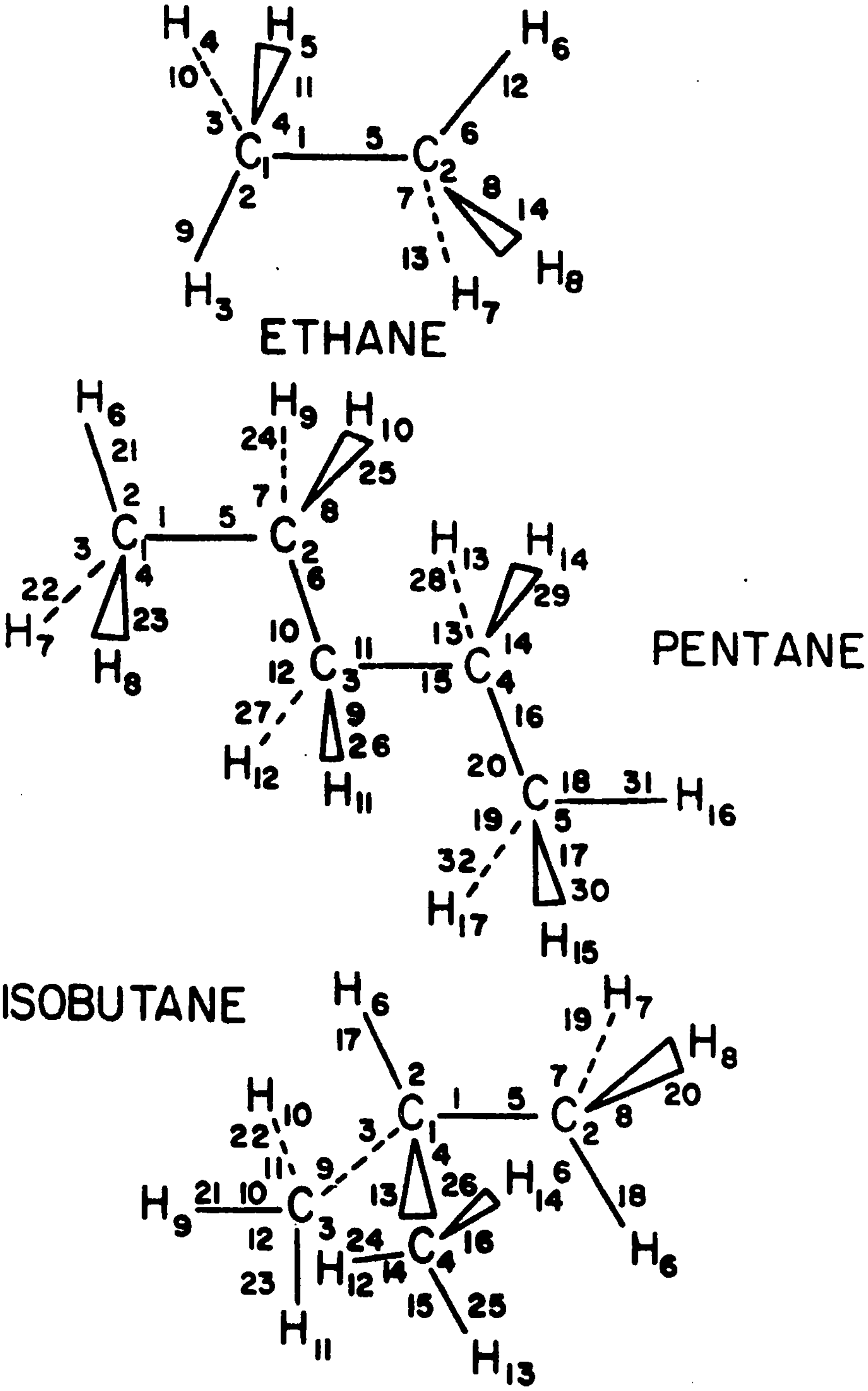


VINYL ETHYNYL METHANE



ISOPROPYL ACETYLENE

Figure 1 (Continued)



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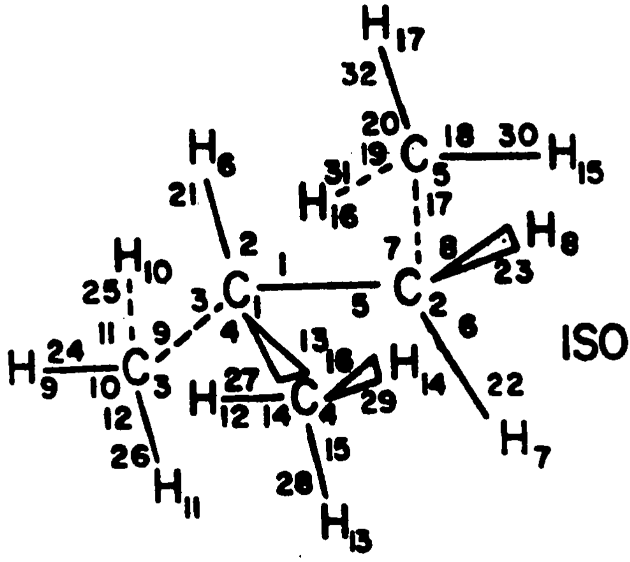
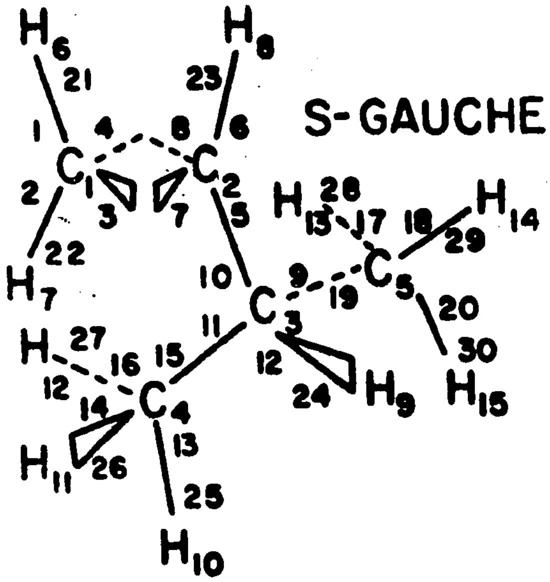
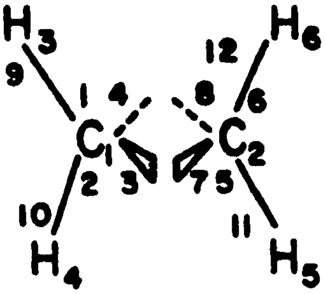


ISOPENTANE



S-GAUCHE-ISOPROPYL ETHYLENE



ETHYLENE

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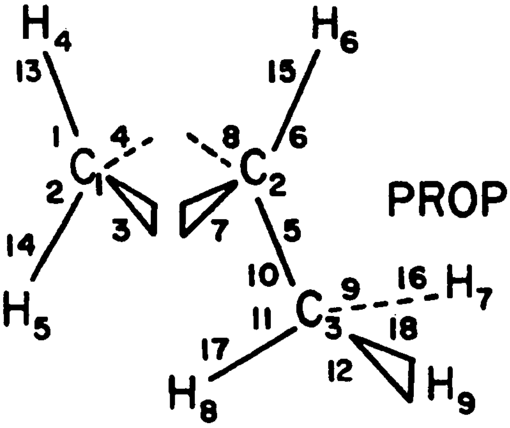
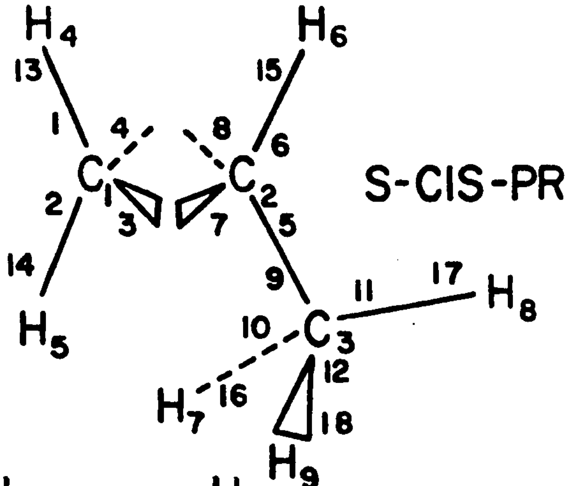
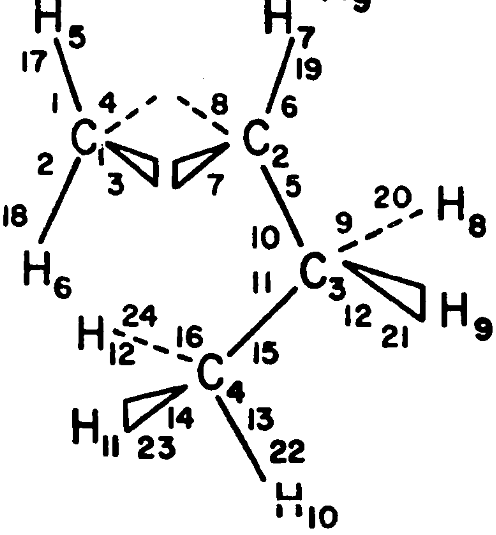


PROPENE



S-CIS-PROPENE



BUTENE

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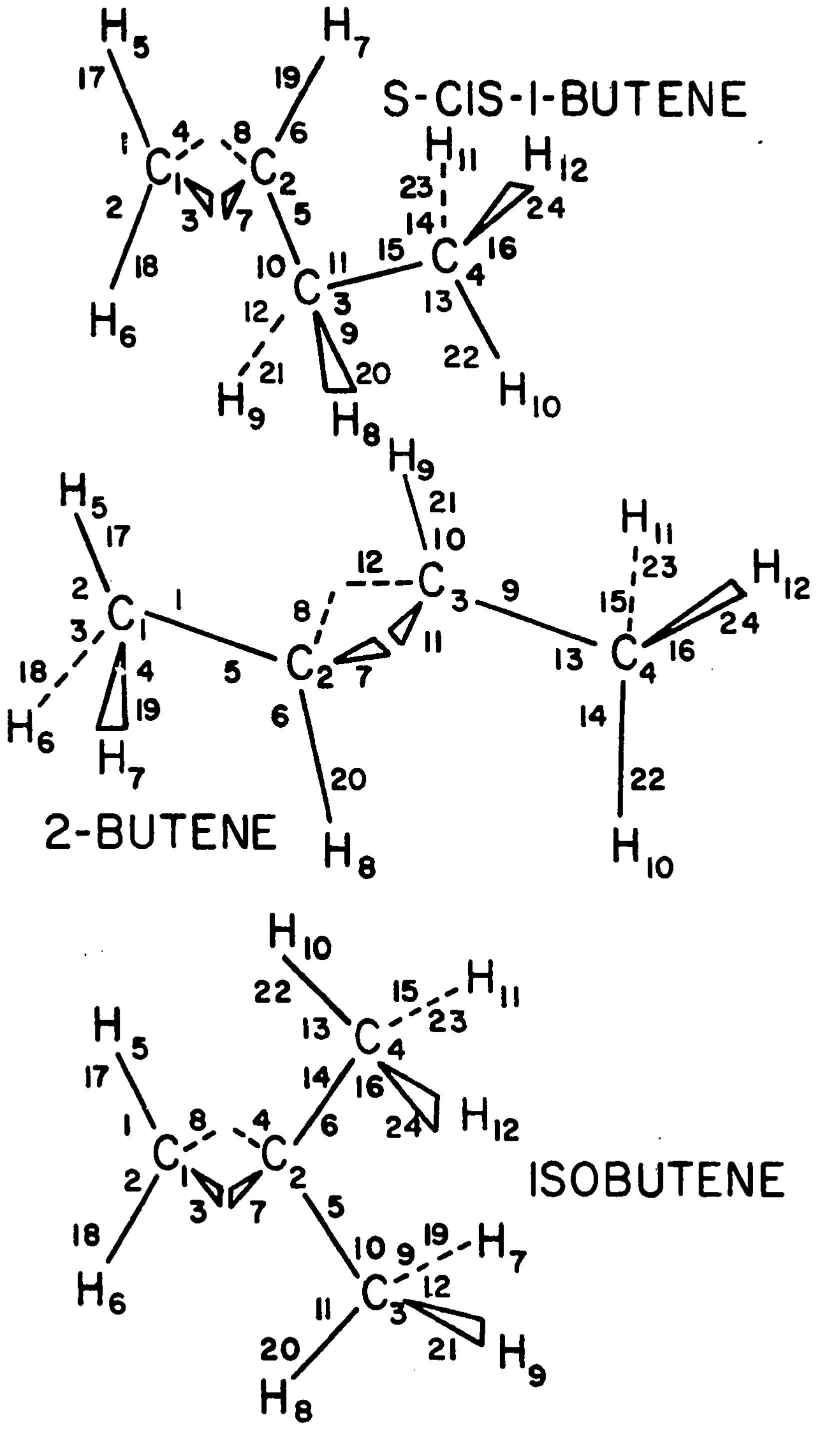

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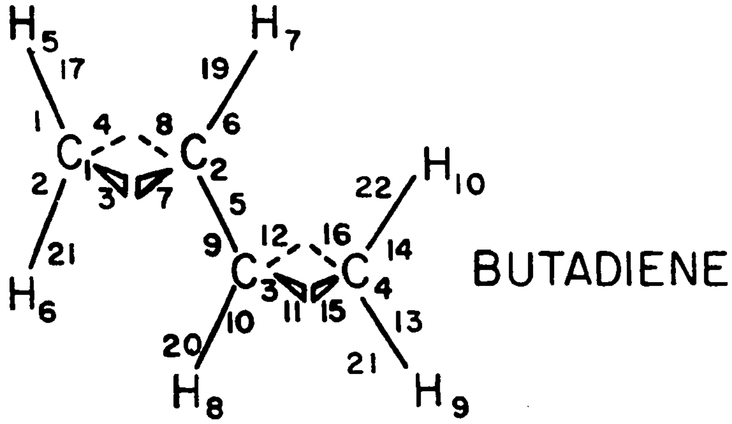
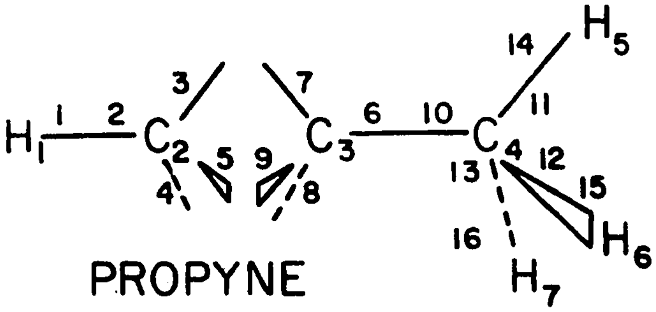
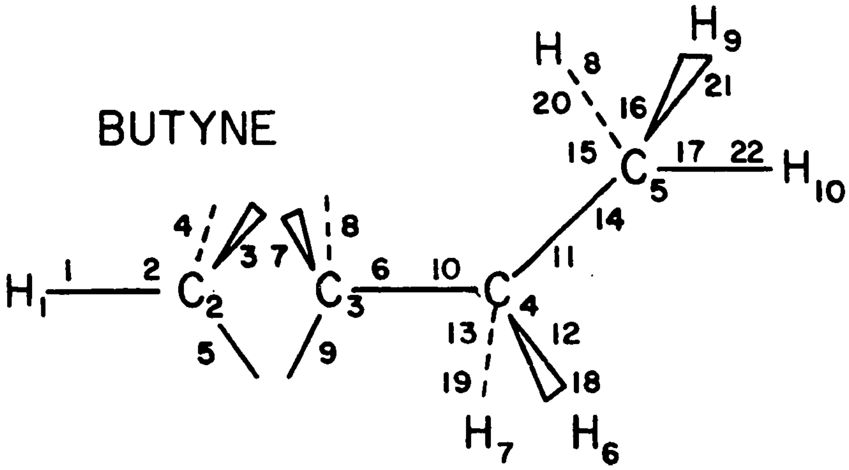


BUTADIENE



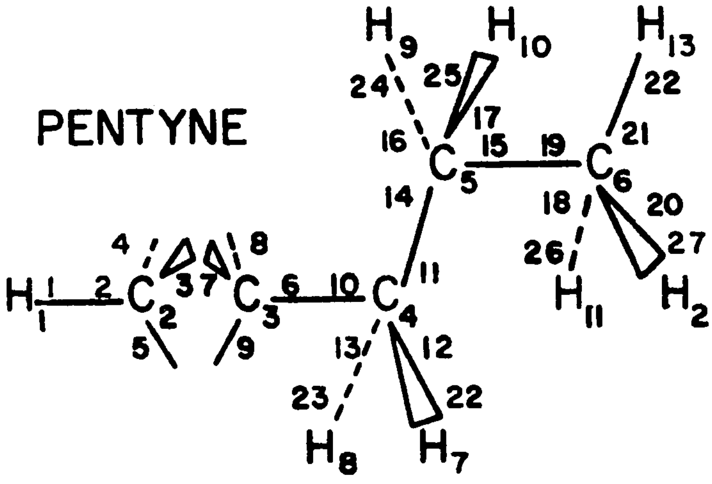
PROPYNE



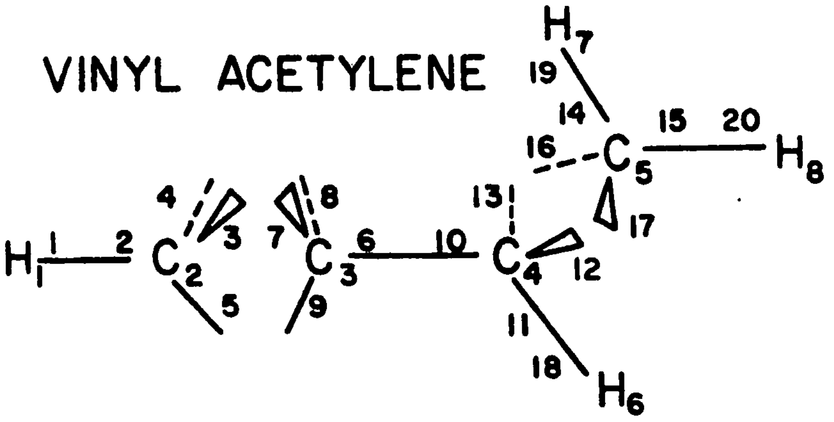
BUTYNE

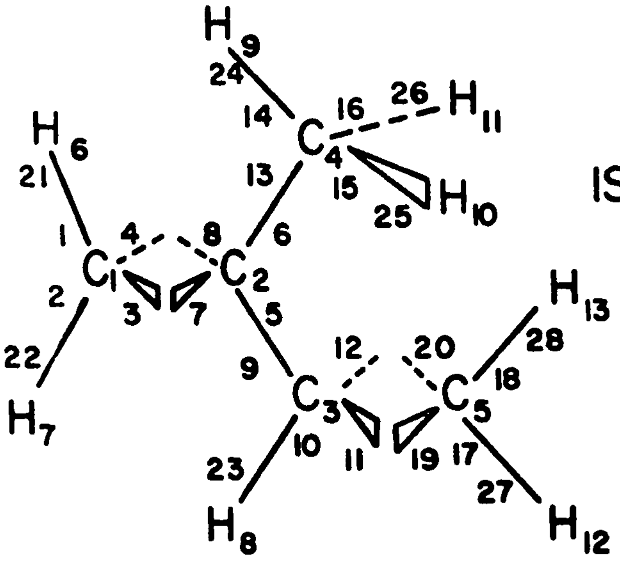
Figure 1 (Continued)

PENTYNE



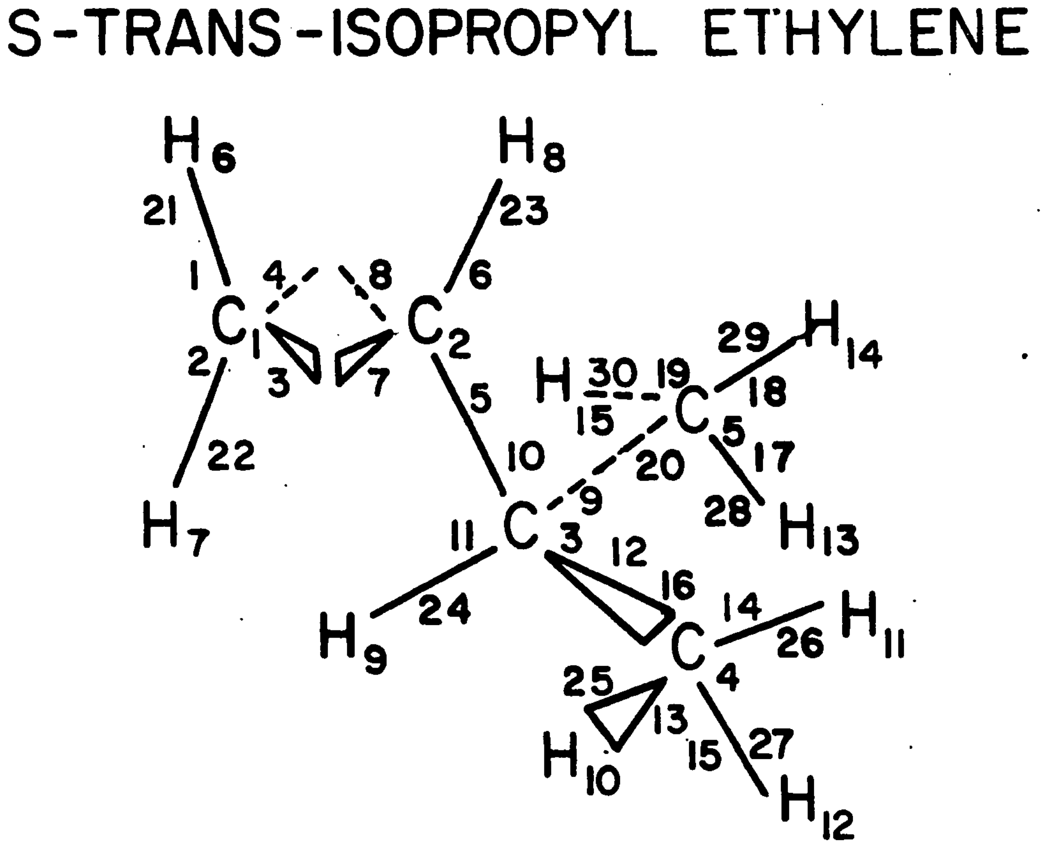
VINYL ACETYLENE





ISOPRENE

Figure 1 (Continued)



S-TRANS-ISOPROPYL ETHYLENE

Figure 1 (Continued)

$C_i, C_j \ldots H_k, H_l \ldots$. The numbers next to each atom label the (hybrid) AO's contributed by that atom. E.g. in propane, the tetrahedral hybrids on the carbon atom C_2 carry the identification numbers 5,6,7,8 and the hydrogen 1S orbital on H_8 is labeled number 17. Thus each single bond exhibits at its two ends the labels of its two constituent (hybrid) AO's. Double and triple bonds are depicted by indicating the four or six hybrids that are used to form the two or three banana bonds. Thus the hybrids 3,4 on C_1 and 7,8 on C_2 form a double bond in ethylene and the hybrids 2,3,4 on C_1 and 6,7,8 on C_2 form a triple bond in acetylene.

The cartesian coordinates for these molecules were calculated with the 'Model-Builder' program (47), and appear in Tables 1-33 in Angstrom units. Bondlengths (Table 34) representing averaged experimental values and tetrahedral (109.5°), trigonal (120°) or linear (180°) angles are assigned automatically by the program, making it especially convenient. These values are basically those adopted in organic chemistry models (79).

Pair Equivalent Hybrids in Mutually Perpendicular Planes

These are two pairs of equivalent hybrids whose centroids lie in mutually perpendicular planes. They will be designated g(+), g(-) and h(+), h(-), with the former lying in the xz plane and the latter in the yz plane. If A and B are the angles measured from the positive and negative z-axes, respectively, toward the positive x- and y-axes, respectively, in a right-handed system, then

$$g(\pm) = (s)\cos Q + \sin Q\,[(z)\cos A \pm (x)\sin A] \qquad (8)$$

$$h(\pm) = (s)\cos R + \sin R\,[(z)\cos B \pm (y)\sin B] \qquad (9)$$

TABLE 1. GEOMETRY AND LCAO-MO'S FOR PROPANE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.539999962
3	C	-1.451925888	-0.000000001	2.053333283
4	H	1.027661100	0.0	-0.363333067
5	H	-0.513830551	-0.889980619	-0.363333067
6	H	-0.513830549	0.889980620	-0.363333067
7	H	0.513830551	-0.889980619	1.903333028
8	H	0.513830550	0.889980619	1.903333028
9	H	-1.965756437	-0.889980621	1.690000218
10	H	-1.965756439	0.889980618	1.690000216
11	H	-1.451925888	0.000000002	3.143332482

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10
1 2S	57	226	-3696	-3560	-94	3592	-94	3592	-45	-57
1 PX	-270	128	-55	-5581	-47	-2785	-47	-2784	-540	270
1 PY	443	0	0	0	-27	-4842	27	4843	0	443
1 PZ	-35	262	-6013	2204	-65	-2179	-65	-2179	103	35
2 2S	-3470	-17	-3630	17	-74	-74	-74	-74	3630	3470
2 PX	-2975	121	-165	-380	-112	-192	-112	-192	-5634	2975
2 PY	4785	0	0	0	437	-437	-437	437	0	4785
2 PZ	-2103	360	6035	5	-164	-51	-164	-51	2167	2103
3 2S	57	3560	45	-226	3592	-94	3592	-94	3696	-57
3 PX	-123	-218	82	-290	-2983	-77	-2983	-77	5687	123
3 PY	443	0	0	0	4842	27	-4842	-28	0	443
3 PZ	-243	5996	544	-33	-1899	-23	-1899	-23	-1952	243
4 1S	167	-138	18	-7136	68	-134	68	-134	442	-167
5 1S	150	21	10	132	11	7116	0	-120	-144	440
6 1S	-440	21	10	132	0	-120	11	7116	-144	-150
7 1S	-7121	-158	21	158	425	-150	-150	425	-21	-138
8 1S	138	-158	21	158	-150	425	425	-150	-21	7121
9 1S	150	-132	144	-21	-120	0	7116	11	-10	440
10 1S	-440	-132	144	-21	7116	11	-120	0	-10	-150
11 1S	167	7136	-442	138	-134	68	-134	68	-18	-167

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10
1	-1	340	-7055	129	-103	-91	-103	-91	66	1
2	-181	142	-157	-6973	-67	151	-67	151	-494	181
3	-164	-14	-89	-138	10	6986	-28	137	168	-462
4	462	-14	-89	-138	-28	137	10	6986	168	164
5	86	-321	-7041	4	104	7	104	7	-62	-86
6	86	-4	62	321	7	104	7	104	7041	-86
7	-6941	144	-140	-144	-440	178	178	-440	140	173
8	-173	144	-140	-144	178	-440	-440	178	140	6941
9	-164	138	-168	14	137	-28	6986	10	89	-462
10	-1	-128	-66	-340	-91	-103	-91	-103	7055	1
11	462	138	-168	14	6986	10	137	-28	90	164
12	-181	6973	494	-142	151	-67	151	-67	157	181
13	167	-138	18	-7136	68	-134	68	-134	442	-167
14	150	21	10	132	11	7116	0	-120	-144	440
15	-440	21	10	132	0	-120	11	7116	-144	-150
16	-7121	-158	21	158	425	-150	-150	425	-21	-138
17	138	-158	21	158	-150	425	425	-150	-21	7121
18	150	-132	144	-21	-120	0	7116	11	-10	440
19	-440	-132	144	-21	7116	11	-120	0	-10	-150
20	167	7136	-442	138	-134	68	-134	68	-18	-167

TABLE 2. GEOMETRY AND LCAO-MO'S FOR ECLIPSED ETHANE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.539999962
3	H	1.027661100	0.0	-0.363333067
4	H	-0.513830551	-0.889980619	-0.363333067
5	H	-0.513830549	0.889980620	-0.363333067
6	H	1.027661100	0.0	1.903333028
7	H	-0.513830551	0.889980619	1.903333028
8	H	-0.513830551	-0.889980619	1.903333028

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7
1 2S	56	-56	3692	-3577	56	3577	3577
1 PX	252	-252	0	2795	-504	5590	-2795
1 PY	-437	-437	0	-4841	0	0	-4841
1 PZ	-41	41	6030	2189	-41	-2189	-2191
2 2S	-3577	3577	3692	57	-3577	-56	-55
2 PX	2795	-2795	0	252	-5590	504	-252
2 PY	-4841	-4841	0	-437	0	0	-437
2 PZ	-2190	2189	-6030	41	-2189	-41	-41
3 1S	-237	237	-6	122	346	7115	-123
4 1S	-237	-347	-5	123	-237	-123	7115
5 1S	346	237	-6	-7115	-237	-122	-123
6 1S	123	-122	-6	-238	-7115	-346	237
7 1S	-7115	-122	-6	346	123	237	237
8 1S	123	7115	-6	-238	122	237	-347

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7
1	-7	7	7068	107	-7	-107	-108
2	246	-246	105	-138	-371	6985	138
3	246	371	105	-138	246	138	6985
4	-371	-246	104	-6985	246	138	138
5	107	-107	7068	-7	107	7	7
6	-138	138	105	246	-6985	371	-245
7	-6985	138	105	-371	-138	-246	-245
8	-138	6985	105	246	-138	-246	372
9	-237	237	-6	122	346	7115	-123
10	-237	-347	-5	123	-237	-123	7115
11	346	237	-6	-7115	-237	-122	-123
12	123	-122	-6	-238	-7115	-346	237
13	-7115	-122	-6	346	123	237	237
14	123	7115	-6	-238	122	237	-347

TABLE 3. GEOMETRY AND LCAO-MO'S FOR BUTANE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.539999962
3	C	-1.451925888	-0.000000001	2.053333283
4	C	-1.451925888	0.0	3.593333245
5	H	1.027661100	0.0	-0.363333067
6	H	-0.513830551	-0.889980619	-0.363333067
7	H	-0.513830549	0.889980620	-0.363333067
8	H	0.513830551	0.889980619	1.903333028
9	H	0.513830550	0.889980619	1.903333028
10	H	-1.965756438	-0.889980620	1.690000217
11	H	-1.965756438	0.889980619	1.690000217
12	H	-2.479586988	-0.000000001	3.956666311
13	H	-0.938095338	0.889980619	3.956666311
14	H	-0.938095337	-0.889980618	3.956666312

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13
1 2S	64	-51	-68	-3552	-98	3594	3594	34	-98	223	34	-3708	-64
1 PX	-265	-548	-47	-5578	-50	-2785	-2785	4	-50	136	4	-70	265
1 PY	442	0	0	0	25	4841	-4841	-14	-25	0	14	0	442
1 PZ	-26	100	-89	2217	-70	-2174	-2174	55	-70	257	55	-6022	26
2 2S	-3484	3632	217	20	-79	-75	-75	-94	-78	-5	-94	-3619	3484
2 PX	-2961	-5636	-286	-382	-111	-193	-193	77	-111	71	77	-182	2961
2 PY	4789	0	0	0	-432	438	-438	-25	432	0	25	0	4789
2 PZ	-2105	2117	4	1	-172	-52	-52	13	-172	396	13	6039	2105
3 2S	78	3632	-20	-217	3484	-94	-94	-75	3484	3619	-75	5	-79
3 PX	-111	5636	-382	-286	-2961	-77	-77	193	-2961	-182	193	71	111
3 PY	432	0	0	0	-4789	-25	25	438	4789	0	-438	0	432
3 PZ	-172	-2117	1	4	-2105	-13	-13	52	-2105	6039	52	396	172
4 2S	98	-51	3552	68	-64	34	34	3594	-64	3708	3594	-223	-98
4 PX	-50	548	-5578	-47	-265	-4	-4	2785	-265	-70	2785	136	50
4 PY	-25	0	0	0	-442	-14	14	4841	442	0	-4841	0	-25
4 PZ	-70	-100	2217	-89	-26	-55	-55	2174	-26	-6022	2174	257	70
5 1S	162	446	59	-7138	72	-135	-135	-10	72	-134	-10	20	-162
6 1S	151	-144	-14	132	-2	-121	7117	-8	11	20	12	11	439
7 1S	-439	-144	-14	131	11	7117	-121	12	-2	20	-8	11	-151
8 1S	-7121	-27	21	156	-142	426	-151	11	425	-145	-1	29	-136
9 1S	136	-27	21	156	425	-151	426	-1	-142	-145	11	29	7121
10 1S	142	-27	-156	-21	7121	11	-1	426	-136	-29	-151	145	425
11 1S	-425	-27	-156	-21	-136	-1	11	-151	7121	-29	426	145	-142
12 1S	-72	446	7138	-59	-162	-10	-10	-135	-162	-20	-135	134	72
13 1S	-11	-144	-131	14	439	12	-8	7117	-151	-11	-121	-20	-2
14 1S	2	-144	-131	14	-151	-8	12	-121	439	-11	7117	-20	11

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13
1	8	60	-111	144	-110	-86	-86	65	-110	334	65	-7069	-8
2	-176	-502	-47	-6971	-70	150	150	5	-70	148	5	-173	176
3	-164	169	11	-139	-26	138	6985	9	9	-18	-10	-86	-461
4	460	169	11	-139	9	6985	138	-10	-26	-18	9	-86	164
5	81	-17	105	9	109	8	8	-59	109	-346	-59	-7040	-81
6	68	7029	343	322	1	105	105	-106	1	53	-106	82	-68
7	-6945	126	-6	-145	170	-442	178	6	-440	141	-29	-140	172
8	-172	126	-6	-145	-440	178	-442	-29	170	140	6	-140	6945
9	-170	126	145	6	6945	6	-29	-442	172	140	178	-140	-440
10	-1	7029	-322	-343	-68	-106	-106	105	-68	-82	105	-53	1
11	440	126	145	6	172	-29	6	178	6945	140	-442	-140	170
12	-109	-17	-9	-105	-81	-59	-59	8	-81	7040	8	346	109
13	70	-502	6971	47	176	5	5	150	176	173	150	-148	-70
14	110	60	-144	111	-8	65	65	-86	-8	7069	-86	-334	-110
15	-9	169	139	-11	-460	-10	9	6985	164	86	138	18	-26
16	26	169	139	-11	164	9	-10	138	-460	86	6985	18	9
17	162	446	59	-7138	72	-135	-135	-10	72	-134	-10	20	-162
18	151	-144	-14	132	-2	-121	7117	-8	11	20	12	11	439
19	-439	-144	-14	131	11	7117	-121	12	-2	20	-8	11	-151
20	-7121	-27	21	156	-142	426	-151	11	425	-145	-1	29	-136
21	136	-27	21	156	425	-151	426	-1	-142	-145	11	29	7121
22	142	-27	-156	-21	7121	11	-1	426	-136	-29	-151	145	425
23	-425	-27	-156	-21	-136	-1	11	-151	7121	-29	426	145	-142
24	-72	446	7138	-59	-162	-10	-10	-135	-162	-20	-135	134	72
25	-11	-144	-131	14	439	12	-8	7117	-151	-11	-121	-20	-2
26	2	-144	-131	14	-151	-8	12	-121	439	-11	7117	-20	11

TABLE 4. GEOMETRY AND LCAO-MO'S FOR BUTADIYNE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.199999809
3	C	-0.000000001	0.0	2.579998970
4	C	-0.000000000	0.0	3.779998779
5	H	-0.000000000	0.0	-1.059999466
6	H	-0.000000000	0.0	4.839998245

EXPANSIONS IN SLATER BASIS

		1	2	3	4	5	6	7	8	9
1	2S	-3262	79	540	3262	-79	4870	-3262	79	-73
1	PX	-5186	-434	0	-4734	380	0	451	815	0
1	PY	-2472	-690	0	3255	-722	0	5727	-31	0
1	PZ	-2470	31	42	2470	-31	-5361	-2470	31	-30
2	2S	-3144	-16	-4735	3144	16	-592	-3144	-16	210
2	PX	-5130	439	0	-4683	-384	0	446	-824	0
2	PY	-2466	698	0	3220	729	0	5666	31	0
2	PZ	2582	111	-5211	-2582	-111	207	2582	111	146
3	2S	16	3144	-4735	-16	-3144	210	16	3144	-592
3	PX	-744	3028	0	-679	-2651	0	64	-5679	0
3	PY	-355	4810	0	467	5027	0	822	217	0
3	PZ	111	2582	5211	-111	-2582	-146	111	2582	-207
4	2S	-79	3262	540	79	-3262	-73	-79	3262	4870
4	PX	736	3061	0	672	-2680	0	-64	-5741	0
4	PY	351	4862	0	-462	5082	0	-813	219	0
4	PZ	31	-2470	-42	-31	2470	30	31	-2470	5361
5	1S	35	-30	-337	-35	30	6860	35	-30	42
6	1S	30	-35	-337	-30	35	42	30	-35	6860

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9
1	-371	29	333	371	-29	7243	-371	29	-27
2	-7044	-517	247	7	-19	-6	-7	636	-43
3	-7	636	247	7	517	-6	-7044	19	-43
4	-7	19	247	7044	-636	-6	-7	-517	-43
5	-209	71	-7041	209	-71	-245	-209	71	250
6	-6987	519	6	25	23	-333	-26	-646	32
7	-25	-646	6	25	-518	-333	-6987	-23	32
8	-26	-23	6	6987	646	-333	-25	519	32
9	-71	209	-7041	71	-209	250	-71	209	-245
10	-519	6987	6	-23	-26	32	646	25	-333
11	23	25	6	-646	-6987	32	-519	25	-333
12	646	25	6	519	-25	32	23	6987	-333
13	-29	371	333	29	-371	-27	-29	371	7243
14	517	7044	247	19	-7	-43	-636	7	-6
15	-19	7	247	636	-7044	-43	517	7	-6
16	-636	7	247	-517	-7	-43	-19	7044	-6
17	35	-30	-337	-35	30	6860	35	-30	42
18	30	-35	-337	-30	35	42	30	-35	6860

TABLE 5. GEOMETRY AND LCAO-MO'S FOR 2-BUTYNE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.460C00000
3	H	1.027661855	0.0	-0.363333333
4	H	-0.513830927	0.889981274	-0.363333333
5	H	-0.513830927	-0.889981274	-0.363333333
6	C	0.000000000	-0.000000000	2.660000000
7	C	0.000000000	-0.000000000	4.120000000
8	H	-1.027661855	-0.000000000	4.483333333
9	H	0.513830927	-0.889981274	4.483333333
10	H	0.513830927	0.889981274	4.483333333

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11
1 2S	-29	17	-3533	-3532	171	29	-17	-17	29	-3673	-3532
1 PX	525	-83	2786	2786	0	61	-41	-41	463	0	-5573
1 PY	232	0	4826	-4826	0	570	-71	71	-338	0	0
1 PZ	67	20	2240	2240	220	-67	-20	-20	-67	-5946	2240
2 2S	3192	-92	58	58	-563	-3192	92	92	-3192	-4784	58
2 PX	5228	-699	375	375	0	613	-349	-349	4615	0	-751
2 PY	2310	0	650	-650	0	5683	-605	605	-3373	0	0
2 PZ	2541	-48	107	107	-143	-2541	48	48	-2541	5275	107
3 1S	-383	133	103	103	-22	-93	72	72	-419	-18	-7091
4 1S	93	-72	103	-7092	-22	-419	72	-133	383	-18	103
5 1S	419	-72	-7092	103	-22	383	-133	72	-93	-18	103
6 2S	3192	59	-92	-92	4784	-3192	-59	-59	-3192	563	-92
6 PX	5228	751	-349	-349	C	613	375	375	4615	0	699
6 PY	2310	0	-605	605	0	5683	650	-650	-3373	0	0
6 PZ	-2541	-107	48	48	5275	2542	107	107	2541	-143	48
7 2S	-29	-3533	17	17	3673	29	3533	3533	29	-171	17
7 PX	525	5573	-41	-41	0	61	2786	2786	463	0	83
7 PY	232	0	-71	71	0	570	4826	-4826	-338	0	0
7 PZ	-67	-2240	-20	-20	-5946	67	2240	2240	67	220	-20
8 1S	469	-7091	-72	-72	18	7	-103	-103	333	22	133
9 1S	-7	103	-72	133	18	333	-103	7092	-469	22	-72
10 1S	-333	103	133	-72	.18	-469	7091	-103	7	22	-72

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11
1	43	27	173	174	276	-43	-27	-27	-43	-6986	173
2	394	-64	-137	-137	22	84	-36	-36	412	-120	-6964
3	-84	36	-138	-6964	22	412	-36	64	-394	-120	-137
4	-412	36	-6964	-137	22	-394	64	-36	84	-120	-137
5	271	-26	-39	-39	-273	-271	26	26	-271	-7121	-39
6	7018	-580	562	132	-296	-17	-402	-2	-17	10	-494
7	17	2	-494	562	-296	-7018	580	-402	-17	10	132
8	17	402	132	-494	-296	-17	-2	580	-7018	10	562
9	271	-39	-26	-26	7121	-271	39	39	-271	273	-26
10	7018	628	-519	-119	-10	-17	428	-1	-17	296	463
11	17	1	463	-519	-10	-7018	-628	428	-17	296	-119
12	17	-428	-119	463	-10	-17	-1	-628	-7018	296	-519
13	-383	133	103	103	-22	-93	72	72	-419	-18	-7091
14	93	-72	103	-7092	-22	-419	72	-133	383	-18	103
15	419	-72	-7092	103	-22	383	-133	72	-93	-18	103
16	43	174	27	27	6986	-43	-174	-174	-43	-276	27
17	-462	-6964	36	36	120	-16	137	137	-344	-22	-64
18	16	-137	36	-64	120	-344	138	6964	462	-22	36
19	344	-137	-64	36	120	462	6964	137	-16	-22	36
20	469	-7091	-72	-72	18	7	-103	-103	333	22	133
21	-7	103	-72	133	18	333	-103	7092	-469	22	-72
22	-333	103	133	-72	18	-469	7091	-103	7	22	-72

TABLE 6. GEOMETRY AND LCAO-MO'S FOR 1,4-PENTADIYNE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	H	0.0	0.0	0.0
2	C	0.0	0.0	1.060000000
3	C	-0.000000000	0.0	2.260000000
4	C	-0.000000001	0.0	3.720000000
5	C	1.376501206	0.0	4.206666652
6	C	2.507872060	0.000000000	4.606666639
7	H	3.507249649	0.000000000	4.959999961
8	H	-0.513830907	-0.889981290	4.083333322
9	H	-0.513830907	0.889981290	4.083333322

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12
1 1S	33	-19	6867	18	-35	-52	-350	-33	35	5	-32	24
2 2S	-3229	35	4876	-33	95	94	601	3229	-95	-9	97	-3263
2 PX	-2899	-89	19	86	377	-205	-6	2941	-377	58	-678	5844
2 PY	-5008	48	0	49	598	0	0	-4983	598	0	0	24
2 PZ	-2460	14	-5343	-13	39	38	80	2460	-39	-3	41	-2455
3 2S	-3213	-107	-614	102	-50	-292	-4762	3214	51	14	-5	-3180
3 PX	-2816	79	8	-75	-406	201	98	2857	406	-44	777	5657
3 PY	-4970	-3	0	-3	-632	0	0	-4946	-631	0	0	23
3 PZ	2544	-72	193	69	112	-205	-5228	-2544	-112	7	196	2569
4 2S	46	-46	168	46	3392	-18	-3566	-46	-3392	-168	3566	-18
4 PX	-201	148	-9	-145	-3013	114	227	203	3013	-207	5548	372
4 PY	-473	-469	0	-474	-4777	5	0	-470	-4777	0	0	2
4 PZ	84	-166	-223	159	2130	-354	5965	-84	-2131	-83	2203	10
5 2S	104	3214	-14	-3213	-50	-3180	5	-106	51	614	4762	-292
5 PX	-91	3362	21	-3327	-241	-536	-74	93	241	179	-4961	260
5 PY	-3	-4927	0	-4987	-632	59	0	-3	-632	0	0	0
5 PZ	49	-1875	-39	1778	345	-6190	798	-50	-345	72	-1649	-121
6 2S	-34	3229	9	-3229	95	-3263	-97	34	-95	-4876	-601	94
6 PX	42	-1328	-23	1363	88	4262	265	-42	-88	-5044	77	-104
6 PY	48	-4965	0	-5026	598	60	0	48	598	0	0	0
6 PZ	-77	-3623	53	3523	-369	-4691	-626	78	369	-1762	20	180
7 1S	18	-33	-5	33	-35	24	32	-18	35	-6867	350	-52
8 1S	-497	-176	-21	-497	7060	200	-21	-178	103	21	21	197
9 1S	182	497	-21	184	-103	191	-21	497	-7060	21	21	194

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12
1	33	-19	6867	18	-35	-52	-350	-33	35	5	-32	24
2	-357	13	7234	-12	34	35	346	357	-34	-3	34	-383
3	-7059	18	10	50	633	-28	285	-5	215	18	-217	38
4	5	-50	10	-18	-210	-28	285	7060	-633	18	-221	38
5	49	93	-13	-90	-254	222	292	-49	250	-53	612	-7119
6	-284	-125	-270	120	49	-348	-7072	284	-49	15	141	-243
7	-7025	11	-333	-16	-678	36	40	13	-217	-14	236	-46
8	-13	17	-333	-11	213	37	41	7025	678	-14	241	-46
9	-44	-82	-344	78	268	-209	-79	44	-263	39	-713	-6975
10	-49	120	278	-115	-149	298	-6949	49	149	-12	-124	-18
11	-116	49	12	-49	-149	-18	124	118	149	-278	6949	298
12	464	199	23	464	6919	-162	-153	202	-163	-23	153	-159
13	-205	-463	23	-207	163	-154	-153	-463	-6919	-23	153	-156
14	121	284	-15	-283	49	-243	-140	-124	-49	270	7072	-348
15	-16	15	14	-7025	-678	-44	-233	11	-220	333	-40	35
16	-12	7025	14	-11	209	-49	-244	17	678	333	-41	38
17	79	43	-39	-45	271	-6975	713	-81	-260	344	79	-209
18	-12	357	3	-357	34	-383	-34	12	-34	-7234	-346	35
19	49	-5	-17	-7059	633	37	214	19	218	-10	-285	-27
20	-18	7060	-18	5	-207	38	224	-50	-634	-10	-285	-29
21	-91	-50	53	49	-257	-7119	-612	92	247	13	-292	222
22	18	-33	-5	33	-35	24	32	-18	35	-6867	350	-52
23	-497	-176	-21	-497	7060	200	-21	-178	103	21	21	197
24	182	497	-21	184	-103	191	-21	497	-7060	21	21	194

```
TABLE  7.  GECMETRY AND LCAO-MO'S FOR METHANE
------------------------------------------------------------------

GECMETRY
ATCM NUMBER   ELEMENT          X              Y              Z

       1         C        0.0            0.0            0.0
       2         H        0.0            0.0            1.089999199
       3         H        1.027661100    0.0           -0.363333067
       4         H       -0.513830551   -0.889980619   -0.363333067
       5         H       -0.513830549    0.889980620   -0.363333067

EXPANSICNS IN SLATER BASIS

            1     2     3     4

 1 2S    3671 -3671  3671  3671
 1 PX       0  2830 -2830  5661
 1 PY       0  4902  4902     0
 1 PZ    6004  2001 -2001 -2001
 2 1S    7101   104  -104  -104
 3 1S    -104   104  -104  7101
 4 1S    -104 -7101  -104  -104
 5 1S    -104   104  7101  -104

EXPANSIONS IN HYBRID BASIS

       1     2     3     4

 1  7035  -102   102   101
 2   102  -102   102  7035
 3   102 -7035   102   102
 4   102  -102  7035   102
 5  7101   104  -104  -104
 6  -104   104  -104  7101
 7  -104 -7101  -104  -104
 8  -104   104  7101  -104
------------------------------------------------------------------
```

TABLE 8. GEOMETRY AND LCAO-MO'S FOR ACETYLENE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.199999809
3	H	-0.000000000	0.0	-1.059999466
4	H	-0.000000000	0.0	2.259999275

EXPANSIONS IN SLATER BASIS

		1	2	3	4	5
1	2S	-3247	-4874	3247	636	-3247
1	PX	-5769	0	-3078	0	2690
1	PY	223	0	-4884	0	-5108
1	PZ	-2474	5334	2474	132	-2474
2	2S	-3247	636	3247	-4874	-3247
2	PX	-5769	0	-3078	0	2690
2	PY	223	0	-4884	0	-5108
2	PZ	2474	-132	-2474	-5334	2474
3	1S	32	-6872	-32	-349	32
4	1S	32	-348	-32	-6872	32

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5
1	-358	-7226	358	331	-358
2	-7061	-5	-9	323	9
3	9	-5	7061	323	9
4	9	-5	-9	323	-7061
5	-358	331	358	-7226	-358
6	-7061	323	-9	-5	9
7	9	323	7061	-5	9
8	9	323	-9	-5	-7061
9	32	-6872	-32	-349	32
10	32	-348	-32	-6872	32

TABLE 9. GEOMETRY AND LCAO-MO'S FOR S-GAUCHE-1-BUTENE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.339999199
3	C	-1.316358184	-0.000000001	2.099998951
4	C	-1.397936407	-1.257404703	2.985367965
5	H	0.935307370	0.0	-0.539999962
6	H	-0.935307371	0.0	-0.539999962
7	H	0.935307371	0.000000000	1.879999161
8	H	-2.144844400	-0.000000001	1.391684866
9	H	-1.374098576	0.889980619	2.726655793
10	H	-2.341903404	-1.257404704	3.530367564
11	H	-1.340196015	-2.147385323	2.358711123
12	H	-0.569450192	-1.257404702	3.693682050

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12
1 2S	191	-43	133	-51	211	3279	131	-1	-3593	177	-4056	-3240
1 PX	648	-4	83	-52	-624	61	77	-24	-4744	57	4742	-28
1 PY	13	-52	597	-174	9	5072	-601	-85	32	20	-4	5048
1 PZ	-38	-51	95	-41	25	3758	95	3	3287	50	3244	-3742
2 2S	-4031	95	0	224	-3906	3194	-29	61	175	130	257	-3237
2 PX	4772	-62	27	-228	-4870	144	83	-67	-511	320	543	-102
2 PY	-93	66	-659	168	-16	4880	628	58	2	-21	0	4922
2 PZ	-3213	17	222	100	-3159	-3862	164	29	-107	311	-6	3831
3 2S	-3629	75	3603	-12	137	15	3442	76	-265	-3512	184	34
3 PX	-5204	-358	-494	-338	-174	-54	-529	22	-317	4599	115	41
3 PY	-165	-123	-4881	104	-43	357	4950	316	-21	-191	9	439
3 PZ	2991	-298	3524	131	-385	-214	3375	364	96	3848	-84	339
4 2S	47	-3591	3687	3564	78	253	-39	-3594	38	63	-22	118
4 PX	-500	-4489	268	-5140	-13	-110	-55	-292	-40	427	9	-45
4 PY	69	163	4918	-182	64	275	349	5007	62	125	-50	72
4 PZ	241	-3977	-3428	3088	0	-114	387	3291	-3	263	0	-67
5 1S	-519	14	-80	63	297	9	-84	18	-7075	-133	278	-2
6 1S	278	-1	21	-30	-517	14	22	-15	270	-13	-7054	-11
7 1S	181	7	-117	-2	-7060	-13	-122	-15	301	-424	-509	-1
8 1S	23	-426	-23	-152	-397	-174	-145	155	-47	-7118	-36	163
9 1S	24	149	7	-174	124	-186	7111	-433	81	151	-51	-477
10 1S	-447	132	-19	7133	-51	-148	-181	133	-61	160	22	-72
11 1S	141	119	-11	-132	-13	17	445	-7112	22	155	-24	-2
12 1S	144	-7113	-11	-131	-3	14	-147	120	18	-440	3	-13

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12
1	585	-7	97	-49	-330	402	91	-19	-7002	122	-312	-362
2	-332	0	-21	24	553	315	-17	15	-293	41	-7019	-322
3	65	-84	532	-168	107	7095	-316	-59	290	116	213	86
4	46	-10	-313	78	94	-78	534	62	244	87	220	-7053
5	-7014	106	70	332	-101	165	-8	95	419	-24	-238	-232
6	-264	17	110	8	-6989	369	109	0	-304	429	529	-376
7	143	76	-594	153	217	6984	337	49	135	-142	108	-53
8	275	-18	337	-85	241	82	-551	-32	131	-111	109	-7014
9	31	-7	7031	0	-84	-348	-74	-4	-54	84	38	-126
10	-7013	-101	-94	-317	105	59	-137	-102	-413	27	215	-98
11	-72	441	143	142	400	164	170	-181	21	-6949	63	-200
12	-203	-181	127	148	-145	156	6926	442	-85	-186	51	494
13	-70	94	7041	-120	84	373	31	91	63	8	-46	142
14	503	-150	157	6975	49	159	189	-152	48	-174	-18	63
15	-168	-136	85	138	-6	-16	-462	-6989	-25	-168	25	39
16	-169	-6988	90	136	30	-10	161	-137	-9	461	-5	-9
17	-519	14	-80	63	297	9	-84	18	-7075	-133	278	-2
18	278	-1	21	-30	-517	14	22	-15	270	-13	-7054	-11
19	181	7	-117	-2	-7060	-13	-122	-15	301	-424	-509	-1
20	23	-426	-23	-152	-397	-174	-145	155	-47	-7118	-36	163
21	24	149	7	-174	124	-186	7111	-433	81	151	-51	-477
22	-447	132	-19	7133	-51	-148	-181	133	-61	160	22	-72
23	141	119	-11	-132	-13	17	445	-7112	22	155	-24	-2
24	144	-7113	-11	-131	-3	14	-147	120	18	-440	3	-13

TABLE 10. GEOMETRY AND LCAO-MO'S FOR S-CIS-,S-TRANS-1,4-PENTADIENE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.339999199
3	C	-1.316358184	-0.000000001	2.099598951
4	C	-2.471678884	-0.000000002	1.112257804
5	C	-3.735042244	-0.000000002	1.558924204
6	H	0.935307370	0.0	-0.539999962
7	H	-0.935307371	0.0	-0.539999962
8	H	0.935307371	0.000000000	1.879999161
9	H	-1.374098574	-0.889980619	2.726655795
10	H	-1.374098576	0.889980619	2.726655793
11	H	-2.274331161	-0.000000002	0.050441571
12	H	-4.555928214	-0.000000003	0.857107947
13	H	-3.932389967	-0.000000001	2.620740438

EXPANSIONS IN SLATER BASIS

		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	2S	-128	3982	3272	183	-23	-4081	159	128	-3272	-221	-171	-23	-4	19
1	PX	-85	4761	36	-11	-2	4726	71	85	-36	630	-637	-2	0	3
1	PY	596	0	-5033	0	-9	0	0	596	-5033	0	0	9	0	0
1	PZ	-110	-3275	3752	-183	23	3285	54	110	-3752	-25	9	23	-15	-23
2	2S	29	-183	3230	175	-155	227	120	-29	-3230	3876	4049	-155	-88	-59
2	PX	-95	517	111	-134	86	559	408	95	-111	4892	-4734	86	31	46
2	PY	-612	0	-4917	0	62	0	0	-612	-4917	0	0	-62	0	0
2	PZ	-185	96	-3824	117	-123	-32	315	185	3824	3132	3282	-123	-78	-48
3	2S	-3458	276	-43	127	6	165	-3651	3458	43	-80	3592	6	255	159
3	PX	384	311	-2	-264	211	150	4578	-384	2	81	5364	211	-197	-84
3	PY	-4777	0	-490	0	-469	0	0	-4777	-490	0	0	469	0	0
3	PZ	-3624	-110	-252	236	-105	-124	3866	3624	252	326	-2745	-105	-275	-142
4	2S	95	66	-107	-3948	-3196	157	-4045	-95	107	195	35	-3196	-172	253
4	PX	87	-1	-31	-1326	3662	-79	-4605	-87	31	133	297	3662	-70	-183
4	PY	-577	0	-54	0	-4934	0	0	-577	-54	0	0	4934	0	0
4	PZ	-239	-13	-71	5649	-1169	-127	-3434	239	71	223	-298	-1169	-514	-507
5	2S	74	-19	48	230	-3273	-85	202	-74	-48	-71	227	-3273	3995	-4043
5	PX	13	-28	42	252	-3535	-97	-246	-13	-42	-32	104	-3535	-4683	1486
5	PY	557	0	90	0	-5023	0	0	557	90	0	0	5023	0	0
5	PZ	-8	-6	-28	588	1292	-35	-600	8	28	74	-158	1292	-3375	-5556
6	1S	79	7075	0	-156	17	287	-131	-79	0	-295	495	17	-7	-29
7	1S	-28	-278	11	-216	16	-7024	13	28	-11	526	-294	16	4	-1
8	1S	139	-294	-17	-59	76	-491	-446	-139	17	7080	-188	76	79	33
9	1S	91	-73	-192	-212	-248	-16	29	7091	-485	-132	-20	377	18	5
10	1S	-7091	-73	485	-212	377	-16	29	-91	192	-132	-20	-248	18	5
11	1S	-252	-34	-8	-7032	13	-189	185	252	8	46	-311	13	-302	-517
12	1S	-53	-12	-22	300	-4	-35	-521	53	22	75	-140	-4	7073	276
13	1S	-12	17	5	-529	-11	69	274	12	-5	-34	29	-11	-270	-7057

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	-89	7002	383	172	-24	-355	120	89	-383	328	-553	-24	3	23
2	31	269	331	189	-21	-7039	19	-31	-331	-563	347	-21	4	18
3	305	-265	-56	-30	-3	230	96	538	-7061	-105	-64	10	-10	-5
4	-538	-265	7061	-30	10	230	96	-305	56	-105	-64	-3	-10	-5
5	8	-432	224	244	-200	-277	-90	-8	-224	57	7025	-200	-105	-87
6	-126	298	381	53	-78	513	486	126	-381	6976	330	-78	-60	-21
7	-314	-130	49	3	52	111	-132	-551	-7004	-225	-241	-36	9	3
8	551	-130	7004	3	-36	111	-132	314	-49	-225	-241	52	9	3
9	-173	68	199	193	273	13	-110	6929	493	118	183	-391	0	12
10	128	419	85	-237	207	249	-66	-128	-85	-120	7008	207	98	78
11	57	-4	121	104	-76	53	-7015	-57	-121	-277	-189	-76	412	215
12	-6929	68	-493	193	-391	13	-110	173	-199	118	183	273	0	12
13	260	48	-9	-7013	-360	181	-266	-260	9	-46	304	-360	302	525
14	-17	30	-119	-105	-193	-26	-7015	18	119	314	46	-193	-416	-236
15	353	25	-2	197	-34	83	194	462	79	50	-205	-7012	-130	105
16	-462	25	-79	197	-7012	83	194	-353	2	50	-205	-34	-130	105
17	39	9	16	-336	-381	29	588	-39	-16	-60	150	-381	7004	-308
18	34	-11	-1	568	-324	-63	-327	-34	1	23	-11	-324	295	-7016
19	433	-22	112	117	-7061	-81	64	354	15	-61	180	42	-268	227
20	-354	-22	-15	117	42	-81	63	-433	-112	-61	180	-7061	-268	227
21	79	7075	0	-156	17	287	-131	-79	0	-295	495	17	-7	-29
22	-28	-278	11	-216	16	-7024	13	28	-11	526	-294	16	4	-1
23	139	-294	-17	-59	76	-491	-446	-139	17	7080	-188	76	79	33
24	91	-73	-192	-212	-248	-16	29	7091	-485	-132	-20	377	18	5
25	-7091	-73	485	-212	377	-16	29	-91	192	-132	-20	-248	18	5
26	-252	-34	-8	-7032	13	-189	185	252	8	46	-311	13	-302	-517
27	-53	-12	-22	300	-4	-35	-521	53	22	75	-140	-4	7073	276
28	-12	17	5	-529	-11	69	274	12	-5	-34	29	-11	-270	-7057

TABLE 11. GEOMETRY AND LCAO-MO'S FOR PENTENE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.339999199
3	C	-1.316358184	-0.000000001	2.099998951
4	C	-2.486880825	-0.000000002	1.099260909
5	C	-3.820559913	-0.000000002	1.869260890
6	H	0.935307370	0.0	-0.539999962
7	H	-0.935307371	0.0	-0.539999962
8	H	0.935307371	0.000000000	1.879999161
9	H	-1.374098574	-0.889980619	2.726655795
10	H	-1.374098576	0.889980619	2.726655793
11	H	-2.429140435	0.889980617	0.472604065
12	H	-2.429140434	-0.889980621	0.472604066
13	H	-3.878300303	-0.889980620	2.495917734
14	H	-3.878300305	0.889980619	2.495917731
15	H	-4.649046129	-0.000000003	1.160946804

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1 2S	3271	-3987	-160	3271	-8	86	-219	-86	52	-136	182	-136	-3	4065	3
1 PX	39	-4753	-68	39	5	-1	629	1	-3	-80	632	-80	-8	-4731	8
1 PY	5035	0	0	-5035	0	-33	0	-33	0	598	0	-598	17	0	17
1 PZ	3754	3282	-57	3754	-5	-92	-27	92	-54	-105	-17	-105	6	-3268	-6
2 2S	3228	180	-120	3228	-86	97	3876	-97	266	33	-4052	33	40	-241	-40
2 PX	112	-512	-398	112	39	-68	4891	68	-146	-96	4736	-96	-36	-544	36
2 PY	4918	0	0	-4918	0	72	0	72	0	-626	0	626	-13	0	-13
2 PZ	-3825	-100	-318	-3825	-74	54	3133	-54	202	-183	-3277	-183	32	19	-32
3 2S	-43	-280	3664	-43	220	65	-86	-65	-18	-3456	-3625	-3456	-93	-175	93
3 PX	-6	-306	-4619	-6	-143	-105	90	105	-319	374	-5231	374	26	-134	-26
3 PY	480	0	0	-480	0	-424	0	-424	0	-4787	0	4787	-24	0	-24
3 PZ	-253	110	-3841	-253	-247	188	331	-188	266	-3628	2776	-3628	74	120	-74
4 2S	-102	-37	3635	-102	-21	-3492	194	3492	3610	81	1	81	-74	-42	74
4 PX	-31	19	4645	-31	-194	-325	149	325	-5315	93	-280	93	51	160	-51
4 PY	-43	0	0	43	0	-4793	0	-4793	0	-436	0	436	437	0	437
4 PZ	-88	-38	3822	-88	-331	3609	226	-3609	2867	-181	238	-181	194	-87	-194
5 2S	39	18	-54	39	3555	67	-56	-68	3712	97	-208	97	3592	87	-3592
5 PX	49	34	354	49	-4709	114	-38	-114	5186	32	-140	32	-492	123	472
5 PY	-20	0	0	20	0	-442	0	-442	0	23	0	-23	4841	0	4841
5 PZ	-39	-7	424	-39	-3723	243	79	-242	-3069	-78	236	-78	3500	-38	-3500
6 1S	1	-7075	127	1	-5	-80	-296	80	-41	84	-501	84	13	-283	-13
7 1S	11	274	-12	11	9	-98	525	98	-39	-28	290	-28	0	7041	0
8 1S	-16	295	442	-16	67	-37	7080	37	-131	136	189	136	-16	497	16
9 1S	473	78	-38	-179	20	-415	-130	-139	-142	101	30	-7106	10	32	2
10 1S	-179	78	-38	473	20	139	-130	415	-142	-7106	30	101	-2	32	-10
11 1S	2	-8	-25	-6	-156	-7119	15	-135	-34	142	138	-423	-151	-27	-426
12 1S	-6	-8	-25	2	-156	135	14	7119	-34	-424	138	142	426	-27	151
13 1S	-10	-5	-143	19	-132	-440	-16	-150	-11	-11	-21	3	-121	-17	-7117
14 1S	19	-5	-143	-10	-132	150	-16	440	-11	3	-21	-11	7117	-17	121
15 1S	-15	10	445	-15	7136	163	59	-163	-20	-73	131	-73	-135	15	135

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	383	-7003	-117	384	1	86	329	-86	50	-92	559	-92	-11	336	10
2	328	-280	-20	328	-6	88	-561	-88	55	21	-334	21	0	7027	0
3	7063	267	-98	-57	-6	-41	-105	-5	-10	305	64	-539	14	-227	9
4	-57	267	-99	7063	-6	5	-105	41	-10	-539	64	305	-9	-227	-14
5	222	425	82	222	-108	126	58	-126	339	12	-7027	12	61	254	-61
6	381	-299	-480	381	-52	30	6976	-30	132	-123	-328	-123	10	-516	-10
7	7004	131	134	48	7	59	-226	42	-8	-323	237	562	-11	-110	-7
8	48	131	134	7004	7	-42	-226	-59	-8	562	237	-323	7	-109	11
9	-488	-71	131	192	-6	431	117	168	137	-166	-185	-6937	6	-21	28
10	83	-418	30	83	109	-128	-119	128	-364	123	-7013	123	-59	-241	59
11	125	0	7034	125	343	-3	-288	3	50	67	134	67	-106	-67	106
12	192	-71	131	-488	-6	-168	117	-431	137	-6937	-185	-166	-28	-21	-6
13	-65	-50	-11	-65	-8	60	83	-60	7033	-107	314	-107	8	-179	-8
14	-39	1	127	22	145	-6947	-8	168	134	-173	-130	444	177	29	441
15	-121	-27	7026	-121	-325	71	322	-71	-80	0	-49	0	106	35	-106
16	22	1	127	-39	145	-168	-8	6947	134	443	-130	-173	-441	29	-177
17	74	37	54	74	-141	14	-91	-14	7075	107	-311	107	-89	153	89
18	12	3	167	-16	139	462	13	163	90	-8	19	24	138	18	-6984
19	-16	3	167	12	139	-163	13	-462	90	24	19	-8	6984	18	-138
20	9	-9	-499	9	6972	-178	-48	177	169	71	-145	71	150	-16	-150
21	1	-7075	127	1	-5	-80	-296	80	-41	84	-501	84	13	-283	-13
22	11	274	-12	11	9	-98	525	98	-39	-28	290	-28	0	7041	0
23	-16	295	442	-16	67	-37	7080	37	-131	136	189	136	-16	497	16
24	473	78	-38	-179	20	-415	-130	-139	-142	101	30	-7106	10	32	2
25	-179	78	-38	473	20	139	-130	415	-142	-7106	30	101	-2	32	-10
26	2	-8	-25	-6	-156	-7119	15	-135	-34	142	138	-423	-151	-27	-426
27	-6	-8	-25	2	-156	135	14	7119	-34	-424	138	142	426	-27	151
28	-10	-5	-143	19	-132	-440	-16	-150	-11	-11	-21	3	-121	-17	-7117
29	19	-5	-143	-10	-132	150	-16	440	-11	3	-21	-11	7117	-17	121
30	-15	10	445	-15	7136	163	59	-163	-20	-73	131	-73	-135	15	135

TABLE 12. GEOMETRY AND LCAO-MO'S FOR VINYL ETHYNYL ETHANE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	H	0.0	0.0	0.0
2	C	0.0	0.0	1.059999466
3	C	-0.000000000	0.0	2.259999275
4	C	-0.000000001	0.0	3.719958360
5	C	1.433069276	0.0	4.226664861
6	C	2.451575406	0.000000000	3.355893296
7	C	-0.725962945	-1.257404703	4.233331681
8	H	-0.513830551	0.889980619	4.083331426
9	H	1.630416999	-0.000000000	5.288481094
10	H	2.254227683	0.000000001	2.294077064
11	H	3.469809099	0.000000000	3.715893271
12	H	-0.725962946	-1.257404703	5.323330880
13	H	-1.753624045	-1.257404703	3.869998614
14	H	-0.212132396	-2.147385323	3.869998614

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1 1S	-14	-353	14	2	12	14	-6871	-35	-35	27	17	43	-35	-45	26	-38
2 2S	28	607	-29	-3	-24	-27	-4873	100	3210	-3253	-35	-80	100	78	-3253	55
2 PX	63	-14	113	-28	-2	-159	-5	354	1743	5704	89	162	-659	84	-3973	345
2 PY	43	-3	-61	6	-95	1	20	589	-5524	-1223	43	-5	-16	164	-4293	-554
2 PZ	14	79	-13	0	-11	-9	5341	40	2452	-2456	-16	-34	41	32	-2451	42
3 2S	-80	-4787	86	-16	75	53	616	-32	3231	-3190	100	235	-32	-253	-3188	-74
3 PX	-43	54	-96	31	21	175	0	-413	1723	5525	-82	-166	749	-86	-3798	-372
3 PY	-51	-90	31	-2	71	1	9	-670	-5457	-1243	-21	1	23	-154	-4186	625
3 PZ	-52	-5235	49	-14	46	23	-198	165	-2524	2577	63	172	158	-182	2572	87
4 2S	-32	-3555	64	-278	106	-188	-169	3494	-45	11	3	-92	3529	27	-9	3282
4 PX	-306	63	-219	-294	-256	-189	2	-2980	178	381	-114	-169	5619	-6	-232	-2862
4 PY	111	-176	429	-20	300	-4	-9	-4839	-436	-132	-351	39	166	-110	-269	4859
4 PZ	-108	5956	175	-148	176	-9	226	2128	-101	23	117	257	2204	-323	30	2060
5 2S	221	100	-3254	186	55	-241	16	13	-54	-282	-3214	3906	4001	107	161	-14
5 PX	-221	40	-2967	-265	-62	-373	-16	-161	49	274	-3022	753	-5516	-62	-158	-80
5 PY	166	-16	4948	2	59	1	-1	-644	80	14	-4902	15	94	68	71	611
5 PZ	-106	490	2405	-458	-35	-404	21	176	9	-13	2397	5751	-1484	-30	-17	165
6 2S	-49	161	-3239	-3986	-6	4087	18	132	-79	-89	-3279	-221	-182	-36	119	132
6 PX	-5	10	2823	-5583	-16	-597	-11	-21	-39	-45	2818	426	-424	31	66	-26
6 PY	-174	16	5029	29	-87	2	2	594	-36	-1	-5045	-8	-13	-54	-44	-558
6 PZ	-63	81	-2450	-1491	-17	-5733	-5	134	63	75	-2487	446	-472	-31	-114	130
7 2S	3584	43	112	37	-3615	14	11	3667	-147	69	-252	-50	-38	-3579	-245	-30
7 PX	-5654	34	18	-24	-2706	-10	12	2767	-100	-12	-13	4	508	104	-145	-315
7 PY	-170	53	68	60	5003	43	20	4899	-115	63	-273	-75	-53	163	-266	354
7 PZ	-1896	535	-82	-32	1911	-11	22	-1953	-30	3	156	5	231	-5995	-40	224
8 1S	-169	21	-474	77	-428	35	25	8	457	250	181	-138	-19	160	90	7088
9 1S	-8	-422	7	293	-4	497	-34	-135	21	137	19	7071	-195	-16	-57	-145
10 1S	-28	2	-7	273	-15	7016	-19	34	96	107	-12	522	-303	1	-160	33
11 1S	62	-133	3	-7072	21	-279	-1	-79	58	56	-2	-291	504	11	-83	-84
12 1S	-138	-432	0	15	129	0	-35	-27	104	-37	-7	26	-158	-7129	149	-167
13 1S	7121	136	-76	-60	130	-23	13	-25	-1	-19	147	47	447	139	-14	-172
14 1S	-128	133	-6	23	-7102	25	12	-17	-3	-6	-19	5	-135	128	-16	448

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	-14	-353	14	2	12	14	-6871	-35	-35	27	17	43	-35	-45	26	-38
2	8	350	-9	-2	-8	-11	-7230	37	349	-376	-11	-28	37	28	-379	35
3	75	284	7	-13	-73	-102	7	609	-43	63	54	37	-314	191	-7118	-108
4	6	284	58	-13	58	-56	-19	-312	7053	12	-33	-3	-90	-60	23	606
5	-24	102	-119	21	-30	112	5	-120	-39	-7107	-85	-178	581	7	70	-321
6	-92	-7094	95	-21	85	53	268	100	311	-243	114	288	95	-305	-246	14
7	-68	-31	-16	14	69	111	345	-709	23	-67	-40	-55	351	-177	-6976	111
8	15	77	-30	8	-36	55	332	341	7034	-36	14	-7	90	61	-36	-651
9	11	-66	100	-27	9	-126	341	133	25	-6987	80	168	-668	4	-69	343
10	77	-6536	-119	-10	-99	-85	-281	-95	65	-14	-99	-268	-144	293	-30	-143
11	-297	-5	-96	-422	-105	-251	-17	-72	93	324	-57	-110	6989	-84	-185	-117
12	156	-209	475	-76	421	-23	-26	156	-434	-236	-166	125	224	-155	-91	6877
13	-1	40	-131	-47	-3	-16	-13	7000	183	-49	330	69	-11	0	289	-51
14	327	-106	-249	437	90	258	16	83	-72	-370	-181	105	6960	118	220	2
15	9	457	-391	-300	-5	-519	24	125	-16	-133	-382	6985	296	28	55	128
16	150	-137	-34	133	50	-109	-9	-587	52	20	-7004	-221	-163	76	53	321
17	-84	-113	-7032	130	-33	-111	-7	323	-61	0	-70	-243	-297	-20	-47	-543
18	22	26	-324	-271	12	7051	16	-27	-90	-105	-316	-550	337	0	151	-23
19	-49	123	-363	-7005	-20	339	0	96	-58	-66	-400	322	-560	-5	88	91
20	81	80	-7037	242	59	-222	8	-306	34	13	58	-104	-56	-1	8	537
21	-164	103	75	284	-63	-218	12	533	-17	10	-7076	-115	-74	-78	-54	-308
22	-105	-81	135	60	73	36	18	6992	-187	73	-370	-98	84	99	-358	41
23	150	485	-15	-9	-152	-2	24	141	-100	37	9	-40	181	-6981	-158	179
24	6989	-160	65	48	-149	19	-10	138	17	44	-160	-50	-501	-144	8	177
25	135	-157	38	-24	-7002	-24	-10	63	-24	-15	16	8	159	-132	18	-459
26	-169	21	-474	77	-428	35	25	8	457	250	181	-138	-19	160	90	7088
27	-8	-422	7	293	-4	497	-34	-135	21	137	19	7071	-195	-16	-57	-145
28	-28	2	-7	273	-15	7016	-19	34	96	107	-12	522	-303	1	-160	33
29	62	-133	3	-7072	21	-279	-1	-79	58	56	-2	-291	504	11	-83	-84
30	-138	-432	0	15	129	0	-35	-27	104	-37	-7	26	-158	-7129	149	-167
31	7121	136	-76	-60	130	-23	13	-25	-1	-19	147	47	447	139	-14	-172
32	-128	133	-6	23	-7102	25	12	-17	-3	-6	-19	5	-135	128	-16	448

TABLE 13. GEOMETRY AND LCAO-MO'S FOR VINYL ETHYNYL METHANE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	H	0.0	0.0	0.0
2	C	0.0	0.0	1.059999466
3	C	-0.000000000	0.0	2.259999275
4	C	-0.000000001	0.0	3.719998360
5	C	1.433069276	0.0	4.226664861
6	C	2.451575406	0.000000000	3.355893296
7	H	-0.513830551	0.889980619	4.083331426
8	H	-0.513830551	-0.889980619	4.083331426
9	H	1.630416999	-0.000000000	5.288481094
10	H	2.254227683	0.000000001	2.294017064
11	H	3.469809099	0.000000000	3.715893271

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13
1 1S	15	-14	33	15	-34	-2	37	-37	6871	351	34	-22	-44
2 2S	-31	27	-3231	-31	98	4	-98	98	4870	-600	-3231	3266	81
2 PX	104	159	-3010	104	-664	28	-362	362	20	13	-2859	-5860	-164
2 PY	78	0	-4954	-78	0	0	-589	-589	0	0	5040	85	0
2 PZ	-14	10	-2457	-14	40	0	-41	41	-5343	-77	-2457	2454	34
3 2S	94	-53	-3209	94	-26	16	68	-68	-612	4792	-3209	3172	-245
3 PX	-91	-176	-2893	-91	760	-31	399	-399	8	-104	-2747	-5634	169
3 PY	-40	0	-4914	40	0	0	629	629	0	0	5000	85	0
3 PZ	56	-23	2543	56	167	14	-98	97	199	5252	2543	-2585	-176
4 2S	47	186	25	47	3604	283	-3402	3402	172	3632	25	-12	76
4 PX	-184	188	-229	-185	5580	285	2995	-2995	-6	-154	-218	-399	184
4 PY	-488	0	-462	489	0	0	4777	4777	0	0	471	7	0
4 PZ	160	9	79	160	2266	154	-2142	2142	-223	-5936	78	-16	-279
5 2S	-3229	240	115	-3229	4004	-182	8	-8	-17	-93	108	294	-3896
5 PX	-2990	367	-111	-2989	-5535	262	98	-98	17	-41	-104	-287	-764
5 PY	-4938	0	64	4938	0	0	605	605	0	0	-66	-1	0
5 PZ	2397	402	-14	2396	-1472	454	-192	192	-21	-491	-13	10	-5751
6 2S	-3262	-4087	103	-3262	-178	3986	-137	137	-19	-164	100	92	219
6 PX	2826	595	53	2826	-423	5584	28	-28	11	-8	51	45	-428
6 PY	-5013	0	-13	5013	0	0	-595	-595	0	0	13	0	0
6 PZ	-2472	5736	-91	-2472	-468	1492	-132	132	5	-82	-88	-80	-451
7 1S	184	-35	172	-487	-3	-77	91	7080	-25	-8	-479	-185	142
8 1S	-487	-35	-479	184	-3	-77	-7080	-91	-25	-8	183	-174	142
9 1S	12	-496	-43	12	-189	-293	151	-151	34	422	-40	-140	-7073
10 1S	-9	-7015	-133	-9	-303	-273	-34	34	19	0	-129	-112	-525
11 1S	0	280	-73	0	503	7072	85	-85	1	132	-71	-56	294

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13
1	15	-14	33	15	-34	-2	37	-37	6871	351	34	-22	-44
2	-10	11	-360	-10	36	2	-35	35	7230	-347	-360	385	29
3	79	82	-7067	-30	-220	13	-622	-202	8	-280	0	-45	-20
4	-34	79	0	78	-206	13	217	622	8	-281	-7065	-42	-17
5	-103	-114	62	-105	600	-21	230	-244	-16	-297	60	7133	182
6	105	-53	-282	105	106	21	-26	26	-264	7110	-282	226	-295
7	-48	-87	-7015	8	242	-11	675	206	-335	-41	-4	59	34
8	10	-83	-4	-46	226	-11	-222	-674	-335	-39	-7017	57	30
9	92	130	-56	93	-697	27	-251	266	-346	88	-54	6960	-174
10	-115	84	-55	-115	-160	8	154	-154	279	6957	-55	7	280
11	-80	250	-151	-81	7013	419	125	-125	16	-23	-143	-336	108
12	-200	18	-197	491	178	69	-164	6920	24	165	457	157	-117
13	491	18	456	-200	178	69	-6920	164	24	165	-208	146	-117
14	-215	-253	156	-215	6974	-430	-18	18	-17	111	147	388	-95
15	-386	517	38	-386	303	299	-134	134	-24	-455	35	135	-6980
16	-7021	108	49	-37	-241	-129	547	308	8	128	-43	-10	231
17	-37	108	-42	-7021	-241	-129	-308	-547	8	128	50	-9	231
18	-320	-7053	125	-320	335	270	22	-22	-17	-27	121	110	553
19	-380	-340	76	-380	-556	7006	-93	93	0	-123	73	66	-326
20	45	221	-6	-7044	-62	-263	303	539	-10	-94	-24	-12	108
21	-7044	221	-25	45	-62	-263	-539	-303	-10	-94	-5	-12	108
22	184	-35	172	-487	-3	-77	91	7080	-25	-8	-479	-185	142
23	-487	-35	-479	184	-3	-77	-7080	-91	-25	-8	183	-174	142
24	12	-496	-43	12	-189	-293	151	-151	34	422	-40	-140	-7073
25	-9	-7015	-133	-9	-303	-273	-34	34	19	0	-129	-112	-525
26	0	280	-73	0	503	7072	85	-85	1	132	-71	-56	294

TABLE 14. GEOMETRY AND LCAO-MO'S FOR ISOPROPYL ACETYLENE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	H	0.0	0.0	0.0
2	C	0.0	0.0	1.059999466
3	C	-0.000000000	0.0	2.259999275
4	C	-0.000000001	0.0	3.719998360
5	C	1.451925888	0.0	4.233331681
6	C	-0.725962943	-1.257404704	4.233331681
7	H	-0.513830551	0.889980619	4.083331426
8	H	1.451925888	-0.000000001	5.323330880
9	H	1.965756439	-0.889980618	3.869998613
10	H	1.965756438	0.889980619	3.869998615
11	H	-0.725962944	-1.257404704	5.323330880
12	H	-1.753624043	-1.257404706	3.869998614
13	H	-0.212132393	-2.147385323	3.869998614

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1 1S	-35	11	35	354	14	-37	-6873	-34	-27	45	45	-27	11	-14
2 2S	101	-24	-101	-610	-29	98	-4871	3208	3255	-78	-78	3254	-24	29
2 PX	359	-4	694	2	-59	348	-10	2966	2875	-86	184	-5835	85	-66
2 PY	594	-95	14	-4	-41	-602	18	-4978	5077	-163	-7	-108	-44	-30
2 PZ	41	-11	-41	-80	-14	42	5340	2452	2455	-32	-32	2455	-11	14
3 2S	-31	72	31	4786	83	-70	614	3233	3190	252	252	3190	72	-83
3 PX	-414	23	-791	-50	40	-370	-4	2928	2756	86	-177	-5666	-73	64
3 PY	-674	71	-21	87	50	641	7	-4918	4952	154	2	-65	15	9
3 PZ	166	44	-166	5233	54	91	-197	-2521	-2573	182	182	-2573	44	-54
4 2S	3520	103	-3520	3527	38	3310	-167	-59	0	-26	-27	-1	103	-38
4 PX	-2961	-258	-5671	-98	307	-2839	5	242	139	8	-97	-362	-131	55
4 PY	-4838	301	-145	170	-112	4918	-8	-410	339	108	46	37	374	322
4 PZ	2147	173	-2147	-5971	112	2074	227	-106	-26	322	322	-27	173	-112
5 2S	-35	89	-3675	-38	-224	-47	10	-108	-116	-105	3580	253	-3613	3581
5 PX	-201	-40	5635	57	223	-129	-23	105	104	73	190	-315	-2978	3000
5 PY	-459	27	-49	9	-110	444	0	36	-43	-56	8	2	4845	4846
5 PZ	230	-70	1958	-541	145	237	22	-24	-9	15	5992	39	1910	-1892
6 2S	3675	-3613	35	-38	-3581	-47	10	-102	253	3580	-105	-122	89	224
6 PX	2774	-2707	-498	-36	5697	-320	12	-81	156	-102	12	-18	-3	16
6 PY	4905	5002	54	-45	175	334	19	-66	274	-161	-91	-117	49	248
6 PZ	-1958	1910	-230	-541	1892	237	22	-23	40	5992	15	-10	-70	-145
7 1S	-17	-420	17	-10	154	7097	24	478	-184	-162	-162	-174	-420	-154
8 1S	-159	0	26	433	-13	-170	-35	79	65	24	7131	-153	130	-139
9 1S	-136	-3	17	-129	-23	443	12	0	1	3	-129	19	-7105	-128
10 1S	443	-72	25	-142	136	-159	14	-3	21	63	-141	12	130	7123
11 1S	-26	130	159	433	139	-170	-35	76	-153	7131	24	69	0	13
12 1S	-25	130	-443	-142	-7123	-159	14	-3	12	-141	63	21	-72	-136
13 1S	-17	-7105	136	-129	128	443	12	0	19	-129	3	1	-3	23

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	-35	11	35	354	14	-37	-6873	-34	-27	45	45	-27	11	-14
2	37	-8	-37	-352	-9	35	-7228	349	377	-28	-28	377	-7	9
3	626	-84	227	-294	-71	-232	6	-42	7108	-197	22	-60	-12	-30
4	-207	50	220	-287	-13	627	-19	7054	-16	32	35	-17	51	12
5	-241	-10	-626	-294	30	-218	6	-43	-59	26	-197	7109	-83	72
6	101	81	-101	7091	96	19	268	313	246	305	305	247	81	-96
7	-123	73	-252	48	66	243	342	22	6990	181	-32	57	-4	18
8	222	-26	-237	-75	-4	-670	331	7033	39	-35	-38	40	-28	5
9	267	-6	724	47	-19	229	342	24	57	-35	181	6989	73	-66
10	167	420	-167	200	-153	6891	-26	-450	175	152	152	165	420	153
11	-95	-98	99	6935	-77	-141	-280	61	22	-292	-292	23	-98	77
12	-38	-109	-7010	-40	302	-64	-13	137	106	86	0	-304	-5	-6
13	7010	-5	38	-40	6	-64	-13	130	-304	0	86	113	-109	-302
14	181	-16	-141	-487	13	182	24	-75	-66	-39	6979	161	-152	151
15	158	28	-67	153	14	-459	-10	-30	17	12	132	-15	-7000	135
16	80	97	-7004	90	-336	13	17	-133	-140	-117	-95	373	73	-112
17	-451	67	-137	167	-141	169	-11	21	-43	-67	144	-11	-147	6989
18	141	-152	-181	-487	-151	182	24	-71	161	6979	-39	-70	-16	-13
19	137	-147	491	167	-6989	169	-11	22	-12	144	-67	-42	68	141
20	7004	73	-80	90	112	13	17	-125	373	-95	-117	-148	98	336
21	67	-7000	-158	153	-135	-459	-10	-30	-14	132	12	17	28	-14
22	-17	-420	17	-10	154	7097	24	478	-184	-162	-162	-174	-420	-154
23	-159	0	26	433	-13	-170	-35	79	65	24	7131	-153	130	-139
24	-136	-3	17	-129	-23	443	12	0	1	3	-129	19	-7105	-128
25	443	-72	25	-142	136	-159	14	-3	21	63	-141	12	130	7123
26	-26	130	159	433	139	-170	-35	76	-153	7131	24	69	0	13
27	-25	130	-443	-142	-7123	-159	14	-3	12	-141	63	21	-72	-136
28	-17	-7105	136	-129	128	443	12	0	19	-129	3	1	-3	23

TABLE 15. GEOMETRY AND LCAO-MO'S FOR ETHANE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.539999962
3	H	1.027661100	0.0	-0.363333067
4	H	-0.513830551	-0.889980619	-0.363333067
5	H	-0.513830549	0.889980620	-0.363333067
6	H	-1.027661100	-0.000000000	1.903333028
7	H	0.513830551	-0.889980619	1.903333028
8	H	0.513830550	0.889980619	1.903333028

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7
1 2S	-3577	-54	-3690	-54	-54	3577	3577
1 PX	2794	258	0	-517	258	-2794	5588
1 PY	4839	448	0	0	-448	4839	0
1 PZ	2190	40	-6031	40	40	-2190	-2190
2 2S	54	3577	-3690	3577	3577	-54	-54
2 PX	258	2794	0	-5588	2794	-258	517
2 PY	448	4839	0	0	-4839	448	0
2 PZ	40	2190	6031	2190	2190	-40	-40
3 1S	123	-158	5	440	-158	-123	7115
4 1S	-7115	440	5	-158	-158	-123	-123
5 1S	123	-158	5	-158	440	7115	-123
6 1S	158	-123	5	7115	-123	-158	440
7 1S	158	-123	5	-123	7115	440	-158
8 1S	-440	7115	5	-123	-123	-158	-158

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7
1	107	7	-7068	7	7	-107	-107
2	-139	172	-104	-461	172	139	6983
3	-6983	-461	-104	172	172	139	139
4	-139	172	-104	172	-461	6983	139
5	-7	-108	-7068	-107	-107	7	7
6	-172	139	-104	6983	139	172	-461
7	-172	139	-104	139	6983	-461	172
8	461	6983	-104	139	139	172	172
9	123	-158	5	440	-158	-123	7115
10	-7115	440	5	-158	-158	-123	-123
11	123	-158	5	-158	440	7115	-123
12	158	-123	5	7115	-123	-158	440
13	158	-123	5	-123	7115	440	-158
14	-440	7115	5	-123	-123	-158	-158

TABLE 16. GEOMETRY AND LCAO-MO'S FOR PENTANE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.539999962
3	C	-1.451925888	-0.000000001	2.053333283
4	C	-1.451925888	0.0	3.593333245
5	C	-2.903851776	-0.000000001	4.106666566
6	H	1.027661100	0.0	-0.363333067
7	H	-0.513830551	-0.889980619	-0.363333067
8	H	-0.513830549	0.889980620	-0.363333067
9	H	0.513830551	-0.889980619	1.903333028
10	H	0.513830550	0.889980619	1.903333028
11	H	-1.965756439	0.889980618	1.690000216
12	H	-1.965756437	-0.889980621	1.690000218
13	H	-0.938095337	-0.889980618	3.956666312
14	H	-0.938095340	0.889980620	3.956666311
15	H	-3.417682327	0.889980617	3.743333498
16	H	-2.903851776	-0.000000000	5.196665765
17	H	-3.417682325	-0.889980622	3.743333501

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1 2S	-36	225	-3550	52	-5	-3593	36	64	64	3593	-67	-5	96	-96	-3710	-30
1 PX	-4	139	-5576	552	-6	2784	4	-265	-265	-2784	-49	-6	48	-48	-74	-21
1 PY	14	0	0	0	1	-4840	14	-442	442	-4840	0	-1	25	25	0	0
1 PZ	-58	260	2220	-100	-5	2173	58	-25	-25	-2173	-85	-5	67	-67	-6023	-35
2 2S	98	-11	19	-3642	33	75	-98	-3486	-3486	-75	213	33	84	-84	-3612	62
2 PX	-83	77	-379	5650	-53	193	83	-2957	-2957	-193	-284	-53	102	-102	-196	-98
2 PY	22	0	0	0	-14	-438	22	-4788	4788	-438	0	14	-431	-431	0	0
2 PZ	-14	401	0	-2109	18	53	14	-2107	-2107	-53	-5	18	172	-172	6041	4
3 2S	79	3621	-217	-3621	-94	94	-79	79	79	-94	-7	-94	-3497	3497	7	-217
3 PX	-201	-134	-287	-5634	-38	77	201	-113	-113	-77	-399	-38	2958	-2958	74	-91
3 PY	-433	0	0	0	-25	25	-433	-433	433	25	0	25	-4793	-4793	0	0
3 PZ	-48	6024	4	2134	-68	13	48	-173	-173	-13	62	-68	2092	-2092	397	-272
4 2S	-3486	3642	62	11	-75	-33	3486	98	98	33	3612	-75	84	-84	-213	19
4 PX	-2972	105	-28	-404	-114	0	2972	-41	-41	0	-5630	-114	196.	-196	99	-126
4 PY	-4788	0	0	0	438	14	-4788	22	-22	14	0	-438	-431	-431	0	0
4 PZ	-2085	-6030	-94	61	-164	56	2085	-73	-73	-56	2197	-164	39	-39	266	-357
5 2S	64	-53	-30	-225	3593	5	-64	-36	-36	-5	3710	3593	96	-96	66	-3551
5 PX	-112	-89	-40	-291	-2977	7	112	-56	-56	-7	5703	-2977	80	-80	97	235
5 PY	-442	0	0	0	4840	-1	-442	14	-14	-1	0	-4840	25	25	0	0
5 PZ	-241	-554	-8	-45	-1901	4	241	14	14	-4	-1938	-1900	23	-23	18	-5957
6 1S	11	-136	-7140	-449	11	135	-11	162	162	-135	58	11	-70	70	20	31
7 1S	8	20	132	145	-4	121	12	-439	151	7118	-13	-3	-11	-2	10	-8
8 1S	-12	20	132	145	-3	-7118	-8	151	-439	-121	-13	-3	2	11	11	-8
9 1S	-11	-145	155	27	-8	-426	-3	136	-7122	-151	20	12	-424	-143	28	14
10 1S	3	-145	155	27	12	151	11	-7122	136	426	20	-8	143	424	28	14
11 1S	144	-34	-19	34	-1	1	426	144	-426	11	-143	11	-7121	-133	143	-19
12 1S	-426	-34	-19	34	11	-11	-144	-426	144	-1	-143	-1	133	7121	143	-19
13 1S	136	-27	14	145	426	8	7122	-11	3	12	-28	-152	-424	-143	-20	155
14 1S	-7122	-27	14	145	-151	-12	-136	3	-11	-8	-28	426	143	424	-20	155
15 1S	151	-145	-8	-20	7118	3	439	-12	8	-4	-10	-121	2	11	13	131
16 1S	162	449	31	136	-135	-11	-162	11	11	11	-20	-135	-70	70	-58	-7140
17 1S	-439	-145	-8	-20	-121	3	-151	8	-12	-3	-10	7118	-11	-2	13	132

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	-68	338	147	-60	-7	85	68	10	10	-85	-107	-7	106	-106	-7072	-45
2	-5	151	-6969	506	-6	-150	5	-176	-176	150	-49	-6	68	-68	-177	-22
3	-9	-19	-139	-170	0	-138	-10	461	-165	6983	11	3	-9	-26	-86	3
4	10	-19	-139	-170	3	-6983	9	-165	461	138	11	0	26	9	-86	3
5	61	-353	10	5	0	-8	-61	81	81	8	111	0	-107	107	-7038	27
6	113	47	319	-7043	65	-105	-113	62	62	105	338	65	8	-8	96	113
7	-4	141	-145	-123	10	442	-27	-172	-6945	178	-10	-9	439	171	-141	-7
8	27	141	-145	-123	-9	-178	4	-6945	-172	-442	-10	10	-171	-439	-141	-7
9	-170	126	6	-176	-29	29	-442	-170	442	6	141	6	-6950	171	-141	6
10	-110	-37	-344	-7027	-59	106	110	-2	-2	-106	-348	-59	62	-62	-49	-104
11	-2	7027	-104	37	-106	59	2	-110	-110	-59	49	-106	62	-62	348	-344
12	442	126	6	-126	6	-6	170	442	-170	-29	141	-29	-171	6950	-141	6
13	-172	123	-7	-141	-442	-10	6945	-4	27	-9	141	178	439	171	10	-145
14	-6945	123	-7	-141	178	9	172	27	-4	10	141	-442	-171	-439	10	-145
15	62	7043	113	-47	105	-65	-62	113	113	65	-96	105	8	-8	-338	319
16	81	-5	27	353	8	0	-81	61	61	0	7038	8	-107	107	-111	10
17	-165	170	3	19	6983	-3	-461	10	-9	0	86	138	26	9	-11	-140
18	-176	-506	-22	-151	150	6	176	-5	-5	-6	177	150	68	-68	49	-6969
19	461	170	3	19	138	0	165	-9	10	3	86	6983	-9	-26	-11	-139
20	10	60	-45	-338	-85	7	-10	-68	-68	-7	7072	-85	106	-106	107	147
21	11	-136	-7140	-449	11	135	-11	162	162	-135	58	11	-70	70	20	31
22	8	20	132	145	-4	121	12	-439	151	7118	-13	-3	-11	-2	10	-8
23	-12	20	132	145	-3	-7118	-8	151	-439	-121	-13	-3	2	11	11	-8
24	-11	-145	155	27	-8	-426	-3	136	-7122	-151	20	12	-424	-143	28	14
25	3	-145	155	27	12	151	11	-7122	136	426	20	-8	143	424	28	14
26	144	-34	-19	34	-1	1	426	144	-426	11	-143	11	-7121	-133	143	-19
27	-426	-34	-19	34	11	-11	-144	-426	144	-1	-143	-1	133	7121	143	-19
28	136	-27	14	145	426	8	7122	-11	3	12	-28	-152	-424	-143	-20	155
29	-7122	-27	14	145	-151	-12	-136	3	-11	-8	-28	426	143	424	-20	155
30	151	-145	-8	-20	7118	3	439	-12	8	-4	-10	-121	2	11	13	131
31	162	449	31	136	-135	-11	-162	11	11	11	-20	-135	-70	70	-58	-7140
32	-439	-145	-8	-20	-121	3	-151	8	-12	-3	-10	7118	-11	-2	13	132

TABLE 17. GEOMETRY AND LCAO-MO'S FOR ISOBUTANE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.539999962
3	C	-0.725962945	-1.257404703	-0.513333321
4	C	-0.725962942	1.257404704	-0.513333321
5	H	1.027661100	0.0	-0.363333067
6	H	-1.027661100	-0.000000000	1.903333028
7	H	0.513830551	-0.889980619	1.903333028
8	H	0.513830550	0.889980619	1.903333028
9	H	-0.725962944	-1.257404703	-1.603332520
10	H	-0.212132396	-2.147385323	-0.150000254
11	H	-1.753624045	-1.257404703	-0.150000255
12	H	-0.725962943	1.257404704	-1.603332520
13	H	-1.753624042	1.257404706	-0.150000254
14	H	-0.212132392	2.147385323	-0.150000255

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13
1 2S	-3557	35	-35	3557	-98	98	3348	-35	35	98	35	3557	35
1 PX	2706	-89	212	176	-389	430	5694	212	-250	390	-89	-2706	-250
1 PY	-4992	-67	-279	0	-71	0	0	279	-212	-71	67	-4992	212
1 PZ	2100	333	14	6052	181	-65	-2013	14	-123	-181	333	-2100	-123
2 2S	48	-221	3575	3700	-87	-3607	-58	3575	101	87	-221	-48	101
2 PX	264	-64	2797	58	1	5584	523	2797	52	-1	-64	-264	52
2 PY	-474	-109	-4829	0	60	0	0	4828	-20	60	109	-474	20
2 PZ	99	253	2194	-5991	59	-2166	-29	2194	-68	-59	254	-99	-68
3 2S	48	-3575	-101	-48	-87	87	-58	221	-221	-3607	101	3700	-3575
3 PX	310	97	-69	-36	-44	9	450	141	-205	5675	81	2873	-2690
3 PY	-394	184	-50	-79	-18	79	-126	243	-133	156	30	4875	5014
3 PZ	229	5993	18	545	-69	-28	-236	-35	-144	-1910	14	1969	-1892
4 2S	-3700	101	221	-48	3607	87	-58	-101	-3575	87	-3575	-48	-221
4 PX	-2873	81	141	-36	-5675	9	450	-69	-2690	44	97	-310	-205
4 PY	4875	-30	-243	79	156	-79	126	50	-5013	-18	-185	-394	133
4 PZ	-1969	14	-35	545	1910	-28	-236	18	-1892	69	5993	-230	-144
5 1S	34	152	-152	-34	413	-413	7122	-152	152	-413	152	-34	152
6 1S	138	-22	-129	-16	2	-7117	441	-129	-3	-2	-22	-138	-3
7 1S	-442	-16	7134	-24	71	132	-161	-140	-64	1	137	-150	-20
8 1S	150	137	-140	-24	-1	132	-161	7134	-20	-71	-16	442	-64
9 1S	150	-7134	64	442	-1	-71	-161	-137	-16	132	-20	-24	140
10 1S	-442	140	20	-150	71	1	-161	16	137	132	-64	-24	-7134
11 1S	138	129	3	-138	2	-2	441	22	-22	-7117	-3	-16	129
12 1S	24	-20	-137	442	-132	-71	-161	64	140	1	-7134	-150	-16
13 1S	16	-3	22	-138	7117	-2	441	3	129	-2	129	-138	-22
14 1S	24	-64	16	-150	-132	1	-161	20	-7134	-71	140	442	137

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13
1	40	306	-5	7019	107	-7	-69	-5	-89	-107	306	-40	-89
2	-175	-151	151	175	-420	420	6905	151	-151	420	-151	175	-151
3	40	5	89	-40	107	-107	-69	-306	306	-7	-89	7019	5
4	-7019	-89	-306	-40	7	-107	-69	89	5	-107	5	-40	306
5	-61	-330	-113	7039	-95	72	-3	-113	109	95	-330	61	109
6	-162	15	137	72	-27	-6989	-465	137	-11	27	15	162	-11
7	496	13	6977	144	-68	-149	176	148	66	-16	-141	174	37
8	-174	-141	148	144	16	-149	176	6977	37	68	13	-496	66
9	-61	113	-109	61	-95	95	-3	330	-330	72	110	7038	113
10	-174	-6977	-66	-496	16	68	176	141	13	-149	37	144	-148
11	496	-148	-37	174	-68	-16	176	-13	-141	-149	66	144	-6577
12	-162	-137	11	162	-27	27	-465	-15	15	-6989	-11	72	-137
13	-7039	109	330	61	-72	95	-3	-109	113	95	113	61	-330
14	-144	37	141	-496	149	68	176	-66	-148	-16	-6977	174	13
15	-72	-11	-15	162	6989	27	-465	11	-137	27	-137	162	15
16	-144	66	-13	174	149	-16	176	-37	-6977	68	-148	-496	-141
17	34	152	-152	-34	413	-413	7122	-152	152	-413	152	-34	152
18	138	-22	-129	-16	2	-7117	441	-129	-3	-2	-22	-138	-3
19	-442	-16	7134	-24	71	132	-161	-140	-64	1	137	-150	-20
20	150	137	-140	-24	-1	132	-161	7134	-20	-71	-16	442	-64
21	150	-7134	64	442	-1	-71	-161	-137	-16	132	-20	-24	140
22	-442	140	20	-150	71	1	-161	16	137	132	-64	-24	-7134
23	138	129	3	-138	2	-2	441	22	-22	-7117	-3	-16	129
24	24	-20	-137	442	-132	-71	-161	64	140	1	-7134	-150	-16
25	16	-3	22	-138	7117	-2	441	3	129	-2	129	-138	-22
26	24	-64	16	-150	-132	1	-161	20	-7134	-71	140	442	137

TABLE 18. GEOMETRY AND LCAO-MO'S FOR ISOPENTANE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.539999962
3	C	-0.725962945	-1.257404703	-0.513333321
4	C	-0.725962942	1.257404704	-0.513333321
5	C	0.725962945	-1.257404703	2.053333283
6	H	1.027661100	0.0	-0.363333067
7	H	-1.027661100	-0.000000000	1.903333028
8	H	0.513830550	0.889980619	1.903333028
9	H	-0.725962944	-1.257404703	-1.603332520
10	H	-0.212132396	-2.147385323	-0.150000254
11	H	-1.753624045	-1.257404703	-0.150000255
12	H	-0.725962943	1.257404704	-1.603332520
13	H	-1.753624042	1.257404706	-0.150000254
14	H	-0.212132392	2.147385323	-0.150000255
15	H	0.725962945	-1.257404703	3.143332482
16	H	0.212132397	-2.147385323	1.690000216
17	H	1.753624045	-1.257404702	1.690000217

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1 2S	-221	38	3558	-3550	26	-3360	-95	103	-98	-97	40	-35	-16	94	3567	39
1 PX	44	-91	153	2706	-249	-5696	-5	430	-391	-390	-90	250	218	-31	-2708	-203
1 PY	-67	70	36	-4989	208	-5	-46	-8	-70	70	-66	214	-305	0	-4994	-286
1 PZ	-272	332	6037	2117	-129	1999	-68	-61	182	184	339	124	70	83	-2087	-10
2 2S	26	-211	3634	6	94	80	-74	-3498	-87	-90	-225	-100	3631	65	-64	-3471
2 PX	63	-46	-30	190	32	-478	437	5632	3	2	-62	-45	2819	320	-287	-2659
2 PY	-108	77	143	-354	-5	-54	120	-189	51	-56	-94	12	-4877	314	-421	-4962
2 PZ	-368	262	-5999	60	-90	43	-168	-2076	62	58	256	71	2175	173	-108	-2105
3 2S	-38	98	-42	55	-3583	56	-9	78	-88	3608	-3571	222	-96	89	3704	-213
3 PX	-7	79	-39	313	-2690	-450	0	3	-45	-5675	100	205	-63	27	2875	-140
3 PY	20	29	-87	-393	5018	126	36	76	-19	-156	179	133	-57	-62	4870	-252
3 PZ	-11	14	536	231	-1881	234	-26	-22	-69	1912	5996	143	16	-66	1970	28
4 2S	63	-3567	-53	-3711	-219	64	32	91	3609	-87	99	3577	220	-18	-54	107
4 PX	45	104	-38	-2878	-202	-445	12	14	-5671	-44	80	2691	141	-24	-313	72
4 PY	-82	-196	84	4887	130	-134	-51	-82	153	19	-28	5008	-243	30	-386	-58
4 PZ	-18	5994	552	-1957	-143	235	12	-30	1912	-69	14	1854	-43	-4	-228	-18
5 2S	-3550	68	-46	-214	78	90	3595	62	36	-15	-33	33	3709	-3602	-92	68
5 PX	-117	-49	47	141	-21	-14	5684	439	-15	4	4	-37	-2851	2703	54	-327
5 PY	193	84	-83	-257	-75	83	-158	122	55	29	23	34	4932	5007	-65	-318
5 PZ	-6001	14	-540	-35	69	17	-1902	-239	-15	27	8	-11	-1942	1890	-23	-242
6 1S	-16	149	-40	42	155	-7123	0	-413	413	413	151	-153	-141	-19	-31	143
7 1S	155	-23	-33	138	-11	-426	426	-7123	1	5	-16	3	-26	154	-132	145
8 1S	153	-16	-39	155	-30	152	-150	147	-1	67	126	20	-36	-420	430	-7138
9 1S	-1	-19	433	148	144	160	-20	-62	0	-131	-7133	16	62	-94	-26	126
10 1S	28	-63	-157	-446	-7128	165	36	0	71	-133	142	-137	9	-82	-26	-18
11 1S	23	-3	-140	137	131	-440	14	-3	2	7115	128	22	5	-10	-17	-21
12 1S	-59	-7137	446	26	-17	156	-10	-75	-133	0	-19	-141	-134	11	-146	-68
13 1S	13	129	-138	17	-21	-439	-9	-1	7118	2	-4	-130	21	-11	-139	-3
14 1S	16	140	-151	24	137	162	13	1	-132	71	-64	7135	16	-1	440	-20
15 1S	-7137	-59	438	123	-88	-63	-134	162	-9	-16	0	-12	-22	138	69	161
16 1S	134	13	-150	-24	-83	-12	-122	154	11	34	21	-9	-11	-7108	-14	-442
17 1S	130	13	-146	-18	-10	1	7114	-437	-9	14	26	13	-11	122	12	150

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	-347	307	7008	58	-99	50	-107	-1	108	111	314	89	52	119	-24	10
2	4	-151	161	-176	-152	-6909	-32	421	-421	-420	-151	151	149	-2	175	-143
3	-2	-89	-52	36	5	72	7	-100	107	7	6	-307	97	36	7023	307
4	-97	10	0	-7019	299	64	-58	-111	8	107	-88	-4	-333	35	-39	-96
5	332	-333	7012	-49	125	2	108	49	-98	-96	-334	-112	-68	-117	61	87
6	-145	7	109	-134	-5	444	-443	-6947	-28	-30	11	7	141	-179	170	-172
7	9	-103	-28	349	38	-104	8	84	-60	12	2	-56	7044	-8	116	79
8	-143	5	174	-151	30	-180	178	-183	12	-67	-130	-39	145	435	-479	-6938
9	-10	107	55	-56	115	0	13	88	-96	-71	113	330	-109	-7	7038	-334
10	-8	36	-485	-172	-162	-174	17	58	16	148	-6978	-13	-62	102	145	-131
11	-40	64	179	500	-6982	-177	-38	-19	-69	149	-140	142	-28	81	150	23
12	-16	-11	165	-161	-138	463	-12	29	-27	6990	-136	-15	7	3	73	15
13	103	128	57	-7051	-325	13	61	101	-67	-95	106	-106	327	-41	52	119
14	47	-6974	-505	-160	14	-171	5	71	148	16	36	148	148	-5	170	69
15	-11	-138	163	-70	14	463	9	25	6987	-27	-11	137	-19	9	163	-10
16	-13	-149	176	-140	-141	-176	-10	-15	150	-68	66	6976	-17	1	-494	36
17	142	109	54	-337	-25	104	-85	7	68	3	-5	59	7067	90	-107	13
18	-6972	46	-491	-138	99	60	150	-176	4	16	-9	6	172	-164	-65	-175
19	-131	-9	172	27	81	-12	138	-166	-10	-38	-37	11	91	-6991	-15	463
20	-138	-10	172	18	2	27	6987	458	9	-12	-15	-10	87	-139	4	-163
21	-16	149	-40	42	155	-7123	0	-413	413	413	151	-153	-141	-19	-31	143
22	155	-23	-33	138	-11	-426	426	-7123	1	5	-16	3	-26	154	-132	145
23	153	-16	-39	155	-30	152	-150	147	-1	67	126	20	-36	-420	430	-7138
24	-1	-19	433	148	144	160	-20	-62	0	-131	-7133	16	62	-94	-26	126
25	28	-63	-157	-446	-7128	165	36	0	71	-133	142	-137	9	-82	-26	-18
26	23	-3	-140	137	131	-440	14	-3	2	7115	128	22	5	-10	-17	-21
27	-59	-7137	446	26	-17	156	-10	-75	-133	0	-19	-141	-134	11	-146	-68
28	13	129	-138	17	-21	-439	-9	-1	7118	2	-4	-130	21	-11	-139	-3
29	16	140	-151	24	137	162	13	1	-132	71	-64	7135	16	-1	440	-20
30	-7137	-59	438	123	-88	-63	-134	162	-9	-16	0	-12	-22	138	69	161
31	134	13	-150	-24	-83	-12	-122	154	11	34	21	-9	-11	-7108	-14	-442
32	130	13	-146	-18	-10	1	7114	-437	-9	14	26	13	-11	122	12	150

TABLE 15. GEOMETRY AND LCAO-MO'S FOR S-GAUCHE-ISOPROPYL ETHYLENE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.339999199
3	C	-1.316358184	-0.000000001	2.099598951
4	C	-2.486880825	-0.000000002	1.099260909
5	C	-1.397936407	-1.257404703	2.985367965
6	H	0.935307370	0.0	-0.539999962
7	H	-0.935307371	0.0	-0.539999962
8	H	0.935307371	0.000000000	1.879999161
9	H	-1.374098576	0.889980619	2.726655793
10	H	-3.430847821	-0.000000001	1.644260508
11	H	-2.429140434	0.889980616	0.472604064
12	H	-2.429140435	-0.889980621	0.472604067
13	H	-1.340196015	-2.147385323	2.358711123
14	H	-0.569450193	-1.257404701	3.693682052
15	H	-2.341903404	-1.257404704	3.530367564

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1 2S	-3247	80	3987	156	-220	-4067	86	-6	3286	-50	-133	133	-37	-188	57
1 PX	-26	-4	4753	70	622	4731	0	-23	58	-50	-78	84	-3	-634	-8
1 PY	5047	-65	-29	16	-7	-2	51	-86	5064	-174	603	598	-53	-13	-6
1 PZ	-3739	-95	-3282	58	-30	3265	-89	2	3758	-37	-101	101	-44	20	-53
2 2S	-3251	95	-183	117	3895	247	87	54	3207	218	28	-2	102	4033	260
2 PX	-96	-69	516	393	4876	544	-58	-66	138	-220	-96	37	-59	-4732	-147
2 PY	4930	90	-2	-16	15	-1	-83	61	4885	167	-634	-665	63	97	2
2 PZ	3816	53	101	311	3149	-18	48	23	-3852	97	-173	228	24	3238	196
3 2S	59	23	274	-3588	-97	174	83	101	-1	-29	-3322	3531	35	3560	-49
3 PX	-4	-89	307	4623	85	137	-102	-25	-21	-291	357	-359	-260	5296	-249
3 PY	421	-319	20	-158	36	4	367	301	346	109	-4913	-4842	-113	173	42
3 PZ	285	118	-120	3885	302	-118	210	314	-172	157	-3496	3622	-208	-2868	263
4 2S	95	-3584	37	-3704	197	54	-3617	90	-112	-97	62	-50	-222	-41	3562
4 PX	12	-118	-22	-4528	118	-193	-146	80	-28	-46	149	-103	-233	393	-5286
4 PY	-51	-4840	1	-52	0	0	4840	29	-57	-53	-457	-471	-110	10	8
4 PZ	94	3531	40	-3915	240	107	3519	1	-93	-46	-215	274	-118	-321	2820
5 2S	108	-216	-38	53	-86	-14	85	-3609	246	3579	39	3689	-3574	-50	-99
5 PX	-52	-121	41	441	6	14	62	-302	-111	-5135	43	312	-4483	505	-21
5 PY	65	-236	-61	80	-70	-41	48	4995	267	-170	-349	4917	178	-69	-82
5 PZ	-65	81	2	314	-1	-2	-27	3295	-108	3088	-394	-3387	-3981	-234	-5
6 1S	1	-75	7074	-126	-293	283	-81	22	5	62	84	-79	11	506	-41
7 1S	-9	-98	-273	15	522	-7040	-95	-14	13	-28	-27	27	0	-290	-36
8 1S	10	-30	-254	-437	7075	-500	-35	-4	-21	-5	136	-126	-13	-193	-132
9 1S	-461	146	-78	45	-128	-34	-401	-421	-175	-168	-7109	-3	151	-35	-149
10 1S	-83	148	-38	31	-112	-180	140	-1	74	16	158	-146	-15	411	7143
11 1S	19	-7131	3	23	11	24	131	-70	28	65	159	440	137	-144	-146
12 1S	-6	128	9	14	15	26	-7113	-3	-14	4	-438	-138	-22	-129	-136
13 1S	-6	-20	-23	142	6	-24	-1	-7113	18	-129	-446	-17	129	-136	5
14 1S	1	138	-15	-441	23	-1	-71	131	12	-139	159	-25	-7132	-150	65
15 1S	-75	-21	61	144	47	25	0	131	-148	7131	176	-24	139	446	18

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	-366	81	7003	116	325	-335	85	-21	404	-49	-91	95	-5	-566	48
2	-329	88	281	16	-554	-7027	86	11	322	21	19	-24	0	331	61
3	84	-68	-288	109	-113	223	20	-62	7092	-165	313	536	-78	-74	-11
4	-7054	23	-246	86	-102	226	-52	59	-69	81	-539	-310	-3	-55	-3
5	-251	126	-429	-83	86	-250	111	87	181	321	13	65	111	6997	335
6	-387	27	300	472	6982	520	28	-5	377	9	-122	118	27	304	126
7	-44	71	-135	-143	-217	110	-51	52	6988	151	-336	-603	72	-154	-5
8	-7017	-56	-131	-120	-239	112	66	-35	79	-85	560	337	-17	-291	-8
9	-126	300	48	40	72	18	-108	-4	-331	0	56	7010	5	-13	87
10	-97	-106	419	-8	-115	242	-125	-104	57	-301	120	-72	-87	6994	-325
11	-127	3	2	-7024	-275	63	-9	-109	110	88	70	-36	306	-92	-8
12	470	-150	77	-183	124	25	411	421	159	154	-6892	161	-154	232	148
13	79	-174	52	-151	114	218	-175	-14	-75	-34	-174	171	12	-455	6967
14	-35	-6978	-1	-147	-14	-35	-145	69	-51	-65	-177	-499	-140	164	140
15	108	117	26	-7037	311	-39	75	99	-127	-105	7	60	-331	56	-111
16	37	-133	-3	-73	-15	-35	-6990	27	29	10	468	166	14	150	128
17	48	13	24	-166	7	23	25	-6992	-16	137	465	68	-136	163	9
18	-17	-142	9	494	-39	1	68	-149	-11	147	-173	144	-6979	175	-67
19	130	-321	-61	-52	-91	-34	93	72	361	-104	-28	7022	115	65	-106
20	65	18	-48	-168	-48	-19	-16	-150	159	6978	-184	143	-148	-505	-35
21	1	-75	7074	-126	-293	283	-81	22	5	62	84	-79	11	506	-41
22	-9	-98	-273	15	522	-7040	-95	-14	13	-28	-27	27	0	-290	-36
23	10	-30	-294	-437	7075	-500	-35	-4	-21	-5	136	-126	-13	-193	-132
24	-461	146	-78	45	-128	-34	-401	-421	-175	-168	-7109	-3	151	-35	-149
25	-83	148	-38	31	-112	-180	140	-1	74	16	158	-146	-15	411	7143
26	19	-7131	3	23	11	24	131	-70	28	65	159	440	137	-144	-146
27	-6	128	9	14	15	26	-7113	-3	-14	4	-438	-138	-22	-129	-136
28	-6	-20	-23	142	6	-24	-1	-7113	18	-129	-446	-17	129	-136	5
29	1	138	-15	-441	23	-1	-71	131	12	-139	159	-25	-7132	-150	65
30	-75	-21	61	144	47	25	0	131	-148	7131	176	-24	139	446	18

TABLE 20. GEOMETRY AND LCAO-MO'S FOR ETHYLENE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.339999199
3	H	0.935307370	0.0	-0.539999962
4	H	-0.935307371	0.0	-0.539999962
5	H	-0.935307370	-0.000000000	1.879999161
6	H	0.935307371	0.000000000	1.879999161

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6
1 2S	214	-4019	-3264	-3264	214	-4019
1 PX	627	-4757	0	0	-627	4757
1 PY	0	0	4999	-5000	0	0
1 PZ	36	3270	-3787	-3787	36	3270
2 2S	-4019	214	-3264	-3264	-4019	214
2 PX	4757	-627	0	0	-4757	627
2 PY	0	0	4999	-5000	0	0
2 PZ	-3270	-36	3787	3787	-3270	-36
3 1S	-518	-7045	-14	-14	299	253
4 1S	299	253	-14	-14	-518	-7045
5 1S	-7045	-518	-14	-14	253	299
6 1S	253	299	-14	-14	-7045	-518

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6
1	552	-7020	-338	-338	-334	-292
2	-334	-292	-338	-338	552	-7020
3	108	247	16	-7054	108	247
4	108	247	-7054	16	108	247
5	-7020	552	-338	-338	-292	-334
6	-292	-334	-338	-338	-7020	552
7	247	108	16	-7054	247	108
8	247	108	-7054	16	247	108
9	-518	-7045	-14	-14	299	253
10	299	253	-14	-14	-518	-7045
11	-7045	-518	-14	-14	253	299
12	253	299	-14	-14	-7045	-518

TABLE 21. GEOMETRY AND LCAO-MO'S FOR PROPENE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.339999199
3	C	-1.316358184	-0.000000001	2.099998951
4	H	0.935307370	0.0	-0.539999962
5	H	-0.935307371	0.0	-0.539999962
6	H	0.935307371	0.000000000	1.879999161
7	H	-1.374098574	-0.889980619	2.726655795
8	H	-2.144844400	-0.000000001	1.391684866
9	H	-1.374098576	0.889980619	2.726655793

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9
1 2S	137	3995	-3261	-181	208	-4055	187	-137	-3261
1 PX	77	4745	-43	-57	-629	4743	643	-77	-43
1 PY	-600	0	-5037	0	0	0	0	-600	5037
1 PZ	97	-3286	-3756	-52	22	3247	-39	-97	-3756
2 2S	-24	-171	-3211	-124	-3895	256	-4035	23	-3211
2 PX	79	507	-121	-325	-4879	539	4773	-79	-121
2 PY	626	0	-4913	0	0	0	0	626	4913
2 PZ	182	106	3840	-312	-3150	-4	-3237	-182	3840
3 2S	3547	271	23	3619	121	184	-3694	-3547	23
3 PX	-531	318	48	-4654	-182	114	-5242	531	49
3 PY	4835	0	-495	0	0	0	0	4835	495
3 PZ	3525	-84	304	-3764	-418	-80	2913	-3525	304
4 1S	-86	7074	-5	133	300	278	-516	86	-5
5 1S	21	-270	-11	15	-520	-7053	278	-21	-11
6 1S	-129	-302	3	425	-7061	-507	176	129	3
7 1S	-89	-81	-491	-136	129	-52	9	-7102	189
8 1S	-126	49	172	7111	-409	-35	5	126	172
9 1S	7102	-81	189	-136	129	-52	8	89	-491

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9
1	94	7004	-380	-123	-334	-313	579	-94	-380
2	-15	292	-319	-43	556	-7021	-330	15	-319
3	-312	-266	-7062	-104	98	219	53	-537	61
4	537	-266	61	-104	98	219	53	312	-7062
5	4	-414	-200	30	-84	-235	-7027	-4	-200
6	117	303	-372	-429	-6985	527	-275	-117	-372
7	327	-131	-7003	130	228	106	222	558	-53
8	-558	-131	-53	130	228	106	221	-327	-7003
9	134	79	511	148	-139	46	-156	-6972	-189
10	-151	410	-83	-50	104	213	-7040	151	-83
11	139	-26	-192	6991	416	62	-36	-139	-192
12	6972	79	-189	148	-139	46	-156	-134	511
13	-86	7074	-5	133	300	278	-516	86	-5
14	21	-270	-11	15	-520	-7053	278	-21	-11
15	-129	-302	3	425	-7061	-507	176	129	3
16	-89	-81	-491	-136	129	-52	9	-7102	189
17	-126	49	172	7111	-409	-35	5	126	172
18	7102	-81	189	-136	129	-52	8	89	-491

TABLE 22. GEOMETRY AND LCAO-MO'S FOR S-CIS-PROPENE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.339999199
3	C	-1.316358184	-0.000000001	2.099998951
4	H	0.935307370	0.0	-0.539999962
5	H	-0.935307371	0.0	-0.539999962
6	H	0.935307371	0.000000000	1.879999161
7	H	-1.887929125	-0.889980620	1.836675175
8	H	-1.117183299	-0.000000000	3.171646104
9	H	-1.887929125	0.889980619	1.836675176

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9
1 2S	-4000	3261	4045	71	3261	-188	-207	-71	242
1 PX	-4745	39	-4745	1	39	-643	630	-1	104
1 PY	0	-5039	0	-583	5039	0	0	-583	0
1 PZ	3285	3758	-3252	13	3758	39	-27	-13	163
2 2S	168	3209	-260	86	3209	4036	3897	-86	0
2 PX	-509	119	-543	193	119	-4771	4881	-193	215
2 PY	0	-4915	0	608	4915	0	0	608	0
2 PZ	-106	-3839	0	150	-3839	3240	3146	-150	350
3 2S	-262	-22	-161	-3590	-22	3690	-121	3590	3532
3 PX	-336	-49	-165	3276	-49	5249	173	-3276	838
3 PY	0	-477	0	4838	477	0	0	4838	0
3 PZ	60	-307	17	1335	-307	-2903	407	-1335	5959
4 1S	-7071	7	-275	-50	7	517	-305	50	-145
5 1S	269	12	7054	-13	12	-277	523	13	26
6 1S	307	-3	518	-239	-3	-177	7062	239	-309
7 1S	-18	-393	-3	-7092	263	-2	224	-100	-123
8 1S	136	258	98	129	258	-14	-297	-129	7133
9 1S	-18	263	-3	101	-393	-2	224	7092	-123

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9
1	-7006	376	308	36	376	-579	337	-36	146
2	-295	320	7018	34	320	329	-554	-34	0
3	263	-61	-226	-376	7064	-54	-100	-449	193
4	263	7064	-226	449	-61	-53	-100	376	193
5	413	201	234	-25	201	7027	83	26	-10
6	-306	370	-533	248	370	279	6986	-248	295
7	130	51	-106	378	7003	-223	-225	482	-202
8	130	7003	-106	-482	50	-223	-225	-378	-202
9	-409	84	-211	83	84	7039	-106	-83	-185
10	8	413	-9	-6983	-261	68	-224	140	139
11	-133	-280	-91	-139	-280	204	313	139	6972
12	8	-261	-9	-140	413	68	-224	6983	139
13	-7071	7	-275	-50	7	517	-305	50	-145
14	269	12	7054	-13	12	-277	523	13	26
15	307	-3	518	-239	-3	-177	7062	239	-309
16	-18	-393	-3	-7092	263	-2	224	-100	-123
17	136	258	98	129	258	-14	-297	-129	7133
18	-18	263	-3	101	-393	-2	224	7092	-123

TABLE 23. GECMETRY AND LCAO-MO'S FOR BUTENE

GECMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.339999199
3	C	-1.316358184	-0.000000001	2.099998951
4	C	-2.486880825	-0.000000002	1.099260909
5	H	0.935307370	0.0	-0.539999962
6	H	-0.935307371	0.0	-0.539999962
7	H	0.935307371	0.000000000	1.879999161
8	H	-1.374098574	-0.889980619	2.726655795
9	H	-1.374098576	0.889980619	2.726655793
10	H	-3.430847821	-0.000000001	1.644260508
11	H	-2.429140434	0.889980616	0.472604064
12	H	-2.429140435	-0.889980621	0.472604067

EXPANSICNS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12
1 2S	4066	3987	-57	138	-3270	-138	-3270	160	-84	84	-219	164
1 PX	-4731	4754	10	79	-40	-79	-40	70	3	-3	627	631
1 PY	0	0	0	-599	-5034	-599	5034	0	-35	-35	0	0
1 PZ	-3268	-3282	53	105	-3754	-105	-3754	61	91	-91	-28	-22
2 2S	-246	-178	-267	-25	-3225	25	-3225	111	-91	91	3883	-4039
2 PX	-540	510	153	92	-116	-92	-116	396	64	-64	4884	4737
2 PY	0	0	0	628	-4920	628	4920	0	76	76	0	0
2 PZ	15	101	-199	190	3827	-190	3827	312	-50	50	3140	-3263
3 2S	-172	279	31	3442	43	-3442	43	-3661	-61	61	-83	-3637
3 PX	-137	306	263	-366	7	366	7	4662	97	-97	92	-5320
3 PY	0	0	0	4783	-479	4783	479	0	-429	-429	0	0
3 PZ	118	-110	-292	3639	252	-3639	252	3814	-184	184	327	2788
4 2S	-53	36	-3548	-60	103	60	103	-3700	3601	-3601	202	38
4 PX	192	-22	5294	-148	20	148	20	-4527	131	-131	123	-395
4 PY	0	0	0	447	46	447	-46	0	-4846	-4846	0	0
4 PZ	-107	40	-2814	226	95	-226	95	-3949	-3522	3522	245	317
5 1S	-283	7074	40	-85	-1	85	-1	-126	78	-78	-296	-504
6 1S	7040	-274	37	28	-10	-28	-10	13	97	-97	525	290
7 1S	495	-295	134	-141	15	141	15	-437	33	-33	7078	187
8 1S	34	-78	155	-103	-473	-7105	177	32	-147	-414	-132	23
9 1S	34	-78	155	7105	177	103	-473	32	414	147	-132	23
10 1S	179	-38	-7145	-163	-79	163	-79	25	-141	141	-113	-411
11 1S	-25	7	138	-150	-3	-438	6	8	-120	-7113	14	136
12 1S	-25	7	138	438	6	150	-3	8	7113	120	14	136

EXPANSICNS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12
1	336	7004	-47	93	-384	-93	-384	117	-83	83	328	561
2	7027	280	-62	-19	-326	19	-326	17	-88	88	-558	-331
3	-226	-267	6	-306	-7062	-541	57	100	-6	-43	-106	62
4	-226	-267	6	541	56	306	-7062	100	43	6	-106	62
5	245	-423	-344	-2	-216	2	-216	-88	-119	119	70	-7014
6	-518	299	-127	128	-382	-128	-382	471	-28	28	6978	-314
7	-109	-131	6	324	-7005	564	-47	-134	45	62	-227	235
8	-109	-131	6	-564	-47	-324	-7006	-134	-62	-45	-227	235
9	-21	70	-141	167	485	-6932	-191	-145	176	431	117	-186
10	-240	417	340	-129	-82	129	-82	14	122	-122	-114	-7016
11	-63	0	7	-85	-125	85	-125	-7046	9	-8	-287	114
12	-20	70	-141	6932	-191	-167	485	-145	-431	-176	117	-186
13	-217	52	-6963	179	77	-179	77	-164	176	-176	114	453
14	35	-2	-130	167	38	466	-27	-91	133	-6987	-15	-156
15	39	26	126	0	119	0	119	-7053	-94	94	320	-62
16	35	-2	-130	-466	-27	-167	38	-91	6987	-133	-15	-156
17	-283	7074	40	-85	-1	85	-1	-126	78	-78	-296	-504
18	7040	-274	37	28	-10	-28	-10	13	97	-97	525	290
19	495	-295	134	-141	15	141	15	-437	33	-33	7078	187
20	34	-78	155	-103	-473	-7105	177	32	-147	-414	-132	23
21	34	-78	155	7105	177	103	-473	32	414	147	-132	23
22	179	-38	-7145	-163	-79	163	-79	25	-141	141	-113	-411
23	-25	7	138	-150	-3	-438	6	8	-120	-7113	14	136
24	-25	7	138	438	6	150	-3	8	7113	120	14	136

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TABLE 24.  GEOMETRY AND LCAO-MO'S FOR S-CIS-BUTENE
---------------------------------------------------------------------------

GEOMETRY
ATOM NUMBER  ELEMENT          X              Y              Z

      1         C        0.0            0.0            0.0
      2         C        0.0            0.0            1.339999199
      3         C       -1.316358184   -0.000000001    2.099958951
      4         C       -1.034954936   -0.000000000    3.614070315
      5         H        0.935307370    0.0           -0.539999962
      6         H       -0.935307371    0.0           -0.539999962
      7         H        0.935307371    0.000000000    1.879999161
      8         H       -1.887929125    0.889980618    1.836675175
      9         H       -1.887929124   -0.889980620    1.836675176
     10         H       -1.978921932   -0.000000002    4.159069915
     11         H       -0.463383994   -0.889980618    3.877394091
     12         H       -0.463383997    0.889980619    3.877394092

EXPANSIONS IN SLATER BASIS

           1     2     3     4     5     6     7     8     9    10    11    12

 1 2S     83  4048   -41   198 -3270    75   -75  -222  3270 -3993   241    41
 1 PX     51 -4746    -5   652   -46     2    -2   624    46 -4744   112     5
 1 PY      0     0    64     0  5026   566   566     0  5026     0     0    64
 1 PZ     65 -3248   -43   -38 -3763    16   -16   -39  3763  3294   161    43
 2 2S   -238  -258   103 -4037 -3204    92   -92  3917  3204   170    20  -103
 2 PX    243  -544   -55  4783  -129   196  -196  4863   129  -508   175    55
 2 PY      0     0   -28     0  4930  -585  -585     0  4930     0     0   -28
 2 PZ    -65    -1    12 -3195  3838   161  -161  3151 -3838  -107   398   -12
 3 2S     19  -161    73 -3621     0 -3483  3483  -153     0  -253  3593   -73
 3 PX    369  -162  -198 -5165    27  3291 -3291   132   -27  -325   883   158
 3 PY      0     0  -441     0   474 -4782 -4782     0   474     0     0  -441
 3 PZ    -64    29   -18  3065   226  1540 -1540   296  -226    97  5592    16
 4 2S  -3546    50 -3598    52  -126    61   -61  -166   126    67  3706  3598
 4 PX   5075   -22 -3134  -521   110   264  -264   141  -110   -70 -1184  3134
 4 PY      0     0 -4841     0   -33  -438  -438     0   -33     0     0 -4841
 4 PZ  -3207   -77 -1625   209   137   -20    20   116  -137   -76 -5903  1625
 5 1S    -73  -276    15  -523    -4   -53    53  -297     4 -7072  -142   -15
 6 1S     23  7054     0   277   -11   -12    12   521    11   268    24     0
 7 1S    -26   516   -14   182    11  -249   249  7068   -11   300  -299    14
 8 1S    154    -3   161    18  -251 -7103  -121   219  -383   -18   -20   431
 9 1S    154    -3  -431    18   383   121  7103   219   251   -18   -20  -161
10 1S  -7141   -17   136  -449    74   161  -161   129   -74   -68   -22  -137
11 1S    132     2   120   141    -8  -438  -155    -6    21    17    -9  7115
12 1S    132     2 -7115   141   -21   155   438    -6     7    17    -9  -120

EXPANSIONS IN HYBRID BASIS

        1     2     3     4     5     6     7     8     9    10    11    12

 1     58   307   -10   591  -384    38   -38   329   384 -7005   152    10
 2    -15  7019    -2  -331  -319    35   -35  -553   319  -295    -5     2
 3     72  -222     3    58    46   441   359  -113  7062   271   191    88
 4     72  -222   -88    58 -7062  -359  -441  -113   -46   271   191    -3
 5   -336   234   104 -7017  -191   -19    19   109   191   414    50  -104
 6      7  -534    25  -252  -374   257  -257  6987   374  -305   298   -25
 7    -59  -104    14   196   -38  -469  -358  -220  7010   131  -221   -55
 8    -59  -104    55   196 -7010   358   469  -220    38   131  -221   -14
 9    144   -13  -181  -106   275 -6940   177  -199   395     0   141  -443
10    314  -215  -104 -7012   -77    59   -59  -105    77  -413  -135   104
11     12   -81   -10   -17   197    90   -90   196  -197   -95  7039    10
12    144   -13   442  -106  -395  -177  6940  -199  -275     0   141   181
13  -6968     8  -151   507   -86  -176   176  -138    86    53   185   151
14   -139    -1  -138  -166    39   456   163     5     8   -14    80  6986
15    154    94    80   -70  -198     6    -6  -204   198   109  7067   -80
16   -139    -1 -6986  -166    -8  -163  -456     5   -39   -14    80   139
17    -73  -276    15  -523    -4   -53    53  -297     4 -7072  -142   -15
18     23  7054     0   277   -11   -12    12   521    11   268    24     0
19    -26   516   -14   182    11  -249   249  7068   -11   300  -299    14
20    154    -3   161    18  -251 -7103  -121   219  -383   -18   -20   431
21    154    -3  -431    18   383   121  7103   219   251   -18   -20  -161
22  -7141   -17   136  -449    74   161  -161   129   -74   -68   -22  -137
23    132     2   120   141    -8  -438  -155    -6    21    17    -9  7115
24    132     2 -7115   141   -21   155   438    -6     7    17    -9  -120
---------------------------------------------------------------------------
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TABLE 25. GEOMETRY AND LCAO-MO'S FOR 2-BUTENE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.519599504
3	C	1.160473347	0.0	2.189599104
4	C	1.160473347	-0.000000001	3.709598609
5	H	1.027661100	0.0	-0.363333067
6	H	-0.513830551	-0.889980619	-0.363333067
7	H	-0.513830549	0.889980620	-0.363333067
8	H	-0.935307371	0.0	2.059599466
9	H	2.095780717	0.000000000	1.649999143
10	H	0.132812246	-0.000000001	4.073331675
11	H	1.674303897	-0.889980619	4.073331675
12	H	1.674303897	0.889980618	4.073331676

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12
1 2S	185	27	3618	-43	135	3714	43	27	-3540	267	-3540	-66
1 PX	9	-291	5580	21	450	-108	-21	-291	2784	-92	2783	5
1 PY	0	513	0	-63	0	0	-63	-513	4827	0	-4827	0
1 PZ	141	-107	-2139	-53	69	6010	53	-107	2231	312	2231	-104
2 2S	248	-3205	-121	129	-3931	4015	-129	-3205	27	-141	27	181
2 PX	-279	-3262	436	123	5141	-438	-123	-3262	198	-289	198	75
2 PY	0	4949	0	-596	0	0	-596	-4949	615	0	-615	0
2 PZ	461	-1977	-126	2	-2662	-5756	-2	-1977	20	433	20	-6
3 2S	-3931	-3205	-181	-27	248	-141	27	-3205	-129	4015	-129	121
3 PX	-5141	3262	75	198	279	289	-198	3262	123	438	123	436
3 PY	0	4949	0	615	0	0	615	-4949	-596	0	596	0
3 PZ	2662	1977	-6	20	-461	-433	-20	1977	2	5756	2	-126
4 2S	135	27	66	3540	185	267	-3540	27	43	3714	43	-3618
4 PX	-450	291	6	2783	-9	92	-2783	291	21	108	21	5580
4 PY	0	513	0	4827	0	0	4827	-513	-63	0	63	0
4 PZ	-69	107	-104	2231	-141	-312	-2231	107	-53	-6010	-53	-2139
5 1S	-32	172	7119	-13	-406	-6	13	171	127	46	127	-3
6 1S	-54	191	-137	-75	125	-9	-110	-496	-7110	-77	92	9
7 1S	-54	-496	-137	110	125	-9	75	191	92	-77	-7110	9
8 1S	-510	6	422	23	-7066	-192	-23	6	125	-283	125	-13
9 1S	-7066	6	13	-125	-510	-283	125	6	-23	-192	-23	-422
10 1S	-406	171	2	-127	-32	46	127	171	12	-6	13	-7119
11 1S	125	191	-9	-92	-54	-77	-7110	-496	-110	-9	75	137
12 1S	125	-496	-9	7110	-54	-77	92	191	75	-9	-110	137

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12
1	215	-79	-43	-67	127	7062	67	-79	162	404	162	-124
2	59	-193	6983	11	415	33	-11	-193	-141	-31	-141	1
3	47	-199	148	29	-136	166	59	527	-6964	80	-137	-5
4	47	527	148	-59	-136	166	-29	-199	-137	80	-6964	-5
5	-233	-236	33	72	-96	7018	-72	-236	0	-436	0	109
6	529	-350	-430	-11	-6991	278	11	-350	-116	299	-116	48
7	94	-10	132	-306	197	-241	-537	-7010	551	-77	-318	109
8	94	-7010	132	537	197	-241	306	-10	-318	-77	551	109
9	-96	-236	-109	0	-233	-436	0	-236	-72	7018	-72	-33
10	-6991	-350	-48	116	529	299	-116	-350	11	278	11	430
11	197	-10	-109	318	94	-77	551	-7010	-537	-241	306	-131
12	197	-7010	-109	-551	94	-77	-318	-10	306	-241	-537	-131
13	127	-79	124	-162	215	404	162	-79	67	7062	67	43
14	415	-193	-1	141	59	-31	-141	-193	-11	33	-11	-6983
15	-136	-199	5	137	48	80	-6964	527	59	166	-29	-148
16	-136	527	5	6964	48	80	-137	-199	-29	166	59	-148
17	-32	172	7119	-13	-406	-6	13	171	127	46	127	-3
18	-54	191	-137	-75	125	-9	-110	-496	-7110	-77	92	9
19	-54	-496	-137	110	125	-9	75	191	92	-77	-7110	9
20	-510	6	422	23	-7066	-192	-23	6	125	-283	125	-13
21	-7066	6	13	-125	-510	-283	125	6	-23	-192	-23	-422
22	-406	171	2	-127	-32	46	127	171	12	-6	13	-7119
23	125	191	-9	-92	-54	-77	-7110	-496	-110	-9	75	137
24	125	-496	-9	7110	-54	-77	92	191	75	-9	-110	137

TABLE 26. GEOMETRY AND LCAO-MO'S FOR ISOBUTENE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.339599199
3	C	-1.316358184	-0.000000001	2.099598951
4	C	1.316358185	0.000000001	2.099598951
5	H	0.935307370	0.0	-0.539599962
6	H	-0.935307371	0.0	-0.539999962
7	H	-1.374098574	-0.889980619	2.726655795
8	H	-2.144844400	-0.000000001	1.391684866
9	H	-1.374098576	0.889980619	2.726655793
10	H	2.144844401	0.000000001	1.391684865
11	H	1.374098576	-0.889980618	2.726655794
12	H	1.374098575	0.889980619	2.726655795

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12
1 2S	3263	136	-188	-188	136	-136	-184	136	3263	-4028	-184	-4028
1 PX	0	-74	50	-50	-74	-74	-645	74	0	4734	645	-4734
1 PY	5066	573	0	0	-573	-573	0	-573	-5066	0	0	0
1 PZ	3725	96	-57	-57	96	-96	53	96	3725	3264	53	3264
2 2S	3141	-40	-84	-84	-40	40	3946	-40	3141	209	3946	209
2 PX	0	-49	240	-240	-49	-49	-4882	49	0	431	4882	-431
2 PY	4838	-612	0	0	612	612	0	612	-4838	0	0	0
2 PZ	-3905	157	-259	-259	157	-157	3137	157	-3905	-77	3137	-77
3 2S	-28	-75	221	3605	-75	-3558	3702	3558	-28	192	-119	-268
3 PX	-57	-50	192	-4675	-50	520	5209	-520	-57	116	227	-312
3 PY	484	34	0	0	-34	4840	0	4840	-484	0	0	0
3 PZ	-307	38	-205	-3753	38	-3519	-2944	3519	-307	-89	406	82
4 2S	-28	3558	3605	221	3558	75	-119	-75	-27	-268	3702	192
4 PX	57	520	4675	-192	520	-50	-227	50	57	312	-5209	-116
4 PY	484	-4840	0	0	4840	-34	0	-34	-484	0	0	0
4 PZ	-307	3519	-3753	-205	3519	-38	406	38	-307	82	-2944	-89
5 1S	2	15	33	124	15	82	517	-82	2	292	-277	-7079
6 1S	2	-82	124	33	-82	-15	-277	15	2	-7079	517	292
7 1S	487	-12	4	-138	38	-7101	-15	-89	-180	-48	-115	80
8 1S	-176	31	-98	7119	31	132	-13	-132	-176	-54	407	-41
9 1S	-180	38	4	-138	-12	89	-15	7101	487	-48	-115	80
10 1S	-176	-132	7119	-98	-132	-31	407	31	-176	-41	-13	-54
11 1S	487	7101	-138	4	-89	12	-115	38	-180	80	-15	-48
12 1S	-180	-89	-138	4	7101	-38	-115	-12	487	80	-15	-48

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12
1	362	-13	-49	-121	-13	-92	-584	92	363	-311	328	-7006
2	362	92	-121	-49	92	13	328	-13	362	-7006	-584	-311
3	7065	516	-110	-110	-294	-516	-44	-294	-99	239	-44	239
4	-99	-294	-110	-110	516	294	-44	516	7065	239	-44	239
5	219	75	-324	15	75	-6	7012	6	219	-215	106	394
6	219	6	15	-324	6	-75	106	75	219	394	7012	-215
7	6958	-540	115	115	325	540	-200	325	115	129	-200	129
8	115	325	115	115	-540	-325	-200	-540	6958	129	-200	129
9	-507	-41	0	148	8	-6978	146	132	178	46	132	-78
10	76	-92	343	-78	-92	134	7033	-134	76	222	-65	-404
11	196	-26	99	6992	-26	-141	79	141	196	69	-438	24
12	178	8	0	148	-41	-132	146	6978	-507	46	132	-78
13	196	141	6992	99	141	26	-438	-26	196	24	79	69
14	76	-134	-78	343	-134	92	-65	-92	76	-404	7033	222
15	-507	6978	148	0	132	41	131	8	178	-78	146	46
16	178	132	148	0	6978	-8	131	-41	-507	-78	146	46
17	2	15	33	124	15	82	517	-82	2	292	-277	-7079
18	2	-82	124	33	-82	-15	-277	15	2	-7079	517	292
19	487	-12	4	-138	38	-7101	-15	-89	-180	-48	-115	80
20	-176	31	-98	7119	31	132	-13	-132	-176	-54	407	-41
21	-180	38	4	-138	-12	89	-15	7101	487	-48	-115	80
22	-176	-132	7119	-98	-132	-31	407	31	-176	-41	-13	-54
23	487	7101	-138	4	-89	12	-115	38	-180	80	-15	-48
24	-180	-89	-138	4	7101	-38	-115	-12	487	80	-15	-48

TABLE 27. GEOMETRY AND LCAO-MO'S FOR BUTADIENE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.339999199
3	C	-1.264396296	-0.000000001	2.069958741
4	C	-1.264396296	-0.000000000	3.409997941
5	H	0.935307370	0.0	-0.539999962
6	H	-0.935307371	0.0	-0.539999962
7	H	0.935307371	0.000000000	1.879999161
8	H	-2.199703667	-0.000000001	1.525998780
9	H	-2.199703666	-0.000000001	3.945997904
10	H	-0.329088925	0.000000001	3.945597903

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11
1 2S	-88	-154	163	3277	154	-4061	-3982	3276	-186	-217	-62
1 PX	-63	-76	34	63	76	4747	-4743	63	-654	626	-12
1 PY	0	758	0	4980	758	0	0	-4980	0	0	0
1 PZ	-71	-111	52	3766	111	3242	3306	3766	66	-32	-67
2 2S	271	-26	179	3152	27	257	154	3152	4051	3897	185
2 PX	-275	-40	259	182	40	530	-482	182	-4782	4882	-113
2 PY	0	-771	0	4901	-771	0	0	-4901	0	0	0
2 PZ	87	-265	339	-3866	265	9	-123	-3866	3141	3133	42
3 2S	-154	-3152	-3897	27	3152	185	-271	27	4051	-179	257
3 PX	-482	182	4882	-40	-182	113	-275	-40	4782	259	-530
3 PY	0	-4901	0	771	-4901	0	0	-771	0	0	0
3 PZ	-123	-3866	3133	-265	3866	-42	87	-265	-3141	339	-9
4 2S	3982	-3276	217	154	3276	-62	88	154	-186	-163	-4061
4 PX	-4743	63	626	-76	-63	12	-63	-76	654	34	-4747
4 PY	0	-4980	0	-758	-4980	0	0	758	0	0	0
4 PZ	3306	3766	-32	-111	-3766	67	-71	-111	-66	52	-3242
5 1S	82	85	-109	0	-85	281	-7077	0	521	-298	24
6 1S	-31	-17	-19	10	17	-7050	271	10	-271	522	-3
7 1S	30	160	-429	-7	-160	-509	302	-7	-155	7064	-16
8 1S	-302	7	-7064	-160	-7	-16	-30	-160	-155	429	-509
9 1S	7077	0	298	-85	0	24	-82	-85	521	109	281
10 1S	-271	-10	-522	17	10	-3	31	17	-271	19	-7050

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11
1	-67	-98	97	399	98	-310	-7003	399	-597	330	-16
2	22	9	48	309	-9	-7025	-295	309	328	-555	0
3	-77	409	97	7034	664	213	282	-9	-37	-107	-64
4	-77	-664	97	-9	-409	213	282	7034	-37	-107	-64
5	387	-95	58	112	95	-222	379	112	7003	76	204
6	-2	-152	425	370	152	527	-302	370	239	6982	44
7	60	-403	-122	6984	-687	99	134	53	-159	-218	51
8	60	687	-122	53	403	99	134	6984	-159	-218	51
9	-379	-112	-76	95	112	204	-387	95	7003	-58	-222
10	302	-370	-6982	152	370	44	2	152	239	-425	527
11	-134	-6984	218	403	53	51	-60	-687	-159	122	99
12	-134	-53	218	-687	6984	51	-60	403	-159	122	99
13	7003	-399	-330	98	399	-16	67	98	-597	-97	-310
14	295	-309	555	-9	309	0	-22	-9	328	-48	-7025
15	-283	-7034	107	-409	-9	-64	77	664	-37	-97	213
16	-282	9	107	664	7034	-64	77	-409	-37	-97	213
17	82	85	-109	0	-85	281	-7077	0	521	-298	24
18	-31	-17	-19	10	17	-7050	271	10	-271	522	-3
19	30	160	-429	-7	-160	-509	302	-7	-155	7064	-16
20	-302	7	-7064	-160	-7	-16	-30	-160	-155	429	-509
21	7077	0	298	-85	0	24	-82	-85	521	109	281
22	-271	-10	-522	17	10	-3	31	17	-271	19	-7050

TABLE 28. GEOMETRY AND LCAO-MO'S FOR PROPYNE

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GEOMETRY
ATOM NUMBER  ELEMENT           X              Y                Z

      1         H         0.0            0.0              0.0
      2         C         0.0            0.0              1.059999466
      3         C        -0.000000000    0.0              2.259999275
      4         C        -0.000000001    0.0              3.719998360
      5         H         1.027661100    0.0              4.083331426
      6         H        -0.513830551    0.889980619      4.083331426
      7         H        -0.513830551   -0.889980619      4.083331426

EXPANSIONS IN SLATER BASIS

             1      2      3      4      5      6      7      8

 1 1S    -6873     36    -31     31    -36    -36    350    -31
 2 2S    -4867    -97   3248  -3248     97     97   -596   3248
 2 PX        0   -352  -3444   2320    352   -704      0   5765
 2 PY        0   -610  -4668  -5316   -610      0      0   -648
 2 PZ     5345    -41   2460  -2460     41     41    -75   2460
 3 2S      606     58   3192  -3192    -58    -58   4792   3192
 3 PX        0    380  -3379   2276   -380    761      0   5656
 3 PY        0    659  -4580  -5216    659      0      0   -636
 3 PZ     -199   -109  -2553   2553    109    109   5265  -2553
 4 2S     -171  -3537    -29     29   3537   3537   3668    -29
 4 PX        0   2794   -324    218  -2794   5588      0    542
 4 PY        0   4839   -439   -500   4839      0      0    -61
 4 PZ      221  -2240    -64     65   2240   2240  -5946    -64
 5 1S       24    100    315   -226   -100   7078     18   -413
 6 1S       24    100    226    413   7078   -100     18    315
 7 1S       24  -7078   -413   -315   -100   -100     18    226

EXPANSIONS IN HYBRID BASIS

       1      2      3      4      5      6      7      8

 1 -6873     36    -31     31    -36    -36    350    -31
 2 -7229    -35    369   -369     35     35   -345    369
 3     1   -287    -25     25    399   -513   -283   7079
 4     1    513   7079     25    287    399   -283    -25
 5     1   -399    -25  -7079   -513    287   -284    -25
 6   261    -41    262   -263     41     41   7119    262
 7   336    316     31    -32   -436    550     -2   7002
 8   336   -550   7002    -31   -316   -436     -2     32
 9   336    436     32  -7002    550   -316     -2     31
10  -277    171     41    -41   -171   -171   6984     41
11   -21   -134   -298    212    134   6978    117    409
12   -21   -134   -212   -409   6978    134    117   -298
13   -21  -6978    409    298    134    134    117   -212
14    24    100    315   -226   -100   7078     18   -413
15    24    100    226    413   7078   -100     18    315
16    24  -7078   -413   -315   -100   -100     18    226
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TABLE 29. GEOMETRY AND LCAO-MO'S FOR BUTYNE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	H	0.0	0.0	0.0
2	C	0.0	0.0	1.059999466
3	C	-0.000000000	0.0	2.259999275
4	C	-0.000000001	0.0	3.719998360
5	C	1.451925888	0.0	4.233331681
6	H	-0.513830551	0.889980619	4.083331426
7	H	-0.513830551	-0.889980619	4.083331426
8	H	1.965756438	-0.889980619	3.869998614
9	H	1.965756438	0.889980620	3.869998616
10	H	1.451925888	-0.000000000	5.323330880

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11
1 1S	-352	-33	37	-46	-13	37	13	-33	35	-24	-6874
2 2S	604	3229	-99	79	26	-99	-26	3229	-99	3272	-4868
2 PX	-5	2956	-365	-187	-77	-365	77	2898	700	-5847	-22
2 PY	0	-4986	-595	0	-60	595	-60	5019	0	-33	0
2 PZ	77	2457	-41	32	12	-41	-12	2457	-40	2457	5342
3 2S	-4791	3212	66	-260	-78	66	78	3212	24	3170	610
3 PX	97	2866	398	180	69	398	-69	2810	-803	-5647	-9
3 PY	0	-4935	634	0	23	-634	23	4968	0	-32	0
3 PZ	-5250	-2539	-100	-186	-49	-100	49	-2539	-174	-2586	-199
4 2S	-3604	-41	-3431	7	-79	-3431	79	-41	-3591	7	-169
4 PX	187	212	2964	117	110	2964	-110	208	-5635	-383	9
4 PY	0	-470	4781	0	439	-4781	439	473	0	-3	0
4 PZ	5951	-83	-2160	-350	-154	-2160	154	-82	-2207	-11	224
5 2S	35	-113	43	-3567	3598	43	-3598	-111	-3668	257	11
5 PX	-53	108	140	-197	2988	140	-2988	105	5660	-323	-23
5 PY	0	33	435	0	4852	-435	4852	-34	0	0	0
5 PZ	538	-17	-242	-5995	-1899	-242	1899	-16	1942	37	22
6 1S	-2	488	121	169	-154	-7091	-434	-181	0	-182	24
7 1S	-2	-177	-7091	169	434	121	154	488	0	-186	24
8 1S	135	-4	149	132	-118	-442	-7103	10	11	18	13
9 1S	135	9	-442	132	7103	149	118	-3	11	18	12
10 1S	-432	74	176	-7132	-132	176	132	73	20	-154	-35

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11
1	-352	-33	37	-46	-13	37	13	-33	35	-24	-6874
2	349	359	-35	29	8	-35	-8	359	-37	388	-7228
3	285	-8	-628	-29	-58	216	-27	7066	224	-35	-8
4	285	7066	210	-30	26	-628	58	-8	230	-35	-8
5	292	-56	242	200	80	237	-79	-55	-630	7127	18
6	-7108	287	-29	-313	-89	-29	89	286	-112	223	264
7	36	15	678	34	30	-221	2	7019	-246	52	334
8	37	7018	-215	35	-1	678	-30	15	-252	52	334
9	-82	41	-261	-185	-71	-255	71	40	734	6969	345
10	-6956	51	155	307	94	155	-94	50	115	13	-279
11	68	128	80	-1	5	80	-5	125	-7034	-313	-12
12	-160	-464	-168	-145	180	-6930	439	205	-132	154	-23
13	-160	200	-6930	-145	-439	-168	-180	-464	-132	159	-23
14	-94	-140	-22	108	-92	-22	92	-136	-7017	382	18
15	-159	-31	-158	-133	135	456	-6998	16	-84	-14	-10
16	-159	16	456	-133	6998	-158	-135	-32	-84	-14	-10
17	483	-71	-187	-6976	154	-187	-154	-70	-151	161	24
18	-2	488	121	169	-154	-7091	-434	-181	0	-182	24
19	-2	-177	-7091	169	434	121	154	488	0	-186	24
20	135	-4	149	132	-118	-442	-7103	10	11	18	13
21	135	9	-442	132	7103	149	118	-3	11	18	12
22	-432	74	176	-7132	-132	176	132	73	20	-154	-35

TABLE 30. GEOMETRY AND LCAO-MO'S FOR PENTYNE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	H	0.0	0.0	0.0
2	C	0.0	0.0	1.059999466
3	C	-0.000000000	0.0	2.259999275
4	C	-0.000000001	0.0	3.719998360
5	C	1.451925888	0.0	4.233331681
6	C	1.451925888	-0.000000001	5.773331643
7	H	-0.513830551	0.889980619	4.083331426
8	H	-0.513830551	-0.889980619	4.083331426
9	H	1.965756439	-0.889980619	3.869998614
10	H	1.965756438	0.889980619	3.869998614
11	H	0.938095340	-0.889980621	6.136664709
12	H	0.938095337	0.889980618	6.136664709
13	H	2.475586988	0.000000002	6.136664709

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1 1S	24	-33	8	14	6876	-45	39	-354	33	-14	-8	-19	37	-39
2 2S	-3281	3225	-11	-28	4866	80	-101	608	-3225	28	11	31	-104	101
2 PX	5847	2878	14	82	27	-183	-358	-6	-2982	-82	-14	-89	706	358
2 PY	59	5030	27	-62	0	0	594	0	4971	-62	27	0	0	594
2 PZ	-2458	2455	-5	-13	-5341	31	-43	78	-2455	13	5	12	-40	43
3 2S	-3160	3216	46	83	-609	-257	74	-4803	-3217	-83	-46	-85	32	-74
3 PX	5641	2791	-8	-73	10	190	391	119	-2892	73	8	71	-814	-391
3 PY	58	4982	-25	26	0	0	-632	0	4923	26	-25	0	0	-632
3 PZ	2601	-2533	41	52	200	-181	-93	-5256	2533	-53	-41	-58	-175	93
4 2S	-3	-40	-94	83	169	-5	-3444	-3594	41	-83	94	215	-3593	3445
4 PX	385	209	-76	-108	-10	68	2950	205	-216	108	76	286	-5639	-2950
4 PY	5	477	-26	434	0	0	-4785	0	471	434	-26	0	0	-4785
4 PZ	5	-85	14	162	-225	-387	-2163	5956	85	-162	-14	5	-2156	2163
5 2S	-248	-108	-74	-3489	-7	-3628	66	-3	112	3489	74	-25	-3603	-66
5 PX	320	103	-194	-2966	22	-163	128	-41	-108	2966	194	389	5608	-128
5 PY	0	-31	437	4799	0	0	-424	0	-31	4799	436	0	0	-424
5 PZ	3	-3	51	2107	-9	-6041	-168	395	3	-2107	-51	6	2105	168
6 2S	76	36	3595	63	18	-3702	102	-217	-37	-63	-3595	3558	51	-102
6 PX	53	10	-2787	-264	9	-66	52	-128	-11	264	2787	5584	544	-52
6 PY	0	-12	4844	442	0	0	25	0	-12	442	4843	0	0	25
6 PZ	-101	-55	2174	29	-19	6017	-76	254	56	-28	-2174	2214	99	76
7 1S	177	-185	0	-435	-25	155	-7093	5	-489	-146	-7	26	6	-118
8 1S	185	489	7	146	-25	155	118	4	177	435	0	26	6	7093
9 1S	-18	10	426	-7109	-13	28	-427	136	5	-134	151	-156	28	-141
10 1S	-18	-5	-151	134	-13	28	141	136	-10	7109	-426	-156	28	427
11 1S	15	-5	-121	151	3	11	-8	-19	-13	438	-7114	-131	143	-1
12 1S	15	13	7114	-438	3	11	1	-19	5	-151	120	-131	143	8
13 1S	-64	-17	-134	162	-15	20	-76	126	18	-162	134	7131	-444	76

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	24	-33	8	14	6876	-45	39	-354	33	-14	-8	-19	37	-39
2	-393	357	-4	-9	7226	31	-36	351	-357	9	4	12	-39	36
3	30	7063	18	-28	10	-26	219	287	8	-60	20	-17	222	626
4	31	-8	-20	61	10	-29	-627	286	-7064	26	-18	-18	233	-209
5	-7131	-60	-19	-84	-22	197	227	295	61	85	18	91	-637	-237
6	-205	294	61	95	-261	-307	-18	-7120	-294	-95	-61	-100	-108	18
7	-56	7021	-17	4	-333	36	-224	42	-15	33	-18	15	-244	-674
8	-57	15	18	-34	-333	39	675	43	-7020	-3	17	16	-256	213
9	-6967	37	10	75	-346	-194	-246	-103	-38	-75	-10	-72	747	256
10	-6	53	-59	-98	280	332	151	-6955	-53	98	59	102	71	-151
11	314	125	-105	0	11	-58	61	90	-131	0	105	343	-7023	-61
12	-153	207	-30	440	23	-142	-6935	-161	467	173	-6	-7	-117	167
13	-161	-467	7	-173	24	-142	-167	-161	-199	-440	30	-7	-116	6935
14	-386	-137	106	68	-19	63	-23	-82	144	-68	-106	-332	-6988	23
15	-121	-57	7	79	-12	-7046	-113	340	59	-79	-7	-7	21	113
16	6	11	-440	-6957	8	-137	434	-132	33	170	-177	144	-119	165
17	5	-33	177	-170	8	-137	-165	-132	-10	6957	440	144	-119	-434
18	-12	6	137	-165	0	-86	-10	16	11	-460	-6988	138	-167	-26
19	126	65	-85	6	26	-7062	118	-329	-68	-6	85	-138	-60	-118
20	-12	-11	6988	460	0	-86	26	16	-6	165	-138	138	-167	10
21	52	11	149	-175	11	-168	72	-139	-11	175	-149	6978	498	-72
22	177	-185	0	-435	-25	155	-7093	5	-489	-146	-7	26	6	-118
23	185	489	7	146	-25	155	118	4	177	435	0	26	6	7093
24	-18	10	426	-7109	-13	28	-427	136	5	-134	151	-156	28	-141
25	-18	-5	-151	134	-13	28	141	136	-10	7109	-426	-156	28	427
26	15	-5	-121	151	3	11	-8	-19	-13	438	-7114	-131	143	-1
27	15	13	7114	-438	3	11	1	-19	5	-151	120	-131	143	8
28	-64	-17	-134	162	-15	20	-76	126	18	-162	134	7131	-444	76

TABLE 31. GEOMETRY AND LCAO-MO'S FOR VINYL ACETYLENE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	H	0.0	0.0	0.0
2	C	0.0	0.0	1.059599466
3	C	-0.000000000	0.0	2.259599275
4	C	-0.000000001	0.0	3.709999084
5	C	1.160473347	0.0	4.379598684
6	H	-0.935307371	0.0	4.249999047
7	H	2.095780717	0.000000000	3.839598723
8	H	1.160473347	-0.000000000	5.459598609

EXPANSIONS IN SLATER BASIS

		1	2	3	4	5	6	7	8	9	10
1	1S	28	-25	35	35	50	28	-350	-57	-6870	26
2	2S	-83	3316	-3216	-3216	-118	-83	594	101	-4868	-50
2	PX	380	-5825	-2928	-2957	-612	380	-4	-176	-37	110
2	PY	-690	16	4969	-4953	0	690	0	0	0	0
2	PZ	-33	2478	-2455	-2455	-47	-33	72	40	5347	-20
3	2S	6	3145	-3213	-3213	143	6	-4780	-318	606	163
3	PX	-429	-5623	-2847	-2875	656	-429	169	161	-13	-90
3	PY	718	16	4952	-4935	0	-718	0	0	0	0
3	PZ	-163	-2636	2508	2507	-19	-163	-5245	-223	-196	110
4	2S	-3172	30	49	49	-3864	-3172	-3988	157	-187	259
4	PX	-3263	-416	-240	-243	5148	-3263	430	341	21	-270
4	PY	4918	2	678	-676	0	-4918	0	0	0	0
4	PZ	-2045	25	116	117	-2704	-2045	5680	-383	202	458
5	2S	-3253	263	94	95	183	-3253	166	-4006	26	-4058
5	PX	3279	-199	-32	-33	310	3279	-250	-460	-38	-5203
5	PY	4981	-2	-695	692	0	-4981	0	0	0	0
5	PZ	1842	7	-8	-8	-553	1842	569	-5757	23	2485
6	1S	-14	-360	-260	-262	-7041	-14	147	320	45	-521
7	1S	-11	18	-12	-12	-527	-11	263	270	26	-7036
8	1S	-4	-159	-60	-61	319	-4	-504	-7064	-45	273

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10
1	28	-25	35	35	50	28	-350	-57	-6870	26
2	-31	401	-352	-352	-44	-31	346	38	-7231	-18
3	-379	0	-20	-7037	-320	594	280	-13	-13	16
4	594	1	-7037	-20	-317	-383	280	-12	-12	15
5	-361	7135	75	75	431	-358	285	203	32	-119
6	-116	170	-310	-311	82	-116	-7097	-379	263	192
7	396	71	-19	-7010	338	-617	69	16	329	-10
8	-616	71	-7010	-19	335	400	68	16	329	-9
9	418	6959	-9	-10	-466	414	-137	-180	346	100
10	-161	-2	-66	-66	-22	-161	-6940	403	-273	-224
11	-359	322	246	248	-6975	-358	-288	-307	-41	528
12	-39	-186	413	-545	216	-6995	226	124	-7	103
13	-6995	-189	-546	410	216	-39	226	124	-7	103
14	-312	7	34	35	551	-312	-313	-288	-21	-7037
15	-374	158	47	48	-346	-374	561	-7014	34	-313
16	-7022	206	548	-432	79	22	28	256	23	227
17	22	203	-434	547	79	-7022	28	256	23	227
18	-14	-360	-260	-262	-7041	-14	147	320	45	-521
19	-11	18	-12	-12	-527	-11	263	270	26	-7036
20	-4	-159	-60	-61	319	-4	-504	-7064	-45	273

TABLE 32. GEOMETRY AND LCAO-MO'S FOR ISOPRENE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.339999199
3	C	-1.264396296	-0.000000001	2.069998741
4	C	1.316358185	0.000000001	2.099998951
5	C	-1.264396296	-0.000000000	3.409997941
6	H	0.935307370	0.0	-0.539999962
7	H	-0.935307371	0.0	-0.539999962
8	H	-2.199703667	-0.000000001	1.529998780
9	H	2.144844401	0.000000001	1.391684865
10	H	1.374098575	0.889980619	2.726655795
11	H	1.374098576	-0.889980618	2.726655794
12	H	-2.199703666	-0.000000001	3.949997904
13	H	-0.329088925	0.000000001	3.949997903

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1 2S	-154	-134	3278	171	52	181	134	-154	-3279	-192	-189	86	-4034	4016
1 PX	-73	75	20	27	19	657	-75	-73	-20	644	50	63	4738	4731
1 PY	722	-557	5007	0	0	0	-557	-722	5006	0	0	0	0	0
1 PZ	-110	-93	3737	58	64	-79	93	-110	-3737	43	-57	69	3259	-3284
2 2S	-10	35	3080	139	-191	-3966	-35	-10	-3081	3946	-86	-279	208	-192
2 PX	-6	50	63	174	112	4890	-50	-6	-63	4891	233	265	420	404
2 PY	-749	594	4830	0	0	0	594	749	4830	0	0	0	0	0
2 PZ	-238	-156	-3930	286	-70	-3047	156	-238	3930	3122	-255	-101	-64	93
3 2S	-3163	68	22	-3886	-250	-4056	-68	-3163	-22	-168	246	161	193	267
3 PX	172	62	-50	4897	530	-4750	-62	172	50	311	159	486	112	269
3 PY	-4909	-77	760	0	0	0	-77	4909	760	0	0	0	0	0
3 PZ	-3858	-28	-268	3122	2	3167	28	-3858	268	336	-179	118	-51	-87
4 2S	96	-3564	-30	-217	-35	102	3564	96	30	3706	3597	-25	-269	-190
4 PX	-67	-526	59	205	-114	221	526	-67	-59	-5200	4673	-4	312	117
4 PY	40	4843	483	0	0	0	4843	-40	483	0	0	0	0	0
4 PZ	-58	-3513	-308	203	84	-375	3513	-58	308	-2951	-3753	15	84	89
5 2S	-3280	49	155	225	4062	183	-49	-3280	-155	-151	39	-3983	-56	-86
5 PX	59	13	-77	628	4743	-647	-13	59	77	39	24	4748	12	62
5 PY	-4980	-15	-749	0	0	0	-15	4980	-749	0	0	0	0	0
5 PZ	3766	63	-116	-34	3249	51	-63	3766	116	51	42	-3305	61	66
6 1S	82	-16	-3	-100	-24	-522	16	82	3	-276	35	-81	295	7081
7 1S	-10	83	0	-39	9	271	-83	-10	0	519	123	30	-7076	-292
8 1S	14	-12	-167	-7072	504	162	12	14	167	433	-105	297	-37	21
9 1S	-45	136	-176	88	117	-379	-136	-45	176	-18	7124	13	-39	54
10 1S	17	91	-175	-1	-11	109	7100	-36	-484	-15	-141	3	79	47
11 1S	-36	-7100	484	-1	-11	109	-91	17	175	-15	-141	3	79	47
12 1S	1	-42	-85	296	-283	-513	42	1	85	105	-15	-7074	22	82
13 1S	-9	-68	21	-526	7046	280	68	-9	-21	7	-42	272	-1	-30

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	-95	14	381	94	17	602	-14	-95	-381	327	-49	66	-309	7005
2	7	-93	352	55	-9	-327	93	7	-352	-584	-121	-23	-7010	314
3	384	-503	7037	104	58	28	-285	-637	43	-53	-110	75	235	-256
4	-637	285	-43	104	58	28	503	384	-7037	-53	-110	75	235	-256
5	-98	-79	129	73	-219	-6992	79	-98	-129	94	-319	-390	-203	-359
6	-108	-7	218	320	-59	-76	7	-108	-218	7011	10	-14	391	213
7	-396	524	6943	-108	-37	139	315	662	-111	-191	112	-55	122	-132
8	662	-315	111	-108	-37	139	-524	-396	-6943	-191	112	-55	122	-132
9	-129	95	86	-55	229	-6993	-95	-129	-86	-14	329	388	212	380
10	-373	6	158	-6982	-520	-276	-6	-373	-158	-455	102	-295	53	0
11	-6990	-42	391	215	-100	172	-66	-47	683	125	-3	134	49	58
12	-47	66	-683	215	-100	172	42	-6990	-391	125	-3	134	49	58
13	123	133	73	-350	31	48	-133	123	-73	7031	-81	-15	-405	-222
14	36	-151	197	-88	-140	408	151	36	-197	91	6987	-24	23	-68
15	44	-130	176	1	18	-125	6980	-13	508	145	144	-5	-78	-45
16	-13	-6980	-508	1	18	-125	130	44	-176	145	144	-5	-78	-45
17	-398	44	97	-328	317	584	-44	-398	-97	-94	22	-7006	-16	-67
18	-314	63	-12	560	7026	-330	-63	-314	12	-38	57	-291	0	21
19	-7035	-27	-399	111	-217	45	5	8	-660	-91	-8	282	-58	-73
20	8	-5	660	111	-217	45	27	-7035	399	-91	-8	282	-58	-73
21	82	-16	-3	-100	-24	-522	16	82	3	-276	35	-81	295	7081
22	-10	83	0	-39	9	271	-83	-10	0	519	123	30	-7076	-292
23	14	-12	-167	-7072	504	162	12	14	167	433	-105	297	-37	21
24	-45	136	-176	88	117	-379	-136	-45	176	-18	7124	13	-39	54
25	17	91	-175	-1	-11	109	7100	-36	-484	-15	-141	3	79	47
26	-36	-7100	484	-1	-11	109	-91	17	175	-15	-141	3	79	47
27	1	-42	-85	296	-283	-513	42	1	85	105	[illegible]	-7074	22	82
28	-5	-68	21	-526	7046	280	68	-9	-21	7	-42	272	-1	-30

TABLE 33. GEOMETRY AND LCAO-MO'S FOR S-TRANS-ISOPROPYL ETHYLENE

GEOMETRY

ATOM NUMBER	ELEMENT	X	Y	Z
1	C	0.0	0.0	0.0
2	C	0.0	0.0	1.339599199
3	C	-1.316358184	-0.000000001	2.099998951
4	C	-1.397936410	1.257404704	2.985367962
5	C	-1.397936407	-1.257404703	2.985367965
6	H	0.935307370	0.0	-0.539999962
7	H	-0.935307371	0.0	-0.539999962
8	H	0.935307371	0.000000000	1.879999161
9	H	-2.144844400	-0.000000001	1.391684866
10	H	-1.340196021	2.147385323	2.358711118
11	H	-0.569450195	1.257404706	3.693682048
12	H	-2.341903406	1.257404703	3.530367562
13	H	-2.341903404	-1.257404704	3.530367564
14	H	-0.569450192	-1.257404702	3.693682050
15	H	-1.340196015	-2.147385323	2.358711123

EXPANSIONS IN SLATER BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1 2S	4057	39	-8	-3992	-39	214	-176	-52	-8	3258	195	-129	-52	-129	3258
1 PX	-4742	3	-24	-4743	-3	-618	-59	-50	-24	47	653	-83	-50	-84	47
1 PY	0	-67	60	0	-66	0	0	167	-60	-5076	0	-596	-167	596	5076
1 PZ	-3241	47	-3	3288	-47	28	-50	-43	-3	3746	-37	-93	-43	-92	3746
2 2S	-257	-89	65	180	89	-3919	-134	218	65	3218	-4025	5	218	5	3218
2 PX	-547	57	-74	-516	-57	-4859	-318	-223	-74	126	4771	-31	-223	-31	126
2 PY	0	74	-46	0	74	0	0	-164	46	-4893	0	659	164	-659	4893
2 PZ	8	-14	32	-108	14	-3170	-311	98	32	-3852	-3184	-207	98	-207	-3852
3 2S	-182	-99	36	-257	99	156	3388	-32	36	7	-3548	-3533	-32	-3533	7
3 PX	-116	350	22	-317	-350	-166	-4550	-327	22	-48	-5174	496	-327	496	-48
3 PY	0	-73	-211	0	-73	0	0	-62	211	-315	0	4980	62	-4980	316
3 PZ	90	249	278	113	-249	-349	-3952	88	278	-244	3088	-3407	88	-3407	-244
4 2S	21	3605	-3579	36	86	74	-64	3578	-225	249	49	33	-108	-3691	-124
4 PX	-9	4493	-292	-41	38	-15	-423	-5142	-21	-110	-500	50	29	-267	43
4 PY	-49	159	-5013	-61	-18	-63	137	180	138	-267	-77	412	39	4871	68
4 PZ	1	3962	3279	0	-71	5	-271	3077	251	-111	250	-374	82	3460	77
5 2S	21	-86	-225	36	-3605	74	-64	-108	-3579	-124	49	-3691	3578	33	249
5 PX	-9	-38	-21	-41	-4493	-15	-423	29	-292	43	-500	-267	-5142	50	-110
5 PY	49	-18	-138	61	159	63	-137	-39	5013	-68	77	-4871	-180	-412	267
5 PZ	1	71	251	0	-3962	5	-271	83	3279	77	250	3460	3077	-373	-111
6 1S	-277	-12	22	-7075	12	293	134	63	22	5	-521	79	63	79	5
7 1S	7054	0	-16	269	0	-514	12	-29	-16	13	279	-21	-29	-21	13
8 1S	509	-4	-9	299	4	-7059	425	0	-9	-7	187	112	0	112	-7
9 1S	36	414	158	-46	-414	-387	7119	-145	158	-167	36	38	-145	38	-167
10 1S	25	-131	-7131	27	-71	-3	-167	-141	136	11	149	-446	62	24	26
11 1S	-4	7115	129	16	-3	-6	440	-128	-23	16	138	135	2	17	5
12 1S	-23	-130	141	-62	1	-54	-153	7131	-13	-147	-448	163	26	25	66
13 1S	-23	-1	-13	-62	130	-54	-153	26	141	66	-448	25	7131	163	-147
14 1S	-4	3	-23	16	-7115	-6	440	2	129	5	138	17	-128	135	16
15 1S	25	71	136	27	131	-3	-167	62	-7131	26	149	24	-141	-446	11

EXPANSIONS IN HYBRID BASIS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	311	6	-20	-7001	-6	-325	-123	-48	-20	385	590	-96	-48	-96	385
2	7019	0	14	-293	0	549	-39	23	14	317	-333	22	23	22	318
3	-214	-3	37	268	-90	104	-100	71	-48	-96	58	-528	-164	315	7083
4	-214	90	-48	268	3	104	-100	-164	37	7083	58	315	71	-528	-96
5	242	-98	103	425	98	-120	19	324	103	195	-6997	-59	324	-59	196
6	-532	-17	-1	-305	17	-6993	-429	7	-1	374	-250	-104	7	-104	374
7	-110	24	-24	136	80	230	124	-84	40	78	195	588	148	-343	6998
8	-110	-80	40	135	-24	230	124	148	-24	6998	195	-344	-84	588	78
9	-40	110	305	-57	-6	-88	-65	87	6	107	0	-7007	-1	35	-338
10	-217	105	-85	-415	-105	104	-6	-300	-85	73	-6992	80	-300	80	73
11	-65	-420	-153	16	420	384	6913	149	-153	173	-106	-176	149	-176	173
12	-40	6	6	-57	-110	-88	-65	-1	305	-338	0	35	87	-7007	107
13	-25	148	-6980	-26	67	-11	180	149	-141	-13	-177	497	-66	-136	-50
14	5	6990	-137	-9	28	29	-464	135	14	-10	-163	-160	11	-74	10
15	18	148	-150	49	-16	51	168	6978	12	159	508	-183	-40	-147	-60
16	44	-76	109	60	93	78	13	-106	-337	364	-68	-86	-122	-7025	-147
17	18	16	12	49	-148	51	168	-40	-150	-60	508	-147	6978	-183	159
18	5	-28	14	-9	-6990	29	-464	11	-136	10	-163	-74	135	-160	-10
19	-25	-67	-141	-26	-148	-11	180	-66	-6980	-50	-177	-136	149	497	-13
20	44	-93	-337	60	76	78	-13	-122	109	-147	-67	-7025	-106	-86	364
21	-277	-12	22	-7075	12	293	134	63	22	5	-521	79	63	79	5
22	7054	0	-16	269	0	-514	12	-29	-16	13	279	-21	-29	-21	13
23	509	-4	-9	299	4	-7059	425	0	-9	-7	187	112	0	112	-7
24	36	414	158	-46	-414	-387	7119	-145	158	-167	36	38	-145	38	-167
25	25	-131	-7131	27	-71	-3	-167	-141	136	11	149	-446	62	24	26
26	-4	7115	129	16	-3	-6	440	-128	-23	16	138	135	2	17	5
27	-23	-130	141	-62	1	-54	-153	7131	-13	-147	-448	163	26	25	66
28	-23	-1	-13	-62	130	-54	-153	26	141	66	-448	25	7131	163	-147
29	-4	3	-23	16	-7115	-6	440	2	129	5	138	17	-128	135	16
30	25	71	136	27	131	-3	-167	62	-7131	26	149	24	-141	-446	11

TABLE 34. ANGLES IN DEGREES AND BONDLENGTHS IN ANGSTROMS ASSIGNED BY THE MODEL-BUILDER TO ACYCLIC PARAFFINS

	BOND	CH	SINGLE CC BONDS			DOUBLE	TRIPLE
	ANGLE	BOND	TETRAHEDRAL	TRIGONAL	LINEAR	BOND	BOND
TETRAHEDRAL	109.5	1.09	1.54	1.52	1.46		
TRIGONAL	120	1.08	1.52	1.46	1.45	1.34	
LINEAR	180	1.06	1.46	1.45	1.38		1.20

where (s), (x), etc. refer to the 2s, 2px, etc. AO's on carbon. Since there are four parameters, but only three constraints (normalization is automatic)

$$\langle g(+)|g(-)\rangle = 0 \tag{10}$$

$$\langle h(+)|h(-)\rangle = 0 \tag{11}$$

$$\langle g(\pm)|h(\pm)\rangle = 0 = \cos Q\cos R + \sin Q\sin R\cos A\cos B. \tag{12}$$

There is one free parameter and one additional constraint may be imposed. The explicit relations that result from Equations 8-12 for the parameters Q, R, A, B are conveniently displayed as

$$(\sin Q\sin A)^2 = \frac{1}{2}, \tag{13}$$

$$(\sin R\sin B)^2 = \frac{1}{2}, \tag{14}$$

$$\cos^2 Q + \cos^2 R = \frac{1}{2} \tag{15}$$

and

$$\cot^2 A + \cot^2 B = 1. \tag{16}$$

Equations 13 and 14 relate the s-character to the angle in the same hybrid, Equation 15 connects their relative s-characters, and Equation 16 connects their opening angles. With these equations, it is straightforward to adjust the two hybrid pairs to various specific situations.

Tetrahedral carbon (four single bonds)

A first set of hybrids obtains by using the additional constraint to fix the angle between all centroids at 109.5° (the tetrahedral value), i.e.

by setting

$$A = B, \tag{17}$$

and from Equation 16

$$\cos A = \sqrt{3}/3. \tag{18}$$

The remaining parameters follow from Equations 13-14, so

$$g(\pm) = .5(s) + .5(z) \pm .7071(x), \tag{19}$$

$$h(\pm) = .5(s) - .5(z) \mp .7071(y). \tag{20}$$

These are the well-known sp^3 hybrids.

Trigonal carbon (two single bonds and one double bond)

Unlike the tetrahedral, the g's and h's are inequivalent here. Suppose the g's point in the direction of the single bonds and the h's are the bent banana hybrids pointing into the double bond. Thus

$$A = 60^{\circ} \tag{21}$$

which implies that

$$B = 101^{\circ}, \tag{22}$$

giving

$$g(\pm) = .5773(s) + .4082(z) \pm .7071(x) \tag{23}$$

and

$$h(\pm) = .4082(s) - .5773(z) \mp .7071(y). \tag{24}$$

The g's are the usual sp^2 hybrids, while the h's are sp^5, with centroids 50° above and below the bond skeleton. The g's, being single bond hybrids, are always coplanar with vicinal single bond neighbors. This forces the centroids of the h's to lie about five degrees away from exactly cis or trans positions.

Ethynyl Carbon (Single Bond and Triple Bond)

<u>Construction of the hybrids</u>

Let p, p(i), i = 1,2,3 be four normalized linear combinations of p-orbitals satisfying

$$\langle p | p(i) \rangle = 0 \tag{25}$$

and

$$\langle p(i) | p(j) \rangle = -\frac{1}{2}, \; i \neq j \tag{26}$$

i.e., the p(i) lie separated by 120° in a plane orthogonal to p. From p and the 2s AO can be formed 'left' and 'right' hybrids which point directly at the neighbor atoms

$$\ell = (s)\cos Q - (p)\sin Q \tag{27}$$

$$r = (s)\sin Q - (p)\cos Q. \tag{28}$$

The orthogonal, trigonal banana hybrids are formed from the r and the p(i)

$$t(i) = (r + p(i)\sqrt{2})\sqrt{3}/3. \tag{29}$$

They point into the triple bond and are orthogonal to the hybrid ℓ that points into the single bond. Since all of these hybrids are automatically orthogonal, Q is a free parameter. It can therefore be adjusted such that the hybrid ℓ fits as closely as possible the atomic s and p contributions to the actual localized MO's representing the single bonds next to triple bonds. The thirteen cases considered in this study gave

$$\ell = .6736(s) - .7391(p) \tag{30}$$

with deviations the same as those for the other single bonds (sp^3 and sp^2). Note that ℓ is not an exact sp hybrid.

The expression for ℓ implies the expression

$$t(i) = .4267(s) + .3889(p) + .5773p(i) \tag{31}$$

for the banana hybrids pointing into the triple bond. These are approximately sp^5, and form an angle of about 63° with the bond axis. It is striking that these hybrids form almost the same angle with each other as those pointing into the double bonds, namely 101°.

Absolute orientation

Since the ultimate goal is to recognize the similarities among localized orbitals, the free rotation of the t(i) should be removed as consistently as possible. The method chosen was to maximize the overlap between a t(i) and its contribution to one of the banana bond LMO's. Suppose ℓ and r lie along the z-axis, and let the contributions from the perpendicular (xy) plane to the three LMO's in the triple bond be given by

$$L(i) = a(i) \cdot (x) + b(i) \cdot (y), \quad i = 1,2,3. \tag{32}$$

The pair of Equations 25,26 can be expressed as

$$p(i) = -(x)\sin(W + (i-1)\pi/3) + (y)\cos(W + (i-1)\pi/3) \tag{33}$$

and the variation in W describes the rotation of the hybrid triple around the bond axis. Optimal fit of p(i) to L(i) is therefore obtained from the condition

$$d/dW[\langle L(i)|p(i)\rangle] = 0 \tag{34}$$

which yields an angle W(i) given by

$$\tan(W(i)) = -a(i)/b(i). \tag{35}$$

Three values of W(i) are obtained in this way, from which the weighted mean is formed

$$W = \sum_i W(i)\langle L(i)|p(l)\rangle / \sum_i \langle L(i)|p(i)\rangle. \tag{36}$$

The absolute orientation of the p(i), and hence the t(i), about the bond axis is then obtained by inserting this value of W into Equation 33.

Even with this procedure, the triple bonds presented situations not encountered with the others. Because of very slow localization and/or slight molecular asymmetry, their centroids were sometimes not coplanar with those of vicinal single bonds. In the discussion of fragments that will be given later, we have therefore extrapolated these exceptions to coplanar orientations.

ENERGY LOCALIZED MO's

Introduction

Energy localized MO's (LMO's) exploit the invariance of the MO equations to unitary transformations, as was pointed out by Fock (15). The LMO's were themselves proposed later by Lennard-Jones and Pople (81), but remained largely conceptual, even after the advent of computers, until the algorithm of Edmiston and Ruedenberg (5,6) allowed their practical determination. In two papers including some diatomic and small polyatomic localizations (6,7), the authors convincingly demonstrated that these were indeed rigorous quantum mechanical analogs to the bonds and lone pairs of chemical intuition, as had been hoped all along. Various interpretations of LMO's are reviewed in the Appendix.

Localization Equations

At first, the formal discussion of localized orbitals was confined to equivalent MO's, those which carry the regular representation (82) of the symmetry group, i.e., they are permuted among each other by the group operations. In passing, it was also mentioned that they presumably maximize the self-repulsion sum (localization sum)

$$D = \sum_{u} [u^2|u^2] \tag{37}$$

over all occupied MO's, where

$$[u|v] = \iint d^3\underline{x}\, d^3\underline{z}\; u(\underline{x})\; v(\underline{z})/|\underline{x} - \underline{z}|. \tag{38}$$

Edmiston and Ruedenberg (5) extended these ideas to general systems (i.e., the symmetry requirements necessary for equivalent orbitals were dropped) and adopted the maximization of D and the resulting 'localization criteria'

$$[u^2 - v^2|uv] = 0 \tag{39}$$

as the central features for the LMO determinations. This was done by series of successive 2 x 2 transformations (5,6) rather like the Jacobi diagonalization method (83). A remarkable feature of this method is that it has always converged as far as is known, even in those cases where it has led to some ambiguities (6,7). These are readily understood (84).

Semiempirical Energy Localization

In principle, there are as many of these as there are semiempirical theories. Only several have appeared, however: a set of pi orbital localizations (21,22) which used the Mulliken approximation (85) for electron repulsion integrals; and all valence electron localizations using CNDO (86) and INDO (63).

One might wonder what differences obtain between the last two approximations. It has been shown (63) that the retention of the one-center two-electron integrals by INDO gives much better agreement with existing *ab initio* LMO's (INDO LMO's are much closer to the *ab initio* than to the CNDO: in particular, INDO reproduces the *ab initio* banana orbitals while CNDO does not mix the sigma and pi orbitals). Thus, semiempirical LMO's are sensitive to the method of approximating the electron repulsion integrals. This becomes especially important when topics such as hybridization are analyzed, and dictates the use of INDO for studying the paraffins.

Starting Orbitals

The starting orbitals for the energy localization can be selected in a way that is similar to that used for the Hückel orbitals (21), and is possible for two reasons:

1. The canonical closed shell INDO MO's are readily available.
2. The LMO's in these paraffins are largely two-center 'bonds.'

The procedure follows:

1. For each bond, form a perfectly homopolar two-center orbital $(\chi + \chi')/\sqrt{2}$, where χ and χ' are the two hybrids pointing into the bond.
2. Project each of these two-center orbitals into the space of the occupied canonical MO's.
3. Symmetrically orthogonalize these projections.

The details of this have been given elsewhere (21). The starting localized MO's obtained this way turn out to be close approximations to the exact LMO's. This is shown in Table 35 for ethane, which lists the coefficients of the two (CH and CC) orbitals in the hybrid basis. The degree of approximation is typical.

First Order Localization

With starting orbitals as close to the LMO's as the SMO's, it is natural to use a first order scheme for each of the 2 x 2 localization steps discussed after Equation 39. Thus, if

$$u_i = v_i + t_{ij}V_j, \tag{40}$$

$$u_j = v_j + t_{ji}V_i, \tag{41}$$

with

TABLE 35. CCMPARISON OF LOCALIZED, LEAST MEAN SQUARE AND PERTURBATION MO'S IN ETHANE

		LMO 1	SMO 1	PMO 1	LMO 2	SMO 2	PMO 2
	1	-108	-58	-83	7069	7070	7069
	2	140	140	157	104	54	76
H	3	6984	6984	6980	104	54	76
Y	4	140	140	157	104	54	76
B	5	8	57	84	7069	7070	7069
R	6	172	173	176	104	54	76
I	7	172	173	176	104	54	76
D	8	-462	-461	-486	104	54	76
	9	-123	-123	-140	-5	-54	-79
A	10	7115	7115	7114	-5	-54	-79
O	11	-123	-123	-140	-5	-54	-79
S	12	-158	-159	-159	-5	-54	-79
	13	-158	-159	-159	-5	-54	-79
	14	441	441	464	-5	-54	-79

$$t_{ij} = -t_{ji}, \tag{42}$$

then the u's are normalized to first order. Substitution of this expansion in Equation 39 yields for t_{ij} the expression

$$t_{ij} = [ii - jj|ij]/|4[ij|ij] - [ii - jj|ii - jj]| \tag{43}$$

where all integrals are calculated with the MO's v_i. It leads to the following change in the localization sum D

$$D' = ([ii - jj|ij])^2/|[ij|ij] - [ii - jj|ii - jj]/4| \geq 0 \tag{44}$$

with each i,j transformation. The procedure is applied to all distinct orbital pairs and iterated until the total change in D is less than some predetermined criterion. Note that this method requires that only three kinds of repulsion integrals be calculated, which gives it a further advantage over the original algorithm (which requires the calculation of all types of repulsion integrals).

LMO's as Two-Center Orbitals Perturbed by Bond-Bond Interactions

In the same context, it is of interest to compare a theory of Pople and Santry (87-89) with energy localization. These authors applied the perturbation theory of Coulson and Longuet-Higgins (90-93) to some simple paraffins by using a hybrid basis analogous to the present one and assuming that the unperturbed orbitals were two-center bonds. Only one-electron core energies and bond-bond interactions were included, and although the method strictly provides just the population matrix, coefficients can be extracted from it in several reasonable ways, all of which give about the same results. In order to make the comparison as favorable and simple as possible, the actual LMO's were truncated to two centers and used as the unperturbed functions with the appropriate INDO one-electron matrix elements.

The results (PMO's) for ethane are also shown in Table 35, and again are typical of the other molecules. The agreement with the LMO's is similar to that obtained for the SMO's and thus provides another interesting interpretation: LMO's can be thought of as arising from perturbed, perfectly two-center orbitals. This has two consequences:

1. It gives particular motivation to such concepts as 'delocalization' and 'overflow' which will be applied later.

2. The PMO's anticipate some of the dependences on relative bond orientations, types and distances that will play a great role in the LMO analysis.

Energy Localized Orbitals from Pseudo-Eigenvalue Equations

Ruedenberg (8) has shown that LMO's satisfy the pseudo-eigenvalue equations (see also the work of Gilbert (94), which is closely related)

$$(F + L)|n\rangle = \gamma_{nn}|n\rangle \ , \ n = 1,\ldots,N \qquad (45)$$

where F is the Fock operator,

$$L = \sum_{i \neq k}^{N}\sum^{N} |i\rangle(C_{ik} - \gamma_{ik})\langle k| \ , \qquad (46)$$

with

$$\gamma_{ik} = \langle i|F|k\rangle \qquad (47)$$

and

$$C_{ik} = |\langle ii - kk|ik\rangle|. \qquad (48)$$

It was hoped that LMO's could be obtained with an SCF iteration process.

The SMO's provided an interesting chance to test this, being very close to the LMO's and thus presumably requiring few iterations for convergence. This was not the case however, for all attempts at iterative solution of Equation 46 failed: the C_{ik}, though small initially (for propane the largest were around .0025 a.u.), did not become successively smaller.

The LCAO Expansions

The complete LCAO LMO's for each molecule are also presented in Tables 1-33. They are given in two bases, the INDO basis of Slater orbitals, and the previously described hybrid basis. The rows in the former are labelled by the AO type, preceded by the number of the atom centering it; and the rows in the latter are labelled by the numbers assigned the hybrids in Figure 1. The LMO's are also labelled by numbers and these form the column headings. The ordering of the molecules is the same as that in Figure 1. Further discussion of the LMO's will be in terms of the hybrid basis only and deferred until suitable molecule-independent coefficients have been determined.

Localization was terminated when an iteration (each set of N(N-1)/2 transformations) left D stable to ten decimals. It was found that even in the worst cases this gave coefficients stable to several parts in ten in the fourth decimal place. Due to the development of the first order method toward the end of the work, the usual Edmiston-Ruedenberg scheme was used, normally taking fifteen minutes or less on an IBM 360/50, but needing more than thirty minutes in some of the larger or triply bonded molecules. The first order method is both faster and easier to program, but the impracticality of repeating calculations, machine changes, etc., made a thorough comparison of relative times difficult. However, they improved by factors of two to five, even without taking full advantage of the fewer integral types required. Thus, the savings is certainly worthwhile.

MOLECULE INVARIANT LMO FRAGMENTS

Local Delocalization and LMO Fragments

It is clear from the LCAO expansions in the hybrid basis (Tables 1-33) that the LMO's are not confined to two centers. This fact is related to the occurrence of long range bond orders, which was pointed out by Pople and Santry (87,88), but seems not to have been widely appreciated, perhaps because such delocalization appears intuitively unappealing. However, recent studies from this laboratory have revealed the importance of such 'local delocalization' in many contexts: the origin of aromatic stability is due to geminal delocalization (21,22), and the origins of rotation barriers (18,19,69,70) as well as the systematic interpretation of bond dipole moments and energies (20) is intimately connected with vicinal delocalization. There are therefore good reasons to devote an essential part of the present study to the delocalization of the LMO's.

Local delocalization means that each LMO contains contributions from various bond regions. In the present discussion, the term 'bond region' will be used to denote the space lying between two chemically bonded atoms. Each LMO is therefore a sum of several LMO fragments, each of which is associated with a specific bond region. The character of these LMO fragments will be the principal objective of the subsequent discussion because, in acyclic paraffins, transferability and regular behavior are most clearly revealed by them. Standard forms for the (LMO) fragments will be cataloged for various conditions in series of tables from which they can be retrieved to construct practically exact LMO's for almost any given acyclic hydrocarbon without solving any equations. For those few exceptions that are not covered by this work, close estimates (to within a few percent) can be obtained by sensible perusal of the discussion of related cases.

An LMO fragment is characterized (1) by the LMO to which it belongs and (2) by the bond region in which it is located. We shall discuss both in turn.

LMO Characteristics of Fragments

The LMO characteristics of a fragment are based on the fact that by far the largest part of each LMO lies in one particular bond region (the coefficients of the hybrids pointing into this region are always about 0.7), so that it is justifiable to say: a particular LMO 'essentially describes' the bond in which it is predominantly concentrated. Thus, LMO number three in pentane (Table 16) essentially describes the single bond between the atoms C_1 and H_6. This principal fragment will be called the bond fragment of that LMO, and it will be used to characterize the LMO itself. Thus the LMO number three will be called a 'CH bond LMO.'

All other fragments of an LMO will be characterized by their location relative to the bond fragment, denoted as geminal fragments, vicinal fragments and third and fourth neighbor fragments. Thus in LMO number three of pentane (Table 16), the fragment between atoms C_1 and C_2 is a geminal fragment, the one between C_2 and C_3 is a vicinal fragment, and those between C_3 and C_4 and C_4 and C_5 are third and fourth neighbor fragments, respectively. Higher fragments will not be considered because of their small coefficients.

We adopt the convention that the bond fragment is positive, which implies that, in each LMO, the coefficients of the hybrids in the bond fragment are positive.

Characterization of LMO Fragments by Bond Regions

The characterization of an LMO fragment with respect to the nature of the bond region in which it lies has to do with the location of that bond region within the total bond skeleton. The character of a bond region, in turn, is determined by the hybrid AO's pointing into it from the two constituent atoms. We start therefore by classifying the character of these hybrids. In the following the term 'hybrid' is always meant to include the hydrogen AO, unless stated otherwise.

Hybrid AO's can be located on four types of atoms

(1) on hydrogen atoms denoted by H;

(2) on alkyl type carbon atoms (>C<);

(3) on vinyl type carbon atoms (=C<) denoted by CV;

(4) on ethynyl type carbon atoms (≡C-) denoted by CE.

The carbon atoms can be further distinguished as

(1) methanic (bonded to hydrogens only);

(2) primary (bonded to one other carbon), denoted by CP;

(3) secondary (bonded to two other carbons), denoted by CS;

(4) tertiary (bonded to three other carbons), denoted by CT;

(5) quaternary (bonded to four other carbons), which will not occur in this investigation.

Finally, the carbon hybrids will be characterized by what kind of bond lies in the coplanar positions(s) vicinal to them, cis or trans. These are denoted by

(1) H, when a CH bond is vicinal;

(2) C, when a CC bond is vicinal;

(3) 2, when a double bond is vicinal;

(4) 3, when a triple bond is vicinal.

The cis are distinguished from the trans by an asterisk, e.g. H* means the CH bond in the vicinal position lies cis.

Thus there exist a considerable number of different hybrid AO's and every bond region can be characterized by the hybrids pointing into it. Since these LMO fragment characteristics will occur again and again in the subsequent discussions, we shall give here a complete description for those that occur in the study, together with the abbreviations to be used in the sequel. Following this, we shall show how the cis and trans fragment abbreviations are used.

1. CPH = single bond between primary alkyl carbon and hydrogen.
2. CSH = single bond between secondary alkyl carbon and hydrogen.
3. CTH = single bond between tertiary alkyl carbon and hydrogen.
4. CPVH = single bond between primary vinyl carbon and hydrogen.
5. CSVH = single bond between secondary vinyl carbon and hydrogen.
6. CEH = single bond between primary ethynyl carbon and hydrogen.
7. CPCP = single bond between two primary alkyl carbons.
8. CPCS = single bond between primary and secondary alkyl carbons.
9. CPCT = single bond between primary and tertiary alkyl carbons.

10. CPCSV = single bond between primary alkyl and secondary vinyl carbons.

11. CPCTV = single bond between primary alkyl and tertiary vinyl carbons.

12. CPCE = single bond between primary alkyl and secondary ethynyl carbons.

13. CSCS = single bond between two secondary alkyl carbons.

14. CSCT = single bond between secondary and tertiary alkyl carbons.

15. CSCSV = single bond between secondary alkyl and secondary vinyl carbons.

16. CSCE = single bond between secondary alkyl and secondary ethynyl carbons.

17. CTCSV = single bond between tertiary alkyl and secondary vinyl carbons.

18. CTCE = single bond between tertiary alkyl and secondary ethynyl carbons.

19. CSVCSV = single bond between two secondary vinyl carbons.

20. CSVCTV = single bond between secondary and tertiary vinyl carbons.

21. CSVCE = single bond between secondary vinyl and secondary ethynyl carbons.

22. CECE = single bond between two secondary ethynyl carbons.

23. BCPVCPV = one of the double banana bonds between two primary vinyl carbons.

24. BCPVCSV = one of the double banana bonds between primary and secondary vinyl carbons.

25. BCPVCTV = one of the double banana bonds between primary and tertiary vinyl carbons.

26. BCSVCSV = one of the double banana bonds between two secondary vinyl carbons.

27. BCPECPE = one of the triple banana bonds between two primary ethynyl carbons.

28. BCPECSE = one of the triple banana bonds between primary and secondary ethynyl carbons.

29. BCSECSE = one of the triple banana bonds between two secondary ethynyl carbons.

We point out the symbols are 'symmetric,' i.e., CSCP means the same thing as CPCS. The trans fragments are described by adding symbols to these, usually preceded by a dash. For example, CPCT-H23 means that a CH bond, a double bond and a triple bond all lie trans to the CPCT bond. If the double bond lay cis, this would be described as CPCT-H2*3. Many times, the CH will be understood, e.g., the preceding will be written CPCT-2*3.

Finally, we distinguish in each LMO fragment the <u>near</u> hybrid and the <u>far</u> hybrid, according to their position relative to the bond fragment of the LMO.

MI ORBITAL BOND FRAGMENTS

General Properties

The molecule invariant (MI) bond fragments are the only fragments for which the coefficients of both constituent hybrids are positive. Furthermore, all are fairly homopolar with coefficients near 0.7, an order of magnitude greater than those in other fragments.

Geminal influences

The slight polarities of the single bonds follow a general pattern that can be summarized by stating that the coefficients on various types of atoms satisfy the following inequalities

$$\mathrm{CE} > \mathrm{H} > \mathrm{CP} > \mathrm{CS} \approx \mathrm{CT} \approx \mathrm{CSV} \approx \mathrm{CTV} \tag{49}$$

and

$$\mathrm{H} > \mathrm{CPV}. \tag{50}$$

Similarly, the coefficients on banana hybrids in double and triple banana bonds satisfy the inequalities

$$\mathrm{CPV} > \mathrm{CSV} > \mathrm{CTV} \tag{51}$$

and

$$\mathrm{CPE} > \mathrm{CSE}, \tag{52}$$

respectively. In comparing fragments with different geminal character, e.g. P, S and T) and identical vicinal fragments, we shall use the term <u>corresponding</u> fragments.

Vicinal influences

Finer differences between bond fragments within the gross behavior just described are induced by the coplanar vicinal fragments of the same LMO. In particular:

1. If bond and coplanar vicinal fragments are separated by a single bond, the type and orientation of the vicinal fragments usually influences the bond coefficients (in cases where higher fragments come into proximity with the bond fragment, the geometry of the higher fragments has some effect, too).

2. If bond and coplanar vicinal fragments are separated by a double bond, the geometry of the vicinal and higher fragments affects the bond coefficients.

3. If bond and coplanar vicinal fragment are separated by a triple bond, the vicinal fragment has little influence.

The CH bonds are least sensitive to vicinal influences, followed, in order, by CC and double and triple banana bonds. To a good approximation, the influences of several vicinal bonds are simply additive. When comparing bond fragments with the same geminal character, but different vicinal elements, we frequently call the vicinal fragments substituents.

Alkyl CH Bonds

The various types of alkyl CH bond fragments appear in the first two rows of Tables 36-39. The first row contains the carbon sp^3 contributions and the second row lists the hydrogen 1s contributions. The E's and V's in parentheses refer to positions of ethynyl and vinyl carbons, respectively,

TABLE 36. BOND AND GEMINAL FRAGMENTS IN METHANE AND PRIMARY CH LMO'S

	METHANE	CPH H	CPH C	CPH 2	CPH 3	CPH H(E)	CPH C(E)	CPH C(V)
CP	7035	6985	6975	6970	6965	7005	6985	6990
H	7100	7115	7135	7105	7090	7105	7125	7120
CP	100	140	140	140		140	140	
H-H	-105	-120	-130	-130		-120	-130	
CP		150	150	145		150	150	
H-C		-130	-140	-135		-130	-140	
CP		150		135				150
H-2		-130		-90				-140
CP					135			
H-3					-100			
CP		-110						
CP		10						
CP		-90	-130					
CS-H		5	-5					
CP		-85	-145					
CS-C		10	-10					
CP		-90	-120					
CS-2		5	0					
CP						-90	-110	
CS-3						5	0	
CP		-70	-115					
CT-HH		10	-5					
CP		-70	-110					
CT-HC		10	-5					
CP		-75	-120					
CT-H2		10	-10					
CP						-75	-105	
CT-H3						5	0	
CP						-75	-105	
CT-23						5	0	
CP		-50		-150				
CSV-H		30		5				
CP		-45		-165				
CSV-C		30		5				
CP				-135				-80
CTV-HH				5				15
CP					-170			
CE					40			
CP			-155					
CS-H*			-10					

TABLE 37. BOND AND GEMINAL FRAGMENTS IN SECONDARY CH LMO'S

	CSH HH	CSH HC	CSH H2	CSH H3	CSH 23	CSH 33	CSH HH(E)	CSH H2*	CSH 22*
CS	6945	6940	6935	6930	6920	6920	6960	6940	6930
H	7120	7140	7110	7090	7080	7060	7110	7105	7090
CS	170	170	170				170		
H-HH	-135	-145	-145				-135		
CS	180								
H-HC	-145								
CS	185		170					175	
H-H2	-150		-100					-120	
CS				170	165	165			175
H-AB				-120	-90	-105			-90
CS	-85							-90	
CP-H	0							-5	
CS	-80	-80	-85				-80		
CP-C	-10	-10	0				-10		
CS	-80		-75						
CP-2	-10		30						
CS				-85					
CP-3				20					
CS	-65		-65						
CS-HH	0		0						
CS	-65								
CS-HC	0								
CS				-65			-70		
CS-H3				20			0		
CS	-45	-85							
CT-HHH	0	-10							
CS	-25		-135					-60	-60
CSV-HH	25		-5					20	20
CS									-130
CSV-HH*									-10
CS					-130				
CSV-H3					-10				
CS				-150	-150				
CE-H				30	30				
CS				-150					
CE-C				20					
CS						-150			
CE-3						50			

TABLE 38. BOND AND GEMINAL FRAGMENTS IN TERTIARY CH LMO'S

	CTH-H HH	CTH-H H2	CTH-H H3	CTH-H 23
CT	6910	6890	6890	6880
H	7120	7110	7100	7090
CT	-70	-70		
CP-HH	-10	-10		
CT	-65			
CP-HC	-10			
CT	-65	-55		
CP-H2	-10	30		
CT			-65	
CP-H3			15	
CT				-50
CP-23				40
CT	-50			
CS-HHH	-10			
CT	-10	-120		
CSV-HHH	20	-15		
CT				-120
CSV-HH3				0
CT			-140	-145
CE-HH			20	15

TABLE 39. BOND AND GEMINAL FRAGMENTS IN CIS PRIMARY CH LMO'S

	CPH H*	CPH VH*	CPH 2*	CPH 3*
CP	6985	6975	6985	6980
H	7110	7135	7095	7080
CP	140		140	
H-H*	-125		-130	
CP		140	140	
H-2*		-125	-100	
CP				135
H-3*				-100
CP	-110			
CP	10			
CP		-185	-85	
CSV-H		-10	25	
CP				-170
CE				40

which are defined in Figure 2. The VH* in Table 39 distinguishes the cases for which vinyl CH bonds occur cis to primary CH bond fragments.

Polarity

Overall, the fragments are very similar. Except for methane, all bond fragments display a 1s coefficient greater by about 2%, and thus the Mulliken gross atomic populations on the hydrogens are always about 4% larger than those on the carbons.

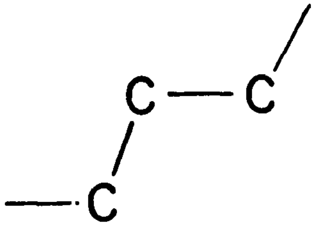
Geminal effects

The geminal effects are seen in that the coefficients for the sp^3 in corresponding fragments, e.g. CPH-2, CSH-2 and CTH-2, decrease by about 40 with each step in the series CPH to CSH to CTH, while the 1s coefficients are almost constant.

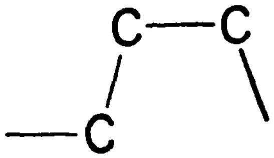
Vicinal effects

Vicinal effects can be assessed by using the CPH-H, CSH-HH and CTH-HHH as prototypes and considering the CC, 2, 3, etc. fragments as substituents. The effects of these 'substitutions' appear in Table 40. The numbers tabulated are those which must be added to the prototype fragment to obtain the substituted fragment, e.g. -10 and 20 must be added to the sp^3 and 1s coefficients of CPH-H, respectively, to obtain those of CPH-C. Inspection of the table reveals that, to a very good approximation, the substituent effects are the same for each of the alkyl CH types. Moreover, according to the CH-23 and CH-33 rows, the effects of several vicinal substituents are simply additive.

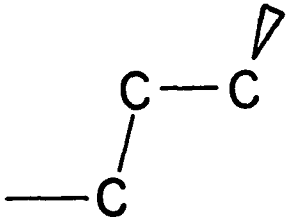
Figure 2. Bond skeleton and relative orientation nomenclatures



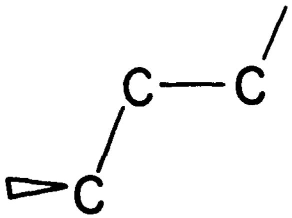
TT-BOND
SKELETON



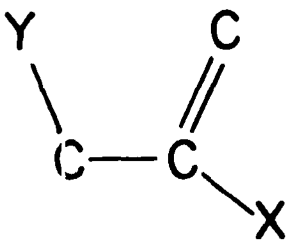
TC-BOND
SKELETON



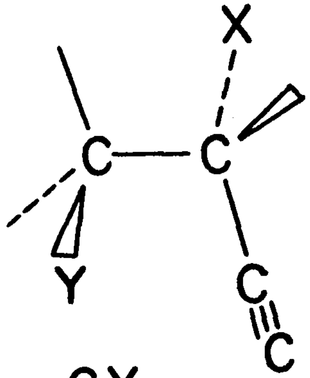
TG-BOND
SKELETON



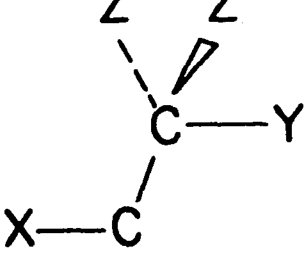
GT-BOND
SKELETON



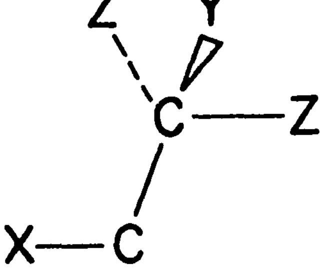
CY
X(V)



CY
X(E)



CX-Y



CX-ZA

TABLE 40. SUBSTITUENT EFFECTS ON CH BOND FRAGMENTS

	CPH	CSH	CTH	CSVH
C	-10	-5		-10
H-C	20	20		20
C	-15	-10	-20	
H-2	-10	-10	-10	
C	-20	-15	-20	
H-3	-25	-30	-20	
C		-25	-30	
H-23		-40	-30	
C		-25		
H-33		-60		
C	20	15		
H-H(E)	-10	-10		
C	0			-5
H-C(E)	10			10
C	5			
H-C(V)	5			
C	0			-5
H-H*	-5			0
C	-10			
H-VH*	20			
C				-5
H-C*				10
C	0	-5		
H-2*	-15	-15		
C	-5			-15
H-3*	-30			-20
C		-15		
H-22*		-30		

Alkyl CC Bonds

Polarity

These are the CC analogs to the alkyl CH, the H being replaced by an alkyl, vinyl or ethynyl carbon. They appear in Tables 41-45 (in Table 41 they are listed in the first two columns, in the remaining tables in the first two rows). The coefficients for a particular fragment are in general more nearly equal than was the case for the alkyl CH, and are slightly larger than the carbon sp^3 coefficients (in the CH). Usually the magnitudes of the coefficients satisfy

$$\mathrm{CE} > \mathrm{CP} > \mathrm{CSV} \approx \mathrm{CTV} > \mathrm{CS} \approx \mathrm{CT}. \tag{53}$$

But when an ethynyl carbon neighbors the fragment, and if the fragment itself contains no ethynyl carbon, the coefficient on the carbon next to the ethynyl becomes largest.

Geminal substitution

There is a difference between the CC and CH alkyl bond fragments here, for if one passes, say, from the CPCP to the CSCP to the CTCP, all coefficients change, while only the sp^3 coefficients changed in the series CPH, CSH and CTH. That is, both coefficients change with geminal substitution in the alkyl CC fragments.

Vicinal substitution

These effects are given in Table 46. The prototype fragments are the CXCP-H, CXCX-HH, CXCXV-HH and CXCE-H, where X is S or T. The regularity

TABLE 41. BOND AND GEMINAL FRAGMENTS IN SATURATED PRIMARY CC LMO'S

	CPC		CPH-H		CPH-C	
CPCP	7070	7070	105	-5		
CPCS-H	7055	7045	90	-10	165	-20
CPCS-C	7070	7040	90	-10	175	-20
CPCS-2	7040	7030	90	-10	160	-20
CPCS-3	7020	7035	85	-10	150	-20
CPCS-H*	7070	7040	80	-10	185	-20
CPCT-HH	7040	7020	75	-15	145	-25
CPCT-HC	7055	7020	70	-15	150	-25
CPCT-H2	7025	7010	70	-15	145	-25
CPCT-H3	7005	7010	70	-20	140	-25
CPCT-23	6990	7000	65	-20	140	-25

TABLE 42. BOND AND GEMINAL FRAGMENTS IN UNSATURATED PRIMARY CC LMO'S

	CPCSV H	CPCSV C	CPCTV HH	CPCE
CP	7040	7065	7030	6985
C	7030	7020	7010	7120
CP	35	35		
H-H	-5	-5		
CP			85	
H-C			-15	
CP	155	165	145	
H-2	-10	-10	-15	
CP				120
H-3				20
CP	205			
H-H*	-15			
CP	70			
H-2*	0			
CP				120
H-3*				20

TABLE 43. BOND AND GEMINAL FRAGMENTS IN SATURATED SECONDARY CC LMO'S

	CSCP H	CSCP C	CSCP 2	CSCP 3	CSCP H*	CSCS HH	CSCS HC	CSCS H3	CSCT HHH
CS	7045	7040	7030	7035	7040	7030	7030	7025	7010
C	7055	7070	7040	7020	7070	7030	7045	6990	7010
CS	140	140	145			125	125	120	110
H-HH	-25	-30	-25			-25	-30	-30	-35
CS		145							175
H-HC		-35							-40
CS	145		130		140	130			
H-H2	-35		5		-20	-40			
CS				130				120	
H-H3				0				-10	
CS	-60								
CP-H	65								
CS						-15	-5	-20	-30
CP-C						55	60	60	55
CS		-85							
CS-HH		55							
CS		-95					-40		
CS-HC		50					60		
CS		-65							
CS-H3		60							
CS	-15		-95		-135				
CSV-HH	90		70		50				
CS						30			
CSV-HC						80			
CS				-115					
CE-H				115					
CS								-70	
CE-C								110	

TABLE 44. BOND AND GEMINAL FRAGMENTS IN UNSATURATED SECONDARY CC LMO'S

	CSCSV HH	CSCSV HC	CSCSV H3	CSCSV HH*	CSCE H	CSCE C	CSCE 3
CS	7015	7015	7015	7010	6960	6955	6950
C	7015	7025	6975	7025	7110	7120	7075
CS	75						
H-HH	-25						
CS	195	185		105			
H-H2	-25	-30		-20			
CS					160	160	
H-H3					0	-5	
CS			180		165		
H-23			-5		-10		
CS							160
H-33							20
CS	110			185			
H-22*	-30			-20			
CS	-115						
CP-H	60						
CS	-30						
CP-2	70						
CS					-70	-90	
CP-3					95	80	
CS	20						
CP-H*	70						
CS		-135					
CS-HH		50					
CS				-190			
CSV-HH				45			
CS					-25		
CSV-H3					110		
CS	65						
CSV-HH*	90						
CS			-160				
CE-H			105				
CS							-125
CE-3							140

TABLE 45. BOND AND GEMINAL FRAGMENTS IN TERTIARY CC LMO'S

	CTCP HH	CTCP HC	CTCP H2	CTCP H3	CTCP 23	CTCS HHH	CTCSV HHH	CTCSV HH3	CTCE HH
CT	7020	7020	7010	7010	7000	7010	6995	6990	6935
C	7040	7055	7025	7005	6990	7010	7000	6960	7090
CT	175	180	175			160	105		
H-HHH	-30	-40	-40			-40	-35		
CT	180		160				230		
H-HH2	-45		-5				-35		
CT				170					200
H-HH3				-20					-10
CT					155			225	210
H-H23					10			-20	-20
CT	-40	-35	-40			-50	-95		
CP-HH	60	55	60			55	55		
CT	-40		-35			0	-10		
CP-HC	50		85			55	65		
CT	-40								
CP-H2	50								
CT				-40					-40
CP-H3				80					90
CT								-10	-40
CP-23								85	80
CT	-25	-60							
CS-HHH	60	50							
CT	10		-75						
CSV-HHH		80		70					
CT					-70				5
CSV-HH3					85				105
CT				-100	-100			-145	
CE-HH				100	100			95	

TABLE 46. SUBSTITUENT EFFECTS ON BOND FRAGMENTS IN CC AND DOUBLE BANANA BONDS

	CSCP	CSCS	CSCSV	CSCE	CTCP	CTCSV	CSVCP	BCSVCPV
C	-5	0	0	-5	0		-10	-20
C-C	15	15	10	10	15		25	30
C	-15				-10			-20
C-2	-15				-15			-25
C	-10	-5	0	-10	-10	-5		
C-3	-35	-40	-40	-35	-35	-40		
C					-20			
C-23					-50			
C	-5		0					0
C-H*	15		10					5
C								-20
C-3*								-40
C								10
C-CSH(E)								-15
C								25
C-CTH(E)								-25
C								-10
C-C(E)								20

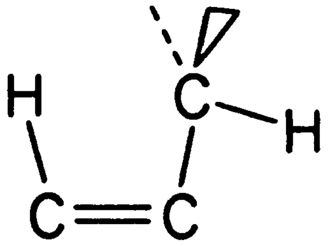
manifest is as observed for the CH, and even the numbers are similar, i.e., the vicinal substituents affect the alkyl CC and CH in about the same ways.

Primary Vinyl CH Bonds

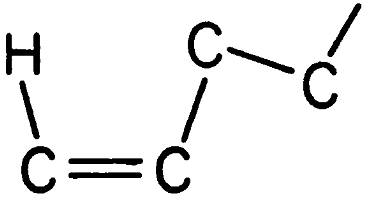
In mono- and disubstituted ethylenes, a primary CH bond can only have single bonds in vicinal positions. Thus there are three kinds of primary bond fragments depending on whether a carbon atom is in cis or in trans or in both vicinal positions. It is found that the bond fragment coefficients depend on bonds beyond the vicinal axes provided they are coplanar with the bond fragment. It is furthermore necessary to distinguish such coplanar bonds as regards their orientation with respect to the bond fragment. The possible cases are illustrated in Figures 3 and 4 and labelled by the abbreviations whose meanings are as follows. The letters T, C, P and L stand for 'trans', 'cis', 'plane' and 'line', respectively. In each three letter symbol, the first letter describes the orientation of the coplanar vicinal bond relative to the bond fragment, the second letter describes the orientation of the double bond relative to the coplanar third bond, and the last letter describes the orientation of the vicinal bond relative to the coplanar fourth bond. The symbol NFN means that there is no coplanar fourth bond. In this case the bond fragment turns out to be independent of the third bond as well, and only the orientation (T or C) of the vicinal bond is required. When no confusion is likely, we shall refer to these as simply NFN.

The bond fragment coefficients of the cis monosubstituted ethylenes differ substantially less from the ethylene coefficients than do those

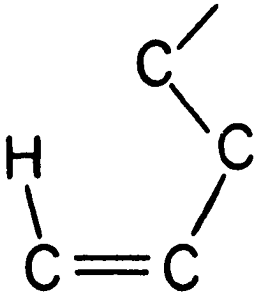
Figure 3. Bond skeletons for primary vinyl CH fragments cis to the substituent



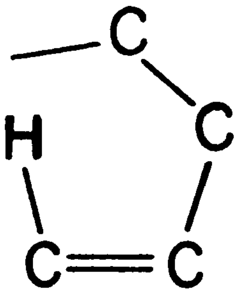
CNFN



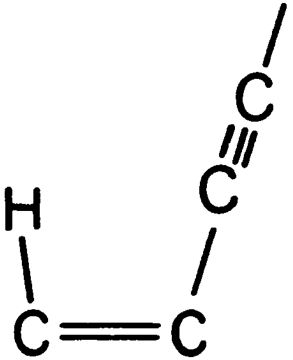
CTT



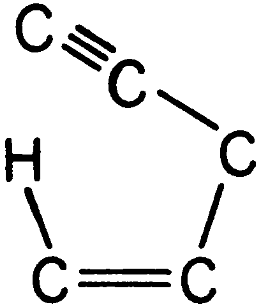
CCT



CCC

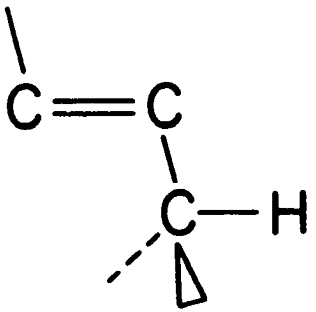


CPL

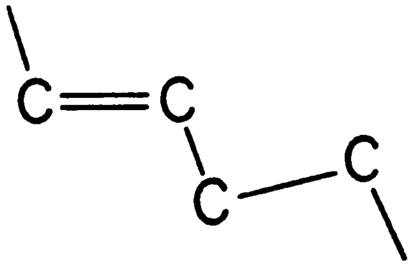


CCP

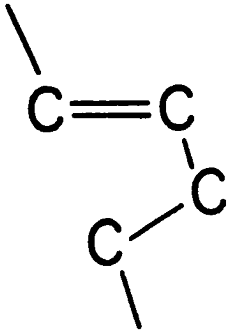
Figure 4. Bond skeletons for primary vinyl CH fragments trans to the substituent



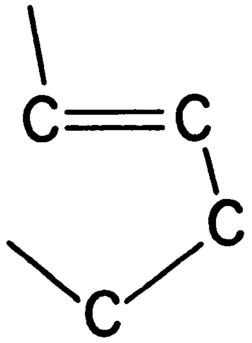
TNFN



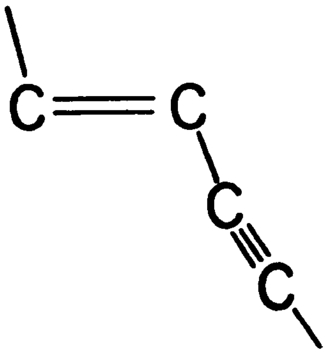
TTT



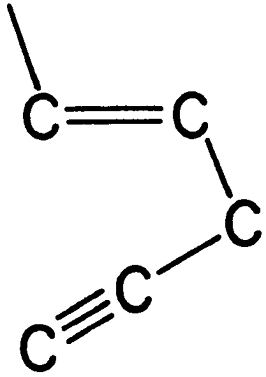
TCT



TCC



TPL



TCP

of the trans monosubstituted ethylenes. The bond fragment coefficients in disubstituted ethylenes display the additive effects of both the cis and trans substituents. This means, in fact, that they behave very much like the trans monosubstituted ethylenes.

Cis substituted ethylenes

Ethylene and the CH fragments in cis monosubstituted ethylenes are listed in Table 47. The ones listed first are not much affected by the substituent, but the three listed last are appreciably changed from ethylene. Examination shows that these are configurations where the coplanar bonds in the molecule 'bend back' toward the bond fragment, so that the effect is partially steric (it is not wholly steric, because it occurs only when the bonds are coplanar). This is therefore a case where the geometric influence is as great as the influence of the type of the coplanar vicinal fragment that was found in the alkyl bonds. If this 'back bending' is absent, the Mulliken populations on the 1s are slightly greater than the sp^2.

Trans substituted ethylenes

For comparing with Table 47, the same bond categories are used in Table 48 to list the bond fragments for trans substituted ethylenes. However, in this case, the bond fragments are practically insensitive to the geometries of the substituents, except for a small change when the double bond is conjugate to a triple bond. The Mulliken populations again favor the 1s over the sp^2, and by amounts slightly larger than the cis cases.

TABLE 47. BOND AND GEMINAL FRAGMENTS IN ETHYLENE AND PRIMARY VINYL CH LMO'S CIS TO THE SUBSTITUENT

	CPVH CPVH	CPVH NFN	CPVH CTT	CPVH CCT	CPVH CCC	CPVH CCP	CPVH CPL
CPV	7020	7020	7025	7025	7040	7050	7035
H	7045	7055	7050	7040	7025	7015	7035
CPV	290	315	315	335	335	340	315
H	-255	-280	-280	-285	-285	-280	-275
BCPV	-245						
CPV	-110						
BCPV		-220		-220	-230	-220	
CSV-H		-110		-110	-110	-110	
BCPV		-215		-220		-220	
CSV-C		-110		-110		-110	
BCPV			-215				
CSV-2			-100				
BCPV			-225				
CSV-H*			-105				
BCPV							-225
CSV-3*							-105

TABLE 48. BOND AND GEMINAL FRAGMENTS IN ETHYLENE AND PRIMARY VINYL CH LMO'S TRANS TO THE SUBSTITUENT

	CPVH	CPVH	CPVH	CPVH	CPVH	CPVH	CPVH
	CPVH	NFN	TTT	TCT	TCC	TCP	TPL
CPV	7020	7000	7000	7000	7000	7000	7015
H	7045	7075	7075	7075	7075	7075	7065
CPV	290	290	290	280	270	270	290
H	-255	-270	-270	-275	-275	-270	-270
BCPV	-245						
CPV	-110						
BCPV		-265			-265	-260	
CSV-H		-130			-130	-140	
BCPV		-245		-245		-240	
CSV-HA		-130		-130		-130	
BCPV		-290			-290	-285	
CSV-C		-135			-135	-135	
BCPV			-285				
CSV-2			-135				
BCPV		-265	-270				
CSV-H*		-130	-130				
BCPV							-255
CSV-3*							-125

Disubstituted ethylenes

Only one substituent is labelled for the disubstituted ethylenes in Table 49: the other is necessarily the corresponding TNFN or CNFN. For example, the CTT in the second column refers to the cis position, the trans being TNFN (written as NFN in the table). The character of the trans substituent is the major determinant, and the bond fragment coefficients differ little from those of the trans monosubstituents (Table 48). If the trans substituent is TNFN, then the various cis substituents run parallel to those of the cis monosubstituted cases (Table 47).

Secondary Vinyl CH Bonds

The bond fragments of secondary vinyl CH bonds (Table 50) resemble more closely the alkyl CH bonds than the primary vinyl CH bonds, which implies that the geminal single bond has a greater influence than the geminal double bond. Similarly, we find that the vicinal substituents beyond the geminal single bond are more important than those beyond the geminal double bond. For example, there is little change in the bond fragment when a CNFN substituent is placed at the end of the double bond (see CSVH-CNFN column). Therefore the other columns deal with bond fragments having various possible vicinal substitutions beyond the single bond. The *differences* in bond fragment coefficients corresponding to these substitutions were also included in the previous Table 40. The agreement with the alkyl CH bonds is perhaps closer than expected.

The column CSVH-CCC corresponds to the case that cis single bonds are in vicinal, third and fourth positions beyond the single bond. This

TABLE 49. BOND AND GEMINAL FRAGMENTS IN ETHYLENE AND PRIMARY VINYL CH LMO'S IN DISUBSTITUTED SYSTEMS

	CPVH	CPVH	CPVH	CPVH
	CPVH	NFN	CTT	TTT
CPV	7020	7005	7010	7005
H	7045	7080	7080	7080
CPV	290	310	310	315
H	-255	-290	-295	-295
BCPV	-245			
CPV	-110			
BCPV		-240		
CTV-HH		-130		
BCPV			-235	-255
CTV-H2			-120	-130

TABLE 50. BOND AND GEMINAL FRAGMENTS IN SECONDARY VINYL CH LMO'S

	CSVH HH	CSVH HC	CSVH HC(E)	CSVH HH*	CSVH HC*	CSVH H3*	CSVH NFN*	CSVH CCC
CSV	6990	6980	6985	6985	6985	6975	6990	7015
H	7060	7080	7070	7060	7070	7040	7065	7030
CSV	85			85			95	
CP-H	-105			-105			-130	
CSV	100	70			110			105
CS-HH	-100	-115			-105			-105
CSV		60						
CS-HC		-120						
CSV			95					
CS-H3			-110					
CSV		60						
CS-HC*		-120						
CSV	120	90						
CT-HHH	-105	-115						
CSV			110					
CT-HH3			-110					
CSV	75							
CSV-HH	-60							
CSV		55						
CTV-HHH		-75						
CSV						25		
CE-H						-80		
BCSV	-235	-235	-245	-225	-220			-200
CPV-H	-95	-105	-105	-100	-115			-120
BCSV	-225	-220	-230					
CPV-C	-105	-110	-110					
BCSV	-220	-215						
CPV-2	-110	-110						
BCSV						-215		
CPV-3*						-80		
BCSV							-200	
CSV-HH							-95	

is an example for a partial steric effect occurring across single bonds. It may be noted that this substitution of the CCC tail beyond the geminal single bond affects the bond fragment in almost the same way as the substitution of the CCC tail beyond the geminal double bond, shown previously in Table 47. The coplanar orientation seems to be more important than the geminal bond.

Vinyl CC Single Bonds

Many of the secondary vinyl CC single bonds were discussed in the previous section on alkyl CC bonds. This applies to all cases listed in Table 51, with the exception of the bonds having a TNFN vicinal substituent beyond the geminal double bond, given in the column CSVCP-NFN. By comparing with Table 48, one sees that this substitution has the same effect on the (CC) bond fragments CSVCP as it had in the (CH) bond fragments CPVH.

Table 52 exhibits secondary and tertiary vinyl CC single bond fragments not including alkyl carbons. The equality of the coefficients in the CSVCTV fragment justify the polarity ranking given in Equation 53, but it should be pointed out that there is a difference between the coefficients in the CSVCSV and CSVCTV bond fragments. In these, and also in the CVCE, one expects geometric and type effects similar to those of the CSVH.

CC Double Bonds

A double bond contains the bond fragments of two LMO's which essentially describe the bond. These bond fragments have 'banana character', i.e., they are bent above and below the nodal plane of the participating pi orbitals.

TABLE 51. BOND AND GEMINAL FRAGMENTS IN VINYL CC(ALKYL) LMO'S

	CSVCP H	CSVCP NFN	CSVCS HH	CSVCS HC	CSVCS H3	CSVCS HH*	CSVCT HHH	CSVCT HH3	CTVCP HH
CV	7030	7020	7015	7025	6975	7025	7000	6960	7010
C	7040	7065	7015	7015	7015	7010	6995	6990	7030
CSV	275	280	265				250		
H-HH	-175	-190	-185				-190		
CSV			315	330	305	330	305	295	
H-HC			-190	-190	-190	-190	-195	-195	
CSV	280								
H-HH*	-175								
CSV			260						
H-HC*			-185						
CTV									105
CP-HH									-65
CTV									95
CSV-HHH									-15
BCV	-220		-235	-235	-240	-240			-200
CPV-H	-55		-65	-65	-65	-65			-45
BCV			-275				-290	-300	
CPV-HA			-50				-55	-55	
BCV							-195		-190
CPV-C							-60		-55
BCV			-145				-155	-165	
CPV-CA			-65				-75	-75	
BCV									
CPV-H									
BCV	-225		-195						
CPV-H*	-55		-60						
BCSV		-240							
CSV-HH		-75							

TABLE 52. BOND AND GEMINAL FRAGMENTS IN VINYL CC(VINYL OR ETHYNYL) LMO'S

	CSVCSV HH	CSVCTV HHH	CSVCE H	CTVCSV HHH
CV	7005	6990	6940	6990
C	7005	6990	7095	6990
CSV	240			
H-HH	-155			
CSV		275		
H-HC		-165		
CSV			290	
H-H3*			-150	
CTV				75
CP-HH				-50
BCV	-160	-170		-140
CPV-2	-40	-45		-30
BCV			-230	
CPV-3*			-30	

Tables 53, 54, and 55 give the coefficients of the constituent hybrids for the cases that the bonded atoms are primary-primary, primary-secondary, primary-tertiary and secondary-secondary carbons.

It is seen that the coefficients do not differ greatly from those found for the single CC bonds. This is so even in the cases of conjugated bonds, which may seem surprising in view of the greater delocalization. The banana bond coefficients are, however, more sensitive to vicinal substituents than are the single bonds. These substituent effects were also included in Table 46. But on the other hand, these substituent effects are quite independent of whether the carbon atoms forming the double bond are secondary or tertiary. This latter result suggests that our observations are likely to hold generally for double bonds although our sampling is limited.

Ethynyl CH Bonds

The ethynyl CH bond fragments (see Table 56) exhibit the strongest polarity encountered in any bond fragments examined in this investigation. Moreover, they are the only CH bonds in which the electron (Mulliken) population on the carbon is greater than that on the hydrogen, in agreement with chemical ideas as regards the 'acidity' of acetylene.

Another characteristic is that the coefficients in the bond fragment are practically insensitive to the substituents on the other side of the triple bond, except if another triple bond is added conjugate with the first. Therefore, Table 56 lists only two classes of ethynyl CH bonds, those with and those without a second conjugated triple bond. Note that

TABLE 53. BOND AND GEMINAL FRAGMENTS ON PRIMARY CARBONS IN DOUBLE BANANA LMO'S

	BCPVCPV	BCPVCSV H	BCPVCSV C	BCPVCSV 2	BCPVCSV CSH(E)	BCPVCSV CTH(E)	BCPVCSV CTC(E)	BCPVCSV H*	BCPVCSV 3*
BCPV	7055	7060	7090	7035	7045	7035	7080	7065	7020
CV	7055	7010	6990	6990	7020	7035	7000	7010	6990
CPV	340	320	320	320	320	320	320	320	320
H-H	15	10	10	10	10	10	10	15	10
CPV		375	400	400	385	365	400	375	380
H-C		0	0	0	0	0	0	0	0
BCPV	-15								
CPV	-15								
BCPV		-60	-80		-45		-60	-50	
CSV-H		50	80		40		70	40	
BCPV		-85	-95			-75			
CSV-C		50	80			35			
BCPV				-10					
CSV-2				50					
BCPV									-20
CSV-3*									40

TABLE 54. BOND AND GEMINAL FRAGMENTS ON PRIMARY AND TERTIARY CARBONS IN DOUBLE BANANA LMO'S

	BCPVCTV HH	BCPVCTV H2
BCPV	7060	7040
CTV	6960	6940
CPV	360	360
H-NFN	0	0
CPV		380
H-TTT		0
CTV	220	220
CP-HH	75	75
CTV		130
CSV-HHH		90
BCPV	-100	
CTV-HH	115	
BCPV		-45
CTV-H2		110

TABLE 55. BOND AND GEMINAL FRAGMENTS ON SECONDARY CARBONS IN BANANA LMO'S

	BCSVCPV H	BCSVCPV C	BCSVCPV 2	BCSVCPV CSH(E)	BCSVCPV CTH(E)	BCSVCPV CTC(E)	BCSVCPV H*	BCSVCPV 3*	BCSVCSV HH
BCSV	7010	6990	6990	7020	7035	7000	7010	6990	7010
CV	7060	7090	7035	7045	7035	7080	7065	7020	7010
CSV	375	370	370				365		350
H-HH	0	-10	-10				-10		-10
CSV	380	380	375	390	390	380			
H-HC	-10	-20	-15	-10	-10	-20			
CSV								360	
H-H3								10	
CSV	200						200		
CP-H	85						85		
CSV									235
CP-C									80
CSV	225	170					190		
CS-HH	90	60					80		
CSV	220								
CS-HC	80								
CSV				215					
CS-H3				80					
CSV	250	185							
CT-HHH	100	75							
CSV					250	180			
CT-HH3					95	60			
CSV			110						
CSV-HH			100						
CSV			130						
CTV-HHH			100						
CSV								160	
CE-H								120	
BCSV	50	80		40		70	40		10
CV-H	-60	-80		-45		-60	-50		10
BCSV	50	80			35				
CPV-C	-85	-95			-75				
BCSV			50						
CPV-2			-10						
BCSV								40	
CPV-3*								-20	

TABLE 56. BOND AND GEMINAL FRAGMENTS ON ETHYNYL CARBONS IN CH AND CC LMO'S

	CEH	CEH (E)	CECP	CECS H	CECS C	CECS 3	CECT HH	CECSV H	CECE
CE	7230	7245	7120	7110	7120	7075	7390	7095	7040
H,C	6875	6860	6985	6960	6955	6950	6935	6940	7040
BCPE	5								
CPE	-335								
BCE	10			-40	-40	-40	-75		
CE-H	-335			-290	-290	-290	-290		
BCE	-10			95	90	80	50		
CE-C	-345			-290	-290	-290	-290		
BCE		-5							-5
CE-3		-335							-250
BCE	0		0						
CE-H*	-335		-285						
BCE	-30							140	
CE-VH*	-345							-285	
BCE	15							-70	
CE-2*	-330							-285	
BCSE			-10						
CSE-HH			-295						

a double bond in conjugation with the triple bond has no noticeable effect. Note also that such conjugation effects were found for the CPVH bonds (Tables 47, 48).

Ethynyl CC Single Bonds

Bond fragments for the CC single bonds next to a triple bond are also listed in Table 56. They behave fairly similar to the analogous CH bonds. The bond fragments are polarized toward the ethynyl carbon, however considerably less so than the CH bonds. The fragments are very insensitive as regards vicinal substitution beyond the triple bond, with the exception of a second conjugate triple bond.

On the other hand, these single bonds can be part of a larger alkyl chain 'this side' of the triple bond. The vicinal substituents of such chains all change the bond fragment coefficients by the increments discussed in Table 46.

If the ethynyl CC bond has a double bond in a second geminal position, the effects discussed for the vinyl CC bonds are expected to add. A single bond fragment between two triple bonds has coefficients more nearly like alkyl and vinyl single bond fragments and is expected to be extremely insensitive to any vicinal substitution.

CC Triple Bonds

A triple bond contains the bond fragments of three LMO's which essentially describe the bond. Like the bond fragments of the double bonds, these too have banana character and their coefficients (Tables 57,58) are close to those of the CC single bond fragments. Another similarity among

TABLE 57. BOND AND GEMINAL FRAGMENTS ON PRIMARY ETHYNYL CARBONS IN BANANA LMO'S

	BCPECPE	BCPECSE CPH*	BCPECSE CSH	BCPECSE CTH	BCPECSE CSVH*	BCPECSE CSC	BCPECSE CTC	BCPECSE 2*	BCPECSE 3
BCPE	7060	7080	7065	7055	7140	7130	7110	7135	7045
CE	7060	7000	7020	7035	6960	6970	6985	6960	6985
CE	360	360	360	360	400	390	380	350	375
H	-30	-35	-35	-35	-25	-25	-25	-35	-35
BCPE	-10								
CPE	-10								
BCPE		-25	-5			-40	-15	-75	
CSE-H		30	10			55	35	10	
BCPE			-60	-40			-65		
CSE-C			45	25			65		
BCPE					0			-75	
CSE-2*					70			20	
BCPE									10
CSE-3									25

TABLE 58. BOND AND GEMINAL FRAGMENTS ON SECONDARY ETHYNYL CARBONS IN BANANA LMO'S

	BCSECPE CPH*	BCSECPE CSH	BCSECPE CTH	BCSECPE CSVH*	BCSECPE CSC	BCSECPE CTC	BCSECPE 2*	BCSECPE 3	BCSECSE HH
BCSE	7000	7020	7035	6960	6970	6985	6960	6985	7020
CE	7080	7065	7055	7140	7130	7110	7135	7045	7020
CSE	265								270
CP	40								45
CSE		295			225				
CS-H		55			10				
CSE		280			205				
CS-C		50			10				
CSE		290			240				
CS-3		50			20				
CSE			310			245			
CT-HH			65			20			
CSE				170			310		
CSV-H				0			70		
CSE								210	
CSE								70	
BCSE	30	10			55	35	10		
CPE-H	-25	-5			-40	-15	-75		
BCSE		45	25			65			
CPE-C		-60	-40			-65			
BCSE				70			20		
CPE-2*				0			-75		
BCSE								25	
CPE-3								10	
BCSE									20
CSE-HH									20

the three is that the coefficient changes occurring in the bond fragments when primary carbons are replaced by secondary carbons (and probably tertiary carbons also) are identical for C-C, CV = CV and CE ≡ CE bonds.

On the other hand, the banana bond fragments of triple bonds are very sensitive to vicinal substitution, inasmuch as it makes a difference whether the near carbon of the vicinal bond is primary, secondary or tertiary, which was not the case for the other bond fragments. This introduces an additive correction to the effects of vicinal CH or CC substitution discussed previously in Table 46 for the other CC bond fragments. It is presumably also true for triple bonds between secondary carbons.

MI ORBITAL GEMINAL FRAGMENTS

Introduction

The coefficients for the geminal fragments were included with their adjacent bond fragment coefficients in Tables 36-58 of the preceding chapter. The geminal fragment coefficients are much smaller than the bond fragment coefficients and have widely varying polarities and nodal properties. Furthermore, the coefficients depend not only on the character of the geminal fragment, but also on that of the adjacent bond fragment. If the type of the far (relative to the geminal fragment) hybrid belonging to the adjacent bond fragment is fixed, and the near carbon hybrid varied over either the alkyl, vinyl, ethynyl or banana types, then concomitant geminal fragment coefficient changes are almost independent of the geminal fragment type. Also, geminal fragment coefficients are influenced by vicinal fragments coplanar with the adjacent bond fragment, and by vicinal fragments coplanar with the geminal fragment itself. Given the adjacent bond fragment type and the geminal fragment type, the effects on the coefficients of the geminal fragment from vicinal fragments lying coplanar with the bond fragment and from vicinal fragments lying coplanar with the geminal fragment are simply additive.

The geminal fragment coefficients are not well represented by SMO's and PMO's such as those given previously in Table 35. The latter types of orbitals tend to produce geminal fragment coefficients that have nodes near the center of the bond region. We shall return to these differences in the last chapter of this work.

Alkyl CH Fragments

Geminal alkyl CH fragments can be characterized by (1) their associated bond fragment, (2) coplanar fragments vicinal to the geminal fragment, (3) fragments lying coplanar and vicinal to the bond fragment. When the latter are changed from CH to CC, systematic changes occur in the geminal fragment coefficients so that geminal fragments adjacent to bond fragments with coplanar vicinal CH fragments can be chosen as prototypes. They are displayed in Tables 59-61 which contain geminal CH fragments with primary, secondary and tertiary carbons, respectively. The columns correspond to various bond fragments with coplanar vicinal CH, the rows correspond to geminal CH fragments characterized by particular vicinal coplanar bonds.

The variation of the coefficients is very similar in the three tables: the difference between two entries (defined by bond fragment and geminal fragment) in one of the tables is generally close to the corresponding differences in the other tables (provided both entries exist in the tables in question). Within one table characteristically distinct behavior is observed for the following groups of bond fragments: (1) CH, (2) C-C(alkyl), (3) C-C(vinyl), (4) C-C(ethynyl). A notable distinction between fragments geminal to CH bonds (group (1)) and the others is that the former have a node near the middle of the fragment, whereas in the latter, the node is towards the atom farthest from the bond fragment.

Tables 62-65 contain the relative changes in the geminal CH due to substitution trans to the bond fragment, e.g. the first and second rows of column one in Table 65 display the numbers which, when added to the

TABLE 59. PROTOTYPE GEMINAL CH FRAGMENTS ON PRIMARY CARBONS

	CPH H	CPCP	CPCS H	CPCT HH	CPCSV H	CPCTV HH	CPCE
C	140	105	90	75	35		
H-H	-120	-5	-10	-15	-5		
C	150		165	145		85	
H-C	-130		-20	-25		-15	
C	150				155	145	
H-2	-130				-10	-15	
C							120
H-3							20
C		105			205		
H-H*		-5			-15		
C					70		
H-2*					0		
C							120
H-3*							20

TABLE 60. PROTOTYPE GEMINAL CH FRAGMENTS ON SECONDARY CARBONS

	CSH HH	CSCP H	CSCS HH	CSCT HHH	CSCSV HH	CSCE H
C	170	140	125	110	75	
H-H	-135	-25	-25	-35	-25	
C	180			175		
H-C	-145			-40		
C	185	145	130		195	
H-2	-150	-35	-40		-25	
C						160
H-3						0
C						165
H-23						-10
C					185	
H-2*					-25	
C					110	
H-22*					-30	

TABLE 61. PROTOTYPE GEMINAL CH FRAGMENTS ON TERTIARY CARBONS

	CTCP	CTCS	CTCSV	CTCE
	HH	HHH	HHH	HH
C	175	160	105	
H-H	-30	-40	-35	
C				
H-C				
C	180		230	
H-2	-45		-35	
C				200
H-3				-10
C				210
H-23				-20

TABLE 62. SUBSTITUENT EFFECTS IN GEMINAL CH FRAGMENTS WITH THE INTRODUCTION OF A CC BOND

	CPH	CSH	CPCS	CPCT	CPCSV	CSCP	CSCS	CSCSV	CSCE	CTCP
	C	C	C	C	C	C	C	C	C	C
C	0	0	0	-5	0	0	0			5
H-H	-10	-10	0	0	0	-5	-5			-10
C	0		10	5		5				
H-C	-10		0	0		-10				
C								10		
H-2								-5		
C									0	
H-3									-5	

TABLE 63. SUBSTITUENT EFFECTS IN GEMINAL CH FRAGMENTS WITH THE INTRODUCTION OF A DOUBLE BOND

	CPH 2	CSH 2	CPCS 2	CPCT 2	CSCP 2	CTCP 2
C	0	0	0	-5	5	0
H-H	-10	-10	0	0	0	-10
C	-5		-5	0		
H-C	-5		0	0		
C	-15	-15			-15	-20
H-2	40	50			30	40

TABLE 64. SUBSTITUENT EFFECTS IN GEMINAL CH FRAGMENTS WITH THE INTRODUCTION OF A TRIPLE BOND

	CPH 3	CSH 3	CPCS 3	CPCT 3	CSCP 3	CSCS 3	CTCP 3
C			-5	-5			
H-H			0	-5			
C			-15	-5			
H-C			0	0			
C	-15	-15			-15	-10	-10
H-3	30	30			35	30	25

TABLE 65. SUBSTITUENT EFFECTS IN GEMINAL CH FRAGMENTS WITH THE INTRODUCTION OF DOUBLE AND TRIPLE BONDS

	CSH 23	CPCT 23	CTCP 23
C		-10	
H-H		-5	
C		-5	
H-C		0	
C	-20		-25
H-23	60		55

CH-H geminal fragment in the CPH-H prototype, give the CH-H adjacent to the CPH-C. Exceptions are the CH-3 and CH-23 of Tables 64 and 65, which are given relative to the CH-2 fragments of the prototypes, there being no prototype CH-3 or CH-23. On the whole, the geminal fragments are only slightly affected by these substitutions, and what changes do occur are fairly regular. The geminal CH-2 adjacent to the CPH-2, CSH-2, etc. in Table 63 are the only ones to change appreciably, and all by about the same amount. Thus, the deductions made for the prototypes also hold in general and, except for the CH-2 just mentioned, the geminal fragments are little changed by substitution trans to the bond fragment.

The additivity of substituent effects follows, e.g. from Table 61. Calculating the differences between the CTH-HH2 (adjacent to the CTCP-H2) and CTH-HHH (adjacent to the CTCP-HH), and similarly for the CTH-HH3 (adjacent to the CTCP-H3), one finds that addition of these two to the CTH-HHH approximately gives the CTH-23 (adjacent to the CTCP-23).

Some coefficient changes due to H → C substitution in the cis position are shown in the first six rows of Table 66, relative to the coefficients of the CH-H* fragment geminal to the CPH-H* bond. (It is interesting that the latter are the same as for the trans case). Although the values for the CH-H* and CH-2* cases are approximately reversed, the changes from the corresponding trans cases are small. This also holds for CH geminal fragments adjacent to CSH bonds. The changes are considerably larger for geminal fragments adjacent to CC bond fragments along axes of hindered rotation (except for ethane).

TABLE 66. SUBSTITUENT EFFECTS IN CIS GEMINAL CH FRAGMENTS

	CPH H*	CPH 2*	CPH 3*
C	0	0	
H-H*	-5	-20	
C	10	0	
H-2*	-5	-5	
C			-15
H-3*			30
C			
H-22*			

Alkyl CC Fragments

The CC prototypes (having CH fragments coplanar and vicinal to their bond fragments) are shown in Tables 67 and 68. Again it can be seen that coefficient changes due to changes in the bond fragment are almost the same for geminal CC fragments centered on secondary and tertiary carbons (the primary carbon series has only one member). Regularities for substitutions trans to the geminal fragment are also observed among those adjacent to corresponding bond fragments (e.g. CPH, CSH, and CTH, or CSCP and CTCP, etc.). However, the geminal fragments CC differ from the (geminal) CH fragments in that no group regularities such as discussed with Tables 59-61 are observed. Also, the geminal CC coefficients are usually opposite in sign to the geminal CH and smaller by a factor of two or three.

The effects of substitution trans to the bond fragment are shown in Tables 69 and 70. Here, because of a smaller sampling, a better perspective is obtained by listing the primary, secondary and tertiary together, which is permissable since the corresponding values never differ by more than 0.0010 (a fact also true of the geminal CH). The relative quantities have the same meaning as for the CH geminal fragments with two exceptions: the CCE-H are taken relative to the prototype's CCSV-H; and the geminal CCS of the CCP-C bond are taken relative to its geminal CSCS-H. Each group of rows labelling the same geminal fragment - e.g., the rows CCP-H, CCP-C, CCP-2, CCP-3 and CCP-23 - is as regular as was the case for the CH geminal fragments. However, the magnitude of the effect is slightly larger for the CC geminal fragments.

TABLE 67. PROTOTYPE GEMINAL CC FRAGMENTS ON PRIMARY AND SECONDARY CARBONS

	CPH	CSH	CSCP	CSCS	CSCT	CSCSV	CSCE
	H	HH	H	HH	HHH	HH	H
C	-110	-85	-60			-115	
CP-H	10	0	65			60	
C		-80		-15	-30		
CP-C		-10		55	55		
C		-80				-30	
CP-2		-10				70	
C							-70
CP-3							95
C	-90	-65					
CS-H	5	0					
C	-85	-65					
CS-C	10	0					
C	-90						
CS-2	5						
C							
CS-3							
C	-70	-45					
CT-H	10	0					
C	-70						
CT-C	10						
C	-75						
CT-2	10						
C	-50	-25	-15				
CSV-H	30	25	90				
C	-45			30			
CSV-C	30			80			
C							-25
CSV-3							110

TABLE 68. PROTOTYPE TERTIARY GEMINAL CC FRAGMENTS

	CTH	CTCP	CTCS	CTCSV	CTCE
	HH	HH	HHH	HH	HH
C	-70	-40	-50	-95	
CP-H	-10	60	55	55	
C	-65	-40	0	-10	
CP-C	-10	50	55	65	
C	-65	-40			
CP-2	-10	50			
C					-40
CP-3					90
C					-40
CP-23					80
C	-50	-25			
CS-H	-10	60			
C	-10	10			
CSV-H	20	80			
C					
CSV-3					

TABLE 69. SUBSTITUENT EFFECTS IN ALKYL GEMINAL CC FRAGMENTS WITH THE INTRODUCTION OF CC BONDS

	CH C	CCP C	CCS C	CCSV C	CCE C
C		5			
CP-H		-5			
C	0		10		
CP-C	0		5		
C				-10	
CP-2				-5	
C					-20
CP-3					-5
C		0			
CS-H		0			
C		-10			
CS-C		-5			
C		-20			
CS-3		5			
C	-40				
CT-H	-10				
C					
CSV-H					

TABLE 70. SUBSTITUENT EFFECTS IN ALKYL GEMINAL CC FRAGMENTS WITH THE INTRODUCTION OF BANANA BONDS

	CH 2	CCP 2	CH 3	CCP 3	CCS 3	CCSV 3	CCE 3	CH 23	CCP 23	CH 33
C	0	0								
CP-H	0	0								
C	-5	5			-5					
CP-C	10	35			5					
C	10									
CP-2	40									
C			-10	0		0				
CP-3			-10	30		20				
C						0		5		
CP-23						25		10		
C	0									
CS-H	0									
C			0							
CS-3			20							
C	-110									
CSV-H	-35									
C								-110	-80	
CSV-3								20	5	
C			-125	-110	-100		-100	-125	-110	
CF-H			5	25	30		30	5	20	
C			-125							
CE-C			-5							
C										-125
CF-3										25

Again with the exception of ethane, the geminal CC fragments which lie along axes of hindered rotation (see Tables 36 and 44), or are adjacent to them (Table 44), change noticeably from the cis to the trans confirmations. In this respect they are directly analogous to the CH geminal fragments.

Finally, the additivity of the substituents also obtains for the CC, as can be seen from the CTCP in Table 68.

Primary Vinyl CH Fragments

The primary vinyl CH geminal fragments form two markedly different classes: (1) the CPVH fragments adjacent to CPVH bond fragments and (2) the CPVH fragments adjacent to banana bond fragments. In each case, the contributions from the carbon (near) hybrids are two to three times larger than was the case for the previously discussed alkyl geminal fragments.

The CPVH geminal fragments adjacent to CPVH bond fragments were included in Tables 47-9. Those whose CPVH bond fragments are cis to the vicinal monosubstituent (Table 47) are about 10% larger than those adjacent to bond fragments trans to the vicinal monosubstituent (Table 48). Both show two classes whose members have nearly equal coefficients: (1) XNFN, XTT and XPL, (2) XCT, XCC and XCP, with X = C (Table 47) or T (Table 48). Ethylene differs from all of these in that the contribution from its hydrogen 1s is smaller, although its carbon hybrid coefficient is identical to those of class (2) in Table 48.

Only members of the first class (the XNFN, XTT and XPL) are represented for the CPVH geminal fragments adjacent to CPVH bond fragments of disubstituted ethylenes in Table 49. These are found to closely resemble the class (1) coefficients of Table 47 (bond fragment cis to the monosubstituent), although the latter have slightly smaller hydrogen orbital coefficients.

The CPVH geminal fragments adjacent to banana bond fragments were given in Tables 53 and 54. They are nodeless. In this way they differ from the CPVH geminal fragments adjacent to CPVH bond fragments, which have pronounced nodes towards the hydrogen atoms. They form basically two classes: (1) CPVH geminal fragments which have a CH fragment in the trans positions, and (2) the CPVH geminal fragments which have a CC fragment in the cis positions. Within each class the carbon and hydrogen hybrid coefficients separately have pretty much the same magnitude. Within the second class the vinyl carbon of the bond fragment that is farthest from the geminal fragment can be tertiary or secondary. In the latter, a finer distinction into two subclasses can be observed, corresponding to the two cases that the banana bond fragment has in trans positions (1) a CC or double bond, (2) a CH or triple bond.

Secondary Vinyl CH Fragments

The secondary vinyl CH geminal fragments adjacent to CSVC single bond fragments (Tables 51-2) noticeably resemble the CPVH geminal fragments adjacent to CPVH single bond fragments. Their coefficients are slightly larger when the bond fragment's carbon atom farthest from the geminal fragment is alkyl (Table 51) then when it is vinyl or ethynyl (Table 52). The variations in these secondary vinyl CH geminal fragments show regularities similar to those previously observed for alkyl geminal fragments. Also, the difference between the geminal fragment coefficients of two enties in Table 51 is close to the difference between the corresponding entries in Table 52 (if such corresponding entries exist). However, the CSVH geminal fragments are insensitive to the orientation of their coplanar vicinal fragments.

The CSVH geminal fragments adjacent to banana bond fragments are shown in Table 54. The relations between them and the CSVH geminal fragments just discussed are very similar to the relations between the two analogous CPVH geminal fragments considered in the preceding section. As in the preceding paragraph, the regularities here are like those of alkyl fragments. There is also an insensitivity to the orientations of the vicinal fragments coplanar with the geminal fragments. Although data are not available for the BCSVCSV and BCSVCTV bond fragments, it is likely that they behave similarly.

Single Bond Vinyl CC Fragments

Like the vinyl CH geminal fragments just discussed, the single bond vinyl CC geminal fragments fall into two clearly distinct classes: (1) the single bond CC geminal fragments adjacent to single bond fragments and (2) the single bond CC geminal fragments adjacent to banana bond fragments.

The fragments in the first class have nodes near the center of the bond region, which is quite different from the alkyl CC geminal fragments. A further distinction is possible in this case: the CC geminal fragments adjacent to CH bond fragments (Table 50) differ from those adjacent to CC bond fragments (Tables 51-2). The greatest variations in the coefficients of the former (Table 50) result from changes in the character of the far carbon atom of the geminal fragment and appear to be independent of the nature of vicinal fragments coplanar with the bond or vicinal fragments. Smaller regular coefficient variations are induced by changes in the vicinal fragments coplanar with the bond fragments. The smallest coefficient variations accompany changes in the vicinal fragments coplanar with the CC geminal fragment itself. Although the sampling of the vinyl CC geminal fragments is limited, the two entries in Table 51 differ from their counterparts adjacent to CH bond fragments (Table 50) by the same amount. This suggests that the same coefficient variations occur in all vinyl CC geminal fragments adjacent to single bond fragments.

The coefficients of the CC single bond geminal fragments adjacent to banana bond fragments (Tables 54-5) are all positive, in sharp contrast with those adjacent to single bonds. In addition, the coefficients of the near hybrid are several times larger than those of the far hybrid. Both features parallel the differences recorded between the vinyl CH geminal fragments adjacent to single bond fragments and the vinyl CH geminal fragments adjacent to banana bond fragments. The observations made for the coefficient variations in the geminal fragments adjacent to CC single bond fragments also apply to the geminal fragments adjacent to banana bond fragments.

The banana bond geminal fragments adjacent to vinyl CC single bond fragments (Tables 51-2) have far hybrid coefficients that are about one half of the far hybrid coefficients found for those adjacent to CH bond fragments. As in the latter case, all of their coefficients are always negative. The highly regular coefficient trends in Tables 51 and 52 are very sensitive to the substituent which is vicinal and coplanar with the banana geminal fragment. There is also a large dependence on the symmetry or asymmetry of the noncoplanar vicinal fragments (see, e.g. BCVCPV-H and BCVCPV-HA in Table 51 and Figure 2). Superimposed on these effects are smaller coefficient dependences on the vicinal fragments coplanar with the adjacent vinyl CC bond fragment. These latter appear to be the same in Tables 51 and 52.

Double Bond Fragments

The banana geminal fragments form three spectacularly different classes: (1) those adjacent to vinyl CH bond fragments, (2) those adjacent to vinyl CC single bond fragments, and (3) those adjacent to banana bond fragments. We shall discuss them in turn.

The coefficients for banana geminal fragments adjacent to vinyl CH bond fragments are always negative. Furthermore, the magnitudes of the near hybrid coefficients are always about twice those of the far hybrids. The adjacent bond fragment can be used to separate these banana geminal fragments into four classes, corresponding to the cases that the vinyl CH bond fragment is (1) primary and cis to its vicinal monosubstituent (Table 47); (2) primary and trans to its vicinal monosubstituent (Table 48); (3) primary in disubstituted ethylenes; and (4) secondary (Table 50). Ethylene (not included in this classification) is similar to some of those in cases (3) and (4). In class (1), all banana geminal fragments have virtually the same value. In class (2), they differ slightly, depending on their coplanar vicinal fragments (these differences are however independent of the monosubstituent trans to the bond fragment). In class (3), the trends are determined by the substituent lying trans to the adjacent CPVH bond fragments. In class (4), the geminal fragment coefficients show very regular variations which are induced by the vicinal fragments (belonging to the alkyl chain on the same side of the double bond as the CH bond fragment) that are coplanar with the adjacent bond fragments and the vicinal fragments coplanar with the banana geminal fragment itself. These variations are of similar magnitude and of the type previously discussed.

The coefficients of banana geminal fragments that are adjacent to banana bond fragments (Tables 53-5) are the smallest of all. Most of these coefficients are rather homopolar. Their nodal properties are completely characterized by the statements: (1) coefficients on primary vinyl carbons (Tables 53-4) are always negative, and (2) coefficients on secondary (Table 55) or on tertiary (Table 54) vinyl carbons are always positive. In each class, small regular coefficient variations occur that are induced by vicinal substitution coplanar with the adjacent bond fragment, and by vicinal substitution coplanar with the geminal fragment itself. The latter differ slightly from class to class.

Ethynyl CH Fragments

Ethynyl CH geminal fragments (Table 57) can only occur adjacent to primary ethynyl triple banana bond fragments. Their near hybrid coefficients are among the largest geminal fragment coefficients found. They all have slight nodes toward the atom farthest from the adjacent bond fragment. Ethynyl CH geminal fragments form five slightly different coefficient classes according to whether the vicinal fragment coplanar with their adjacent bond fragment is (1) an alkyl CH bond, (2) a CC bond, (3) a double bond, (4) a triple bond, and (5) a secondary vinyl CH bond. The CH geminal fragment coefficients for acetylene are the same as those of class (1).

Single Bond Ethynyl CC Fragments

The ethynyl CC single bond geminal fragments can only occur adjacent to secondary ethynyl triple bond fragments. Like the ethynyl CH geminal fragments, their coefficients are strongly polarized toward the near (relative to the bond fragment) carbon atom. These near hybrid coefficients are several times larger than any of the other CC single bond geminal fragment coefficients encountered. Variations among the single bond ethynyl geminal fragment coefficients are primarily characterized by (1) their far hybrid carbon atom, and (2) the vicinal fragment coplanar with the adjacent triple bond fragment. Generally smaller coefficient changes are induced by vicinal fragments on the same side of the triple bond as, and coplanar with, the geminal fragment itself.

Triple Bond Fragments

As was the case for the double bond geminal fragments, the triple bond geminal fragment coefficients form three classes: (1) those adjacent to ethynyl CH bond fragments, (2) those adjacent to ethynyl CC single bond fragments, and (3) those adjacent to banana bond fragments.

There is a characteristic of triple bond geminal fragment coefficients adjacent to single bond fragments (Table 56) which distinguishes them from all others: the *far* hybrid coefficient magnitudes are much larger than those of the *near* hybrid. The banana geminal fragment coefficients adjacent to CH bond fragments are virtually insensitive to any influences. There are, however, two prominent effects on the near hybrid coefficients of the banana geminal fragments adjacent to CC bond fragments: (1) the farthest carbon atom in the adjacent bond fragment, and (2) the vicinal fragment coplanar with, and on the same side of the triple bond as, the geminal fragment itself.

The coefficients for the triple bond geminal fragments adjacent to triple bond fragments (Tables 57-8) are the smallest of the ethynyl geminal fragments, just as their counterparts were the smallest of the vinyl fragments. Most have nodes near the center of the bond region. They can be characterized by (1) the vicinal fragment coplanar with the adjacent triple bond fragment, and (2) the vicinal fragment coplanar with the geminal fragment itself.

MI ORBITAL VICINAL FRAGMENTS

Vicinal Groups

The term 'vicinal group' refers to the collection of vicinal fragments whose near (relative to the bond fragment) hybrids are located on the same carbon atom. Members of vicinal groups are classified as (1) *overflow fragments*, those vicinal and coplanar with the bond fragment, or (2) *gauche fragments*, those vicinal and *non*coplanar with the bond fragment. The character of the overflow fragment will also be used to characterize the vicinal group itself.

Overflow and gauche fragment coefficients for a particular vicinal group will appear together in the tables, always listed in the order, overflow fragment first (usually in the first two rows of the table), and the several possible gauche fragments following. Of the two coefficients for each fragment, the near (relative to the bond fragment) hybrid will be listed first.

Nodal Properties and Coefficient Magnitudes

The two coefficients of a particular vicinal fragment have similar magnitudes and opposite signs. If the overflow fragment is trans to the bond fragment, its near hybrid coefficient is always negative (and its far hybrid coefficient always positive). Its adjacent gauche fragment coefficients are several times smaller, with near hybrid coefficients that are always positive (and far hybrid coefficients always negative). If the overflow fragment is cis to the bond fragment, all coefficient signs are the reverse of the trans case. Also, the cis overflow fragment coefficient magnitudes are about twice those of its adjacent gauche fragments. These facts have proved important for understanding the origins of hindered rotation (18,19,68,70).

Comparison with Geminal Fragments

As a class, vicinal fragment coefficients differ from those of geminal fragments in two interesting ways:

1. Their nodal properties and coefficient magnitudes are much less varied.

2. Their coefficient magnitudes are larger.

The latter seems all the more noteworthy since the vicinal fragments are farther removed from the bond fragment.

Alkyl Vicinal Groups

Alkyl vicinal groups are those whose near (relative to the bond fragment) carbon atom is an alkyl carbon. Their coefficients can be grouped according to whether their overflow fragment is CH or CC. In either case, coefficients for their vicinal fragments form four classes, according to whether their associated bond fragment is (1) CH, (2) CC, (3) double banana or (4) triple banana. Coefficients for a particular vicinal fragment are primarily determined in each category by characterizing both atoms of the bond fragment as either (1) alkyl carbon, (2) vinyl carbon, (3) ethynyl carbon, or (4) hydrogen. Vicinal fragment coefficients whose near hybrids are located on primary carbon atoms differ from corresponding fragment coefficients whose near hybrids are located on secondary or tertiary carbon atoms by amounts that are nearly independent of the character of the bond fragment.

Alkyl CH groups

The coefficients for the primary alkyl CH groups vicinal to CH bond fragments are shown in Table 71 (those of the overflow fragment appear in the first two columns). All overflow fragments lie coplanar with CH bond fragments, but the *gauche* fragment coefficients display variations that are induced by (1) their coplanar vicinal bonds, which lie adjacent to the bond fragment (the CPH-C columns in Table 71), and (2) coplanar bond chains beyond their coplanar vicinal bonds (the TT-CPH-C columns in Table 71).

Coefficients for secondary alkyl groups vicinal to CH bond fragments are listed in Tables 72-3. Regular variations in the gauche fragments are induced as for the primary CH vicinal fragments. Now, however, the fragments and their associated chains need not be adjacent to the bond fragment.

The tertiary CH vicinal fragment coefficients with CH bond fragments appear in Table 74. The observations made for the primary and secondary cases hold here too. There is now a small 'chain' effect (see Figure 2) that can be seen in the overflow fragment coefficients in the last column of Table 74.

The coefficients for alkyl CH groups vicinal to CC bond fragments are shown in Table 75. The overflow fragment coefficients usually appear in the first two columns, but may also occur in columns three and four (e.g. the CSCSV-H row). Their magnitudes are larger than those of the preceding

TABLE 71. OVERFLOW ONTO PRIMARY CH FRAGMENTS IN CH LMO'S

	CPH	CPH-H	TT-CPH-C	CPH-C
CPH	-460 440	170 -160		
CPH*	370 -345	-245 240		
CSH-H	-460 440	165 -150	175 -160	
CSH-C	-465 440	165 -150	175 -160	
CSH-2	-465 445	165 -150	180 -165	190 -180
CSH-3	-455 440	160 -150		185 -175
CSH-2*	-455 430	165 -155	175 -160	
CTH-HH	-465 440		175 -160	
CTH-H2	-465 440		175 -160	185 -175
CTH-H3	-460 445		170 -160	180 -170
CTH-23	-460 450			180 -170
			CPH-2	
CSVH-H	-415 410		140 -130	
CSVH*	315 -295		-225 225	

TABLE 72. OVERFLOW CNTO SECCNDARY CH FRAGMENTS IN CH LMO'S

	CPH	CSH	CSH 2	CSH 3	CTH	CSVH
CS	-440	-440	-445	-435	-445	-400
H-HH	425	425	425	430	425	395
CS	180	175	175	165		
H-HH	-150	-145	-140	-140		
CS	180				180	
H-HC	-150				-150	
CS	180					145
H-H2	-150					-125
CS	105					
CP-H	-105					
CS	105	110	105	110	105	
CP-C	-105	-110	-105	-115	-105	
CS						85
CP-2						-85
CS	105					
CS-HH	-105					
CS	105	105				
CS-HC	-105	-105				
CS	105					
CS-H3	-105					
CS	105					
CT-HHH	-105					
CS	100					
CSV-HH	-105					

TABLE 73. OVERFLOW ONTO SECONDARY CH FRAGMENTS IN ALKYL CH LMO'S

	CPH CSH	CPH CSH-C	CSH CSH-2	CPH CSH-2*	CPH CSH-3	CSH CSH-3
CS	-435	-435	-430	-440	-440	-440
H	420	420	415	430	435	435
CS	180	180				
H-HH	-185	-150				
CS		175	170			
H-H2		-150	140			
CS					180	175
H-H3					-155	-145
CS				180		
H-H2*				-160		
TT-CS	120					
CT-HHH	-120					
TT-CS		120				
CSV-HH		-120				
CS		105		105		
CSV-HH		-95		-105		
CS			130			
CSV-HC			-145			
CS					95	
CE-H					-90	
CS						100
CE-C						-95

TABLE 74. OVERFLOW ONTO TERTIARY CH FRAGMENTS IN ALKYL CH LMO'S

	CPH CTH	CSH CTH	CSVH CTH	CPH CTH-2	CPH CTH-3	CPH CTH-23	GT-CPH CTH-2
CT	-420	-420	-385	-420	-420	-420	-410
H	415	415	385	420	420	430	400
CT	105	100		110			
CP-HH	-95	-90		-100			
CT	105	110					
CP-HC	-95	-100					
CT	110		90				110
CP-H2	-95		-80				-95
CT					110		
CP-H3					-95		
CT	110						
CS-HHH	-95						
TT-CT							125
CSV-HHH							-110
CT	105			105			
CSV-HHH	-95			-85			
CT						105	
CSV-HH3						-90	
CT					100	100	
CE-HH					-80	-85	

TABLE 75. OVERFLOW CNTO PRIMARY AND SECONDARY CH FRAGMENTS IN CC LMO'S

	TT-CPH		CPH-H		TT-CPH-C		CPH-C	
CSCP	-495	440	170	-145				
CSCS-H	-500	445	170	-145				
CSCS-C	-505	450	170	-145				
CSCS-3	-500	445	170	-145				
CSCT-HH	-490	440	170	-145				
CTCP-H	-495	440	160	-140	170	-150		
CTCP-C	-500	445	160	-140	170	-150		
CTCP-2	-500	445	165	-135	170	-145	185	-165
CTCP-3	-490	445	160	-135			180	-160
CTCS-HH	-495	440	165	-140	175	-155		
	TT-CPH		CPH		CPH-H		CPH-C	
CSCSV-H	-455	410	-505	445	160	-140		
CTCSV-HH	-455	410	-505	445	155	-135	170	-150
CTCSV-H3			-500	445	160	-135	180	-160
CSCE	-485	430			160	-135		
CTCE-H	-485	435			155	-130	165	-140
	TT-CSH-C		CSH-HH		CSCP-C			
CTCP-H	-480	430	170	-130	115	-105		

section, but those of the gauche fragments are little changed. The small coefficient variations among all fragments can be understood as in the previous section.

The coefficients for primary CH overflow fragments that are vicinal to double bond fragments appear in the first two columns of Table 76. Those of the secondary and tertiary overflow fragments are shown in the first two rows of Table 77. All have slightly larger magnitudes than their counter parts vicinal to CC bond fragments. The gauche fragment coefficient magnitudes are, however, substantially larger than those vicinal to CC bond fragments. The slightly larger coefficient variations found for all of these vicinal fragments are due to the same factors discussed previously.

Vicinal CH group coefficients with triple bond fragments are shown in Table 78. Their overflow fragment coefficients are like those vicinal to CH bond fragments. However, their gauche fragment coefficients are like those vicinal to double bond fragments. All coefficient variations arise for reasons similar to those previously given.

Alkyl CC groups

As a whole, all alkyl CC group coefficients are smaller than those of corresponding alkyl CH group members. This is particularly evident for the overflow fragments. However, coefficients for a particular vicinal fragment in each of the four bond fragment classes (CH, CC, double and triple banana) stand in about the same relationship as corresponding fragment coefficients in the alkyl CH groups. Similarly, small coefficient

TABLE 76. OVERFLOW ONTO PRIMARY CH FRAGMENTS IN DOUBLE BANANA LMO'S

	CPH		CPH-H		CPH-C		CPH-2	
BCSVCPV	-510	490	190	-170			190	-190
BCSVCSV-H	-525	495	195	-170			200	-190
BCTVCPV-H	-505	485			195	-175	180	-180
BCTVCPV-2	-505	485			195	-175	175	-175
BCSVCPV*	415	-395	-280	260			-260	265

TABLE 77. OVERFLOW ONTO SECONDARY AND TERTIARY CH FRAGMENTS FROM BANANA LMO'S

	BCSVCPV CSH	BCSVCPV CSH-22*	BCSVCPV CSH-3	BCSVCPV CTH	BCSVCPV CTH-3	BCSVCPV CSH*-2
C	-490	-495	-490	-470	-475	390
H	485	485	485	460	475	-380
CS	200					
H-HH	-165					
CS	190					
H-H2	-180					
CS			190			
H-H3			-180			
CS		200				-275
H-22*		-190				250
CS	125					
CP-C	-120					
CS	125					
CP-2	-140					
CS	125					
CS-HC	-120					
CS		120				-205
CSV-HH		-120				200
CS			115			
CE-H			-105			
CT				130		
CP-HH				-110		
CT				125		
CP-H2				-130		
CT					130	
CP-H3					-135	
CT					120	
CE-HH					-195	

TABLE 78. OVERFLOW ONTO CH FRAGMENTS IN TRIPLE BANANA LMO'S

	BCSECSE CPH	BCSECPE CSH	BCSECPE CSH-2	BCSECPE CSH-3	BCSECPE CTH	BCSECPE CTH-2	BCSECPE CPH*	BCSECPE CSVH*
C	-480	-465	-455	-465	-450	-440	420	325
H	495	490	480	495	480	470	-425	-360
CP	190						-255	
H-3	-160						363	
CS		205						
H-H3		-180						
CS			205					
H-23			-180					
CS				205				
H-33				-180				
CS		125						
CP-3		-140						
CS		125						
CS-H3		-140						
CS			120					
CSV-H3			-120					
CS				115				
CE-3				-105				
CT					135			
CP-H3					-115			
CT						135		
CP-23						-130		
CT						120		
CSV-23						-140		
BCSV								-190
CPV*-3*								205

variations for both the gauche and overflow fragments are induced by (1) *their* coplanar vicinal fragments and (2) coplanar bond chains beyond their coplanar vicinal bonds. In addition, small coefficient changes are now also induced by *other* vicinal fragments coplanar with the bond fragment.

Coefficients for alkyl CC groups vicinal to CH bond fragments are listed in Tables 79-82. The overflow fragments having near secondary (tertiary) carbon atoms and far alkyl carbon atoms are shown in Table 79 (Table 80). Those whose near carbon atom is secondary (tertiary) and whose far carbon atom is vinyl or ethynyl appear in Table 81 (Table 82).

The coefficients for groups vicinal to CC bond fragments are given in Table 83. The TG and TC prefixes characterize configurations that are analogous to the previously encountered TT and GT configurations (see Figure 2).

The alkyl CC group coefficients vicinal to double (triple) bond fragments are listed in Table 84 (Table 85).

Single Bond Vinyl Groups

Single bond vinyl groups have overflow fragments that are vinyl single bonds. The bond region between the group and its bond fragment may be either a single or a double bond. The vicinal group coefficients for the two cases can be distinguished, and thus provide two characterizations for these vinyl groups. When the bond fragment and vicinal group are double bonded, we say that there is vicinal 'delocalization through the double bond,' and when they are singly bonded, we say that there is vicinal

TABLE 79. OVERFLOW ONTO SECONDARY ALKYL CC FRAGMENTS IN CH LMO'S

	CPH CSCP	CPH CSCS	CPH CSCS-C	CPH CSCS-3	CPH CSCT	CSVH CSCP	CSVH CSCS	CSVH CSCP*
CS	-320	-320	-320	-335	-330	-285	-290	195
C	340	345	345	345	345	320	320	-205
CS	145	145	145	145	145			
H-HH	-160	-155	-155	-155	-155			
CS					145			
H-HC					-155			
CS						115	115	-200
H-H2						-130	-130	220

TABLE 80. OVERFLOW ONTO TERTIARY ALKYL CC FRAGMENTS IN CH LMO'S

	CPH CTCP	CPH CTCP-C	CPH CTCP-2	CPH CTCP-3	CPH CTCS	CSH CTCP	CSVH CTCP
CT	-305	-300	-300	-305	-310	-310	-275
C	330	325	330	335	335	335	310
CT	150	150	155		150	145	
H-HHH	-150	-155	-160		-150	-145	
CT	155		150				125
H-HH2	-150		-145				-130
CT				155			
H-HH3				-155			
CT	90				90		
CP-HH	-110				-105		
CT					90	95	
CP-HC					-105	-120	
CT							70
CP-H2							-90
CT	90	100					
CS-HHH	-110	-125					
TT-CT			105				
CSV-HHH			-125				
CT	85		85				
CSV-HHH	-110		-105				
CT				75			
CE-HH				-95			

TABLE 81. OVERFLOW ONTO UNSATURATED SECONDARY ALKYL CC FRAGMENTS IN CH LMO'S

	TT-CPH CSCSV	TG-CPH CSCSV	TC-CPH CSCSV	CPH CSCE	CSVH CSCSV	CSVH CSCE	CSVH CSCSV*
CS	-340	-315	-315	-305	-275	-280	235
C	355	330	335	315	315	295	-245
CS		140					
H-HH		-155					
CS	140	150					
H-H2	-155	-175					
CS			145				
H-H3			-170				
CS				120			
H-23				-140			
CS					145		
H-H2*					-155		
CS					120		-195
H-22*					-130		215

TABLE 82. OVERFLOW ONTO UNSATURATED TERTIARY ALKYL CC FRAGMENTS IN CH LMO'S

	TT-CPH CTCSV	TG-CPH CTCSV	CPH CTCSV-3	CPH CTCE	CSVH CTCE
CT	-325	-300	-295	-295	-270
C	335	320	325	305	290
CT		150			
H-HHH		-145			
CT	150	155			
H-HH2	-150	-170			
CT				150	
H-HH3				-160	
CT			155	155	125
H-H23			-170	-160	-140
CT		90			
CP-HH		-105			
CT	85	85			
CP-H2	-105	-120			
CT				85	
CP-H3				-120	
CT					70
CP-23					-100
CT				85	
CSV-HH3				-120	
CT			75		
CE-HH			-90		

TABLE 83. OVERFLOW ONTO SECONDARY ALKYL CC FRAGMENTS IN CC LMO'S

	CSCP CSCP	CSCS CSCP	CTCP CSCP	CSCSV CSCP	CSCE CSCP	CSCP CTCP	CSCP CSCS	CSCP CSCSV	CSCP CSCE
C	-345	-355	-350	-315	-340	-335	-350	-365	-330
C	335	340	335	310	330	330	340	340	305
C	140	140	135	130	130	150	140		
H-H	-145	-145	-140	-140	-135	-140	-145		
C			150						
H-C			-145						
C								135	
H-2								-140	
C									140
H-3									-155
CT						100			
CP-H						-110			

TABLE 84. OVERFLOW ONTO ALKYL CC FRAGMENTS IN DOUBLE BANANA LMO'S

	BCSVCPV CSCP	BCSVCPV CTCP	BCSVCPV CTCP-3
C	-350	-335	-330
C	375	360	370
C	165	175	
H-H	-175	-165	
C	155	160	
H-2	-185	-175	
C			165
H-23			-180
CT		105	
CP-HH		-125	
CT		105	
CP-H2		-145	
CT			100
CE-HH			-115

TABLE 85. OVERFLOW ONTO ALKYL CC FRAGMENTS IN TRIPLE BANANA LMO'S

	BCECPE CSCP	BCECPE CSCS	BCECPE CSCSV	BCECPE CSCE	BCECPE CTCP	BCECPE CTCP-2	BCECPE CTCSV
C	-315	-315	-335	-300	-305	-305	-325
C	380	385	390	350	375	375	380
C	155	155	150		175		
H-3	-185	-180	-180		-185		
C						175	160
H-23						-185	-190
C				160			
H-33				-200			
CT					105		
CP-H3					-140		
CT							105
CP-23							-140
CT						100	
CSV-H3						-140	

'delocalization through the single bond.' The coefficients occurring in *both* cases can be classified with the scheme used for the alkyl groups. Furthermore, the *intra*- and *inter*-class variations show values similar to those between the analogous alkyl group classes.

Delocalization through the double bond

When the delocalization occurs through the double bond, the vicinal group contains only two fragments. One is trans to the bond fragment, and the other is cis to the bond fragment. *We shall call the trans fragment the overflow fragment*. Coefficient magnitudes for both coplanar fragments are always substantially larger than those of the analogous cis or trans alkyl vicinal fragments.

The overflow fragment coefficients for delocalization through the double bond are shown in the first two *columns* of Table 86 for primary vinyl CH groups, and in the first two *rows* of Table 87 for secondary vinyl CH groups. The three letter symbols at the *left end* of Table 86 refer to the relative orientation of the overflow fragment and its coplanar chain beyond the bond fragment, whereas the three letter symbols in the *body* of Table 86, and those labelling the columns of Table 87, refer to the relative orientation of the bond fragment and its coplanar chain beyond the cis vicinal fragment. All of these were defined on the previous Figures 3 and 4. The sensitivity of the vinyl vicinal fragment coefficients to these is comparable to the sensitivity of the alkyl vicinal fragment coefficients to the TT, GT, etc. orientations.

The coefficients for the various cases of delocalization through the

TABLE 86. OVERFLOW THRU THE DOUBLE BOND ONTO PRIMARY VINYL CH FRAGMENTS

	CPVH		CPVH-H		CPVH-C		
CPVH	-550	520	335	-300			
CSVH	-555	520			NFN	330	-300
CSVH	-560	525			CTT	335	-300
CSVH	-560	525			CCT	335	-295
CSVH	-565	525			CCC	330	-295
CSVH	-550	525			CCP	325	-295
CSVH	-550	525			CPL	345	-320
NFN							
CSVCP	-580	515	330	-275			
CSVCS	-585	520	330	-280			
CSVCT	-590	520	335	-280			
TTT							
CSVCS	-590	525	330	-275			
CSVCSV	-595	520	330	-270			
CSVCTV	-585	515	330	-280			
TCT							
CSVCS	-560	505	330	-290			
CSVCT	-565	505	330	-290			
TCC							
CSVCS	-555	495	345	-295			
TCP							
CSVCS	-555	505	335	-305			
CSVCT	-560	505	335	-305			
TPL							
CSVCE	-560	505	315	-265			
DI							
CSVCTV	-600	520			NFN	330	-270
CTVCP	-585	515			TTT	330	-280

TABLE 87. OVERFLOW THROUGH THE DOUBLE BOND ONTO SECONDARY CH FRAGMENTS IN PRIMARY AND SECONDARY VINYL CH LMO'S

	CVH NFN	CPVH CTT	CPVH CCT	CPVH CCC	CPVH CCP	CPVH CPL
CSV	-525	-525	-520	-515	-520	-530
H	510	510	500	490	500	520
CSV	235					
CP-H	-215					
CSV	235					
CP-C	-215					
CSV	235	235	245			
CS-HH	-215	-215	-240			
CSV			255			
CS-HC			-240			
CSV					255	
CS-H3					-250	
CSV				280		
CS-HH*				-250		
CSV	240		250			
CT-HHH	-215		-240			
CSV					260	
CT-HH3					-250	
CSV	220					
CSV-HH	-215					
CSV		230				
CTV-HHH		-220				
CSV						225
CE-H						-190

double bond onto CC groups are shown in Tables 88 and 89. The first (second) of the column labels characterizes the bond fragment (overflow fragment). The three letter symbols appearing as the last column labels describe the relative orientation of the bond fragment and its coplanar chains beyond the overflow fragment (see Figures 3 and 4).

Delocalization through the single bond

When the delocalization onto the single bond vinyl group occurs through a single bond, the vicinal group consists of a vinyl CC or CH overflow fragment and two banana gauche fragments. The overflow fragment coefficient magnitudes are nearly the same as their alkyl counterparts, but those of the banana gauche fragments are slightly larger than those of the alkyl CC gauche fragments.

The (secondary) vinyl CH group coefficients are listed in Tables 90 and 91 for CH and CC bond fragments, respectively. Those for the (tertiary) CC vinyl groups appear in Table 92.

Delocalization Through the Triple Bond

When the vicinal group and the bond fragment are separated by a triple bond region, the former can contain only one member. We shall call this ethynyl single bond fragment an overflow fragment since it lies along the same line as its bond fragment. Its coefficient magnitudes are about those of cis overflow fragments, with nodal properties like those of trans overflow fragments.

The ethynyl single bond overflow fragment coefficients are listed in Table 93. The column labels characterize the bond fragment (which is

TABLE 88. OVERFLOW THROUGH THE DOUBLE BOND ONTO VINYL UNSATURATED CC FRAGMENTS

	CPVH CSVCP NFN	CSVCP CSVCP NFN	CPVH CSVCS NFN	CPVH CSVCS TTT	CPVH CSVCS TCT	CPVH CSVCS TCC	CPVH CSVCS TCP	CPVH CSVCT NFN	CPVH CSVCT TCT	CPVH CSVCT TCP
CSV	-415	-435	-420	-415	-425	-430	-430	-425	-430	-435
C	410	405	415	415	420	420	420	415	420	420
CSV	300	300	305					305		
H-HH	-300	-285	-300					-300		
CSV					300	300	300		300	300
H-HC					-295	-295	-295		-295	-295
CSV	305									
H-HH*	-305									
CSV				300						
H-HC*				-300						

TABLE 89. OVERFLOW THROUGH THE DOUBLE BOND ONTO VINYL CC FRAGMENTS IN PRIMARY VINYL CH LMO'S

	CPVH CSVCSV TTT	CPVH CSVCTV TTT	CPVH CSVCSE TPL	CPVH CTVCP NFN	CPVH CTVCSV TTT
CV	-380	-390	-405	-395	-360
C	385	390	380	405	380
CSV	300				
H-HH	-300				
CSV		300			
H-HC		-300			
CSV			305		
H-H3*			-320		
CTV				215	215
CP-HH				-220	-220
CTV				205	
CSV-HHH				-210	

TABLE 90. OVERFLOW ONTO SECONDARY VINYL CH FRAGMENTS IN CH LMO'S

	CPH	CSH	CTH	CSVH	CPH H*
CSV	-430	-430	-430	-425	295
H-HH	425	425	425	430	-310
BCSV	130	110			
CPV-H	-105	-85			
BCSV		140	125		
CPV-C		-115	-100		
BCSV				120	
CPV-2				-95	
BCSV	130				
CSV-HH	-110				
BCSV					-205
CPV-H*					195

TABLE 91. OVERFLOW ONTO SECONDARY VINYL CH FRAGMENTS IN CC LMO'S

	CSCP	CSCS	CTCP	CSCSV	CSCE	CTCE	CTVCP	CSCP H*	CSCSV H*
CSV	-470	-480	-470	-485	-455	-455	-455	300	305
H	435	440	435	445	420	420	435	-300	-310
BCSV	135	135	120	130	130	115		-220	-205
CPV-H	-100	-100	-85	-95	-95	-80		190	180
BCSV			145			135			
CPV-C			-110			-105			
BCTV							125		
CPV-2							-90		

TABLE 92. OVERFLOW ONTO TERTIARY VINYL CC FRAGMENTS IN CH LMO'S

	CPH	CSVH	CPH
CTV	-325	-320	
CP-H	345	350	
CTV			-320
CSV-HH			330
βCTV	115		
CPV-HH	-110		
βCTV		110	110
CPV-H2		-105	-110

TABLE 93. OVERFLOW THRU THE TRIPLE BOND

	CEH	CECP	CECS	CECT	CECSV	CECE
CE	-330	-345	-350	-350	-345	-335
H	350	350	350	355	350	335
CE	-260	-275				
CP	275	275				
CE	-270					
CT	280					
CE	-265					
CSV	275					
CE	-245					
CE	250					

necessarily an ethynyl single bond also), and the row labels characterize the overflow fragment.

Double Bond Groups

Double bond vicinal groups are those whose overflow fragment near (banana) hybrids point into double bond regions. Their vicinal fragment coefficients can be classified with the scheme used for the single bonds and, among classes of coefficients, usually have values and variations similar to those found there.

The vicinal group coefficients having CH bond fragments are shown in Tables 94 and 95. The overflow fragment coefficient magnitudes are similar to those of the *trans* CH vicinal fragments observed for the delocalization through the double bond. Their other banana vicinal fragments, which lie *gauche* to the bond fragment, have coefficients that are larger than those of previous *gauche* fragments. (In fact, they are similar to the *cis* CH vicinal fragment coefficients found for the delocalization through the double bond.) However, the single bond gauche fragments have coefficient magnitudes that are slightly smaller than those observed previously.

Double bond vicinal group coefficients having CC *or* banana bond fragments are given in Table 96. Those vicinal to CC or *triple* bond fragments are in the same relation to those vicinal to CH bond fragments (Tables 94 and 95) as previously observed. However, those vicinal to *double* bond fragments have *decidedly larger magnitudes* (relative to the double bond groups vicinal to CH, CC or triple bond fragments). These

TABLE 94. OVERFLOW ONTO DOUBLE BANANA FRAGMENTS IN CH LMO'S

	CPH 2	CSH 2	CSH 22*	CSH 23	CTH 2	CTH 23	CPH 2*	CSH 2*	CSH 22*
BCSV	-560	-560	-550	-545	-560	-545	470	470	465
CPV-H	540	540	540	540	540	535	-440	-440	-435
CSV	120	110							
H-HH	-130	-125							
CSV		120	125	135	120	130			
H-HC		-135	-140	-150	-135	-145			
CSV							-250	-260	-260
H-HH*							240	250	250
CSV									
H-HC*									
BCSV	380	325	315	310					
CPV-H	-310	-305	-305	-305					
BCSV		335			335	320			
CPV-C		-315			-315	-310			
BCSV							-380	-360	-355
CPV-H*							375	360	355

TABLE 95. OVERFLOW ONTO SECONDARY-SECONDARY AND TERTIARY DOUBLE BANANA FRAGMENTS IN CH LMO'S

	CPH	CPH	CPH
	2	2	2
eCV	-550	-540	-525
CV	535	515	505
CSV	115		
H-HH	-125		
CTV		75	
CP-HH		-90	
CTV			80
CSV-HH			-95
eCSV	320		
CSV-HH	-305		
eCTV		325	
CPV-HH		-295	
eCTV			315
CPV-H2			-285

TABLE 96. OVERFLOW ONTO DOUBLE BANANA FRAGMENTS IN CC AND BANANA LMO'S

	CSCP	CTCP	CTCP	BCSVCPV	BCTVCPV	BCSVCPV	BCSECPE
	2	2	23	2	2	2	2*
BCSV	-595	-595	-585	-685	-685		550
CPV	530	530	535	665	660		-550
BCTV						-665	
CPV-H2						640	
CSV	110	105		150			
H-HH	-115	-110		-160			
CSV		120	125		160		
H-HC		-125	-135		-165		
CSV							-250
H-H3*							260
CTV						110	
CP-HH						-125	
BCSV	335	335	325				
CPV-H	-315	-310	-305				
BCSV		345					
CPV-C		-315					
BCSV				405	390		
CPV-2				-410	-400		
BCSV							-415
CPV-3*							435
BCTV						395	
CPV-H2						-385	

larger magnitudes are not acquired at the expense of any other particular fragment coefficients, and in fact are the only strong conjugation effects found in the present study.

Triple Bond Groups

Triple bond vicinal groups are those whose three members all have near hybrids that point into triple bond regions. Their coefficients which occur vicinal to CH (CC and banana) bond fragments are shown in Table 97 (Table 98). The latter overflow fragment coefficients (Table 98) have the largest magnitudes encountered in this work. The triple bond gauche fragments have coefficient magnitudes intermediate to the double bond and single bond gauche fragments of the preceding section. With the exception of the strong conjugation effects, which are not found here, coefficient classes and trends are similar to those of the double bond vicinal groups.

TABLE 97. OVERFLOW CNTO TRIPLE BANANA FRAGMENTS IN CH LMO'S

	CPH 3	CSH 3	CSH 23	CSH 33	CTH 3	CTH 23	CPH 3*	CSVH 3*
BCSE		-675	-675	-675	-670	-670	570	465
CPE-H		630	625	630	630	625	-535	-430
BCSE	-680							
CSE-HH	640							
BCSE		220	225	215				
CPE-H		-215	-220	-210				
BCSE		260					-370	
CPE-CSCP		-245					345	
BCSE		245						
CPE-CSCS		-230						
BCSE			250					
CPE-CSCSV			-230					
BCSE				270				
CPE-CSCSE				-255				
BCSE					235	240		
CPE-CTCP					-225	-230		
BCSE						250		
CPE-CTCSV						-220		
BCSE								-335
CPE-2*								320
BCSE	215							
CSE-HH	-200							

TABLE 98. OVERFLOW ONTO TRIPLE BANANA FRAGMENTS IN CC AND BANANA LMO'S

	CSCP 3	CSCS 3	CSCSV 3	CSCE 3	CTCP 3	CTCP 23	CTCSV 3	BCECE 3	BCVCV 3*
BCSE	-735	-745	-705	-715	-715	-715	-685	-750	615
CPE	630	635	605	610	625	630	600	740	-595
BCSE	250	250	235	240	220	220	205		-420
CPE-H	-230	-230	-215	-220	-205	-205	-190		360
BCSE					270		255		
CPE-CTCP					-245		-225		
BCSE						265			
CPE-CTCSV						-240			
BCSE									-395
CPE-2*									380
BCSE								250	
CPE-3								-250	

THIRD AND FOURTH NEIGHBOR FRAGMENTS

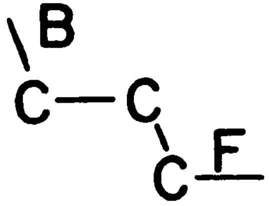
Third Neighbors

Third neighbor fragments are those that are two bond regions removed from the bond fragment. Six types of so-called 'overflow onto third neighbor fragments' are considered: (1) T, (2) C, (3) S, (4) S', (5) L, and (6) P. These symbols are defined on Figure 5 and refer to the relative orientation of the bond fragment (B) and a particular third neighbor fragment (F, which is usually coplanar with the bond fragment). An asterisk following the symbol designates rotation of the fragment F through 180° for the type in question (e.g. T and T* on Figure 5).

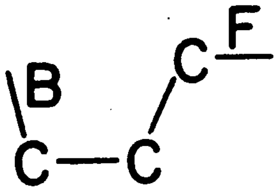
Distinct nodal properties, magnitudes and variations obtain for third neighbor fragment coefficients. However, partly because they are small, and partly because we have found no applications involving them, we shall content ourselves with listing them in the tables. The F fragment coefficients will always be given first, and for all third neighbor fragments we use the order (1) near (relative to the bond fragment) hybrids, (2) far hybrids.

The coefficients for T and C third neighbor F fragments are listed in the first two columns of Tables 99 and 100, respectively. The CH and CC column labels characterize the fragments adjacent to F. The row labels (e.g. CH-C) characterize the bond fragment (CH in our example) and the F fragment (CC in our example), respectively. The T* and C* cases are denoted by the asterisk immediately following the F fragment label (e.g. CH-C* in Tables 99 and 100).

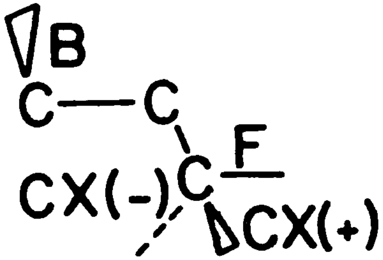
Figure 5. Bond skeletons for third neighbor overflow



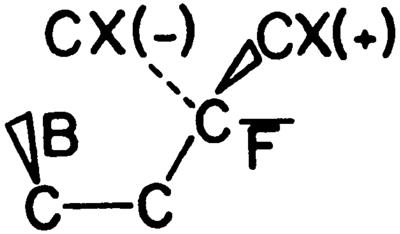
T



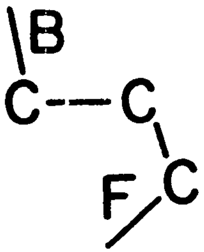
C



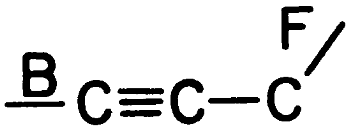
S



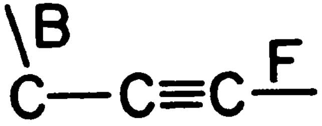
S'



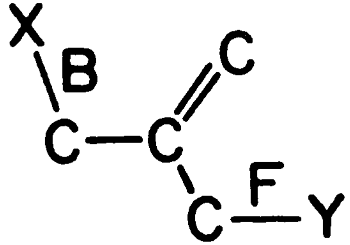
T*



L



P



CX-CY(V)

TABLE 99. T OVERFLOW ONTO THIRD NEIGHBOR FRAGMENTS

	F		CH		CC	
CH-H	140	-135	-15	20	0	5
CSVH-H	115	-115	-15	15		
CC-H	145	-130	-20	20		
BCVCV-H	160	-150	-15	15		
BCECE-H	160	-150	-15	15		
CH-CPVH	145	-145	0	25		
CC-CPVH	150	-140	-10	25		
BCECE-CPVH	160	-160	5	20		
CH-CSVH	125	-135			-5	-10
CC-CSVH	130	-130			-10	-10
BCECE-CSVH	135	-140			-10	-10
CH-C	100	-105	-5	20	0	10
CC-C	110	-105	-10	20		
BCECE-C	120	-125	-5	20		
CH-2	150	-165	10	-5	-85	80
CH-3	180	-195			-30	25
CC-3	195	-195			-40	25
BCECE-3	210	-220			-35	25
CH-H(V)	100	-100	0	5		
CSVH-H(V)	90	-90	0	0		
CH-CSVH(V)	100	-105			-5	10
CH-H*	-25	45	80	-80	55	-60
CH-CSVH*	-5	25			60	-70
CSVH-CSVH*	-45	45			50	-60
CH-C*	5	25	70	-75	50	-60

TABLE 100. C OVERFLOW ONTO THIRD NEIGHBOR FRAGMENTS

	F		CH		CC	
CH-H	-90	100	-10	-5		
CSVH-H	-140	130	5	-5		
CH-CPVH	-120	125	-50	20		
CC-CPVH	-125	135	-20	-10		
CSVH-CPVH	-95	105	-50	30		
CSVH-CSVH	-55	60			-5	30
CH-C	-80	90	-10	-5		
CH-CSVC	-110	125	-50	15		
CH-3	-100	120			10	-15
CH-H*	-65	45	-45	45	-40	45
CSVH-H*	-60	35	-50	55		
CH-C*	-65	40	-15	30		
CH-CCSV*	-55	25	-15	30		
CH-CCE*	-85	55	-15	30		

The S and S' third neighbor fragment coefficients are shown in Table 101 and the upper half of Table 102, respectively. Note that neither have F fragments coplanar with the bond fragment. The fragments CX(+) and CX(-) are defined in Figure 5. The X's in the tables indicate that the coefficients for the fragments in question are almost independent of type. Remaining labels have the same meaning as in Tables 99 and 100.

The remaining two third neighbor fragment coefficient categories, L and P, are also given in Table 102. In the former, *all* third neighbor fragments lie on a coplanar chain with the bond fragment. In the latter, there is only *one* third neighbor fragment. The X's in (the lower half of) Table 102 stand for either C or H, and the column labels characterize the third neighbor fragments.

Fourth Neighbors

Fourth neighbor fragments are *three* bond regions removed from the bond fragment. The *nine* classes are described in Figure 6: (1) TT, (2) TC, (3) TP, (4) CT, (5) CC, (6) CP, (7) PL, (8) LP, and (9) LL. The symbols B, F, and the asterisk have meanings directly analogous to those used for the third neighbor fragments. Here, however, the bond fragment (B) and fourth neighbor fragment F are always coplanar.

For the same reasons as were given for the third neighbor fragments, we shall content ourselves here with describing the coefficient tabulations. The F fragment coefficients are given first, in the order (1) near hybrid, (2) far hybrid, and the latter order is also used for the fourth neighbor fragments adjacent to F.

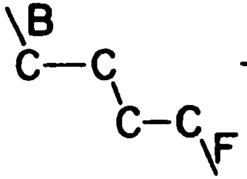
TABLE 101. S CVERFLCW ONTO THIRD NEIGHBCR FRAGMENTS

	F		CX(+)		CX(-)	
CH-H	-65	70	-30	10	15	10
CSVH-H	-50	50	-30	10	10	5
CC-H	-60	60	-30	10	10	5
BCVCV-H	-65	70	-40	10	20	-10
BCECE-H	-55	55	-50	50	20	0
CH-CPVH	90	-80	-20	30		
CH-CSVH	-30	35	-60	50	45	-10
BCECE-CSVH	-25	30	-55	30	45	-5
BCVCV-C	-65	75	-40	0	20	-5
BCECE-C	-55	65	-35	-5	10	10
CH-CSVC	70	-65	-10	25		
BCVCV-3	-90	100	40	-55	-10	35
BCECE-3	-80	90	15	-50	10	20
CH-H(V)	-25	30	-40	-10	10	40
CH-CSVH(V)	-5	10	-65	5	40	25
CH-CPVH(V)	90	-80	-15	15		
BCVCV-CSVH*	-10	-10	0	-15	-80	110

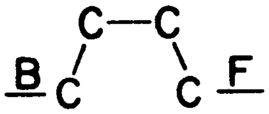
TABLE 102. S', L AND P OVERFLOW ONTO THIRD NEIGHBOR FRAGMENTS

		F		CX(+)		CX(-)	
	BCVCV-H,C	85	-75	-40	10	10	20
	CH-CPVH	-35	10	-40	50		
S'	BCECE-CPVH	-35	15	-50	60		
	CH-CSVH	-25	15	-15	-5	-55	90
	BCVCV-CSVH	80	-75	-50	5	35	-10
		CH		CC			
L	CEH-CX	20	-25	10	-20		
	CEH-CSVH	40	-45	5	-25		
		CEH					
	CX	35	-35				
P	CSVH	45	-50				
	BANANA	30	-30				

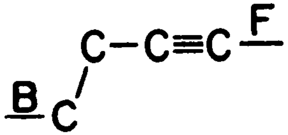
Figure 6. Bond skeletons for fourth neighbor overflow



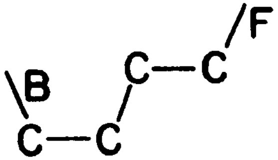
TT



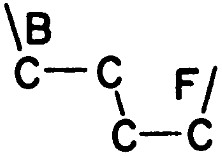
TC



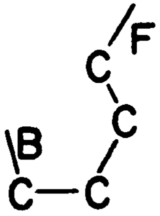
TP



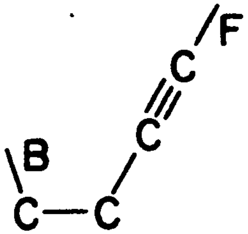
CT



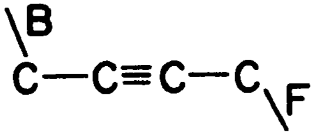
TT*



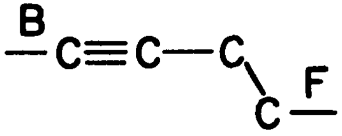
CC



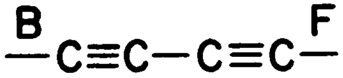
CP



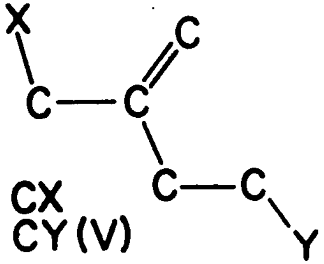
PL



LP



LL



CX
CY (V)

The TT, TC, and TP fourth neighbor fragment coefficients appear in Table 103. The upper column labels CX indicate that the fragment occurring adjacent to the F fragment have coefficients almost independent of their character. The first of the row labels (e.g. CH in CH-h) characterizes the bond fragment, and the second (e.g. H in CH-H) characterizes the F fragment.

The CT, CC, and CP fourth neighbor fragment coefficients are listed in Table 104. All labels have the same meaning as in Table 103. This is also true of the PL, LP, and LL fragment coefficients given in Table 105.

TABLE 103. TT, TC AND TP OVERFLOW ONTO FOURTH NEIGHBOR FRAGMENTS

	F		CX	
		TT		
CH-H	-50	60	10	-15
CH-CSVH	-60	80	10	-10
CH-CPVH	-60	75	15	-25
CSVH-CPVH	-60	75	25	-35
CPVH-CPVH(V)	-65	80	20	-30
		TC		
CPVH-H	50	-40	0	5
CPVH-CSVH	50	-35	25	-20
CPVH-H(V)	25	-15	5	-5
CH-CPVH	50	-40	60	-40
CH-CPVH(V)	20	-15	60	-40
	TP			
CH-CEH	-30	45		
CPVH-CEH	-35	50		

TABLE 104. CT, CC AND CP OVERFLOW ONTO FOURTH NEIGHBOR FRAGMENTS

	F		CX	
		CT		
CPVH-CSVH	20	-35	-5	5
CPVH-CPVH(V)	15	-25	-5	5
		CC		
CPVH-H	-220	180	35	-25
CPVH-H(V)	-140	115	20	-10
CSVH-CPVH	-170	155	-190	215
CPVH-CSVH*	-180	190	-85	80
	CP			
CPVH-CEH	20	-25		

TABLE 105. PL, LP AND LL OVERFLOW ONTO FOURTH NEIGHBOR FRAGMENTS

	F		CX	
		PL		
CH-H	65	-135	-35	70
		LP		
CEH-H	-25	35	10	-10
CEH-CSVH	-25	35	10	-10
CEH-CPVH	-35	45	20	-25
CEH-C	-10	25	10	-10
CEH-3	-40	55	15	-20
	LL			
CEH-CEH	-30	40		

BOND FRAGMENTS AND BOND PROPERTIES

Introduction

Since more than 95% of an LMO's population is within the bond fragment, it is natural to wonder if bond properties can be predicted with them. Two such properties that come to mind immediately are bond moments and bond energies, which receive a great deal of attention in the textbooks (35-37,79,95-101). Both have been studied previously in this laboratory (20), where it was found that the former receive important contributions from outside the bond region in an LMO description, and therefore cannot be accurately reproduced with bond fragments alone. The latter, however, were found to stem from contributions within the bond region, and hence bond fragments may be useful for their study.

Another property that appears interesting from a bond fragment viewpoint is the nuclear spin coupling constant between directly bonded atoms. Unlike the bond energy, it is possible to make a theoretical argument for this situation (102-105).

Bond Energies

The concept of 'bond energy' cannot be made non-arbitrary theoretically, so, were it not for its spectacular applications by chemists that have made it a topic for discussion in introductory courses, there would probably be no urge to postulate its existence. This being the case, the bond energy for present purposes will be defined

$$E = P(A,B)\cdot e(hy) \tag{54}$$

where P(A,B) is the bond fragment's bond order, i.e., twice the product of its coefficients, and e(hy) depends only on the hybridization within the fragment. The latter are determined by equating E to empirical prototype bond energies, e.g. the e's for sp^3 - H1s and sp^3 - sp^3 hybridizations are determined from methane and ethane, respectively.

The extensive set of empirical bond atomization energies recently published by Sanderson (106) is used for the present study. These are shown in Table 106 under column A (the remaining column labels designate the overflow fragments) and in Tables 107 and 108 as the first number in each of the row-wise groups. All other numbers in the tables are those obtained with Equation 54. The molecules used to determine the e's are methane (sp^3-H), ethane (sp^3-sp^3), ethylene (sp^2-H and double banana), propene (sp^2-sp^3), acetylene (sp-H), propyne (sp-sp^3) and (diatomic) C_2 (triple banana). The overall agreement is good, especially for the CH fragments, and isn't particularly dependent on the overflow type. Each overflow fragment lowers the energy around 0.3 to 0.6 kilocalories per mole by its presence. At this level, then, one can obtain reasonable bond energies by assuming that they depend on the bond fragment's hybridization and bond order, the latter being a function of both the bond and overflow fragment types.

Nuclear Coupling Constants between Directly Bonded Atoms

The classical interaction between the magnetic moment, $\underline{m}$, of an electron and the magnetic field, $\underline{B}$, of a nucleus (at the origin) is (107)

$$H = -\underline{m}\cdot\underline{B} \qquad (55)$$

TABLE 106. COMPARISON OF ALKYL BOND ATOMIZATION ENERGIES AND BOND FRAGMENT ENERGIES IN KILOCALORIES PER MOLE

	A	H	C	2	3	H*	33	23
METHANE	99.1							
CPH	98.5	98.6	98.7	98.3	98.0	98.5		
CSH	98.2	98.1	98.3	97.8	97.5		96.9	97.2
CTH	97.1	97.6		97.2	97.1			96.8
CPCP	84.4							
CPCS	84.1	83.9	84.0	83.6	83.4	84.0		
CPCT	84.7	83.4	83.6	83.2	82.9			82.6
CSCS	84.1	83.4	83.6		82.9			
CSCT	84.4	83.0						

TABLE 107. COMPARISON OF VINYL BOND ATOMIZATION ENERGIES AND BOND FRAGMENT ENERGIES IN KILOCALORIES PER MOLE

	ETHYLENE	PROPENE	BUTADIENE	2-BUTENE
CPVH	98.7	98.7	98.7	
		98.8	98.8	
		98.8	98.8	
CSVH		99.5	99.5	98.5
		98.5	98.5	98.6
CSVC		86.0	86.6	84.3
				86.2
HCVCV	72.3	72.2	72.7	72.7
		71.9	71.4	71.4

TABLE 108. COMPARISON OF ETHYNYL BOND ATOMIZATION ENERGIES WITH BOND FRAGMENT ENERGIES IN KILOCALORIES PER MOLE

	CC	ACETYLENE	PROPYNE	BUTYNE
CEH		101.0	101.0	101.4
			101.0	101.0
CEC			87.8	87.2
				87.4
BCECE	63.0	63.0	62.5	63.0
		62.8	62.4	62.5

where

$$\mathrm{B} = \mathrm{curl}\ \underline{A} \tag{56}$$

and the vector potential $\underline{A}$ is given by (108)

$$\underline{A} = \underline{M} \times \underline{r}/|\underline{r}|^3 \tag{57}$$

with $\underline{M}$ the magnetic moment of the nucleus. This can also be written (108)

$$\begin{aligned} H &= -\underline{m}\cdot\nabla \times (\underline{M} \times \nabla(1/r)) \\ &= (2/3)(\underline{m}\cdot\underline{M})\ 4\pi\delta(\underline{r}) - [(\underline{m}\cdot\nabla)(\underline{M}\cdot\nabla) \\ &\qquad - (1/3)(\underline{m}\cdot\underline{M})\nabla^2](1/r) \end{aligned} \tag{58}$$

where $\delta(\underline{r})$ is the Dirac delta function (39). The first term is the Fermi contact interaction (105,108) and the second gives dipole-dipole interactions (89,105,108) which are not important for the coupling between directly bonded atoms (89,105). Thus, the interaction of interest is

$$V = (2/3)(\underline{m}\cdot\underline{M})\ \delta(\underline{r}). \tag{59}$$

When many nuclei and electrons are present, this becomes (105)

$$V = (2/3)(\underline{m}_i\cdot\underline{M}_A)\ \delta(\underline{r}_i - \underline{r}_A) \tag{60}$$

with repeated indices summed.

Applying V as a perturbation to a closed shell Born-Oppenheimer wave function gives no first order contribution since the total electronic spin is zero. Second order perturbation theory gives contributions like

(105)

$$\langle 0|V|N\rangle\langle N|V|0\rangle/(E_N-E_0),\ N \neq 0 \tag{61}$$

where E_N and E_0 are the N- and ground-state energies, respectively. Making an average energy approximation (103)

$$E_N-E_0 \approx E, \tag{62}$$

closure (105) can be used to obtain

$$\langle 0|V^2|0\rangle/E \tag{63}$$

for the second order contribution to the energy. Therefore

$$\Delta E = -(4/9E)\ \underline{M}_A\cdot\langle 0|\delta(\underline{r}_A-\underline{r}_i)\ \underline{m}_i\underline{m}_j\ \delta(\underline{r}_j-\underline{r}_B)|0\rangle\cdot\underline{M}_B \tag{64}$$

or in tensor form

$$\Delta E = \underline{M}_A\cdot\underline{K}_{AB}\cdot\underline{M}_B \tag{65}$$

where $\underline{K}_{AB}$ is the second rank *reduced coupling tensor* (in dyadic form) between nuclei A and B. If the molecules are rotating rapidly and randomly, $\underline{K}_{AB}$ may be replaced by its spherical average (105), the *reduced coupling constant*

$$K_{AB} = (1/3)\ \mathrm{trace}\ (\underline{K}_{AB})$$

$$= -(4/27E)\langle 0|\delta(\underline{r}_A-\underline{r}_i)(\underline{m}_i\cdot\underline{m}_j)\ \delta(\underline{r}_B-\underline{r}_j)|0\rangle \tag{66}$$

and the interaction energy becomes

$$\Delta E = K_{AB}\,(\underline{M}_A \cdot \underline{M}_B). \tag{67}$$

Thus, in a closed shell molecule with the dipole terms neglected, the interaction between the magnetic moments of the electrons and nuclei leads to a coupling of the nuclear moments, i.e., the electrons couple the nuclear moments.

Introduction of the INDO LCAO-MO closed shell wave function with the approximation that all AO's are zero at the nuclear positions except the local s functions gives (89,105)

$$K_{AB} = (64\pi^2/9E)\, b^2 \langle s_A|\delta(\underline{r}_A)|s_A\rangle\langle s_B|\delta(\underline{r}_B)|s_B\rangle$$

$$\times\ (Ps(A,B))^2 \tag{68}$$

where b is the Bohr magneton (109) and Ps(A,B) the s bond order between atoms A and B. This is the desired expression, showing that the coupling constant between two nuclei is proportional to the square of the s bond order. By replacing Ps(A,B) with Fs(A,B), the s bond order of the bond fragment, one obtains

$$J_{AB} \propto (Fs(A,B))^2/E \tag{69}$$

where J_{AB} is the coupling constant which couples the spins directly (rather than the magnetic moments). It is related to the reduced constant by

$$J_{AB} = (\hbar\, G_A\, G_B/2\pi)\, K_{AB} \tag{70}$$

where the G's are nuclear gyromagnetic ratios that include the charge, mass and nuclear g factors (89,104).

In order to use Equation 69, there must be some way of determining the average energies E, which have magnitudes near those of the lowest excited states in the electronic spectra. The way of doing this presently will be to assume a value of 13.200 electron volts for ethane (89) and then use the experimental CH and CC coupling constants (89) with the theoretical bond orders for ethane, ethylene and acetylene to calculate the E's for the latter two via

$$E_2 = (Fs_2/Fs_1)^2 \cdot (J_1\ /J_2) \cdot E_1. \qquad (71)$$

Slightly different values are obtained with the CH and CC constants, and the number to be used is the weighted (according to the numbers of bonds) average of these. The results are shown in Table 109, where the calculated J's are those obtained with the weighted averages. (In all that follows, the J's will be in cycles per second (cps) and the E's in electron volts (eV).) The differences between the calculated and experimental are at worst about 10%.

If it is assumed that the ethane, ethylene and acetylene values hold for all alkanes, alkenes, and alkynes, respectively, then it is possible to calculate other coupling constants. A check of this is given in Table 110, where the experimental (110) and calculated CH constants in isobutene, propyne and 2-butyne are compared. The agreement is the same as in Table 109 and shows that the assumption is reasonably valid.

TABLE 109. AVERAGE ENERGIES AND COUPLING CONSTANTS IN ETHANE, ETHYLENE AND ACETYLENE

	E			CH		CC	
	CH	CC	AVG.	CALC.	EXPT.	CALC.	EXPT.
ETHANE	13.200	13.200	13.200	126	126	34.6	34.6
ETHYLENE	13.904	11.901	13.567	162	157	59.3	67.6
ACETYLENE	12.125	12.640	12.297	246	249	176	171.5

TABLE 110. COMPARISON OF EXPERIMENTAL AND CALCULATED CH COUPLING CONSTANTS

	CPH		CH	
	CALC.	EXPT.	CALC.	EXPT.
ISOBUTENE	126	126	163	155
PROPYNE	134	132	246	248
2-BUTYNE	134	131		

Table 111 contains some calculated alkyl bond fragment coupling constants for which experimental values aren't known. The upper column labels (CX) characterize the bond fragment, with X defined in the body of the table. The lower column labels characterize the overflow fragment. The row labels specify the type of the alkyl carbon of the bond fragment, e.g. CX with X = H and row label CP means that the bond fragment is CPH. Each row label appears three times, according to whether the bond fragment coupling constants apply to alkanes, alkenes or alkynes, respectively. Overall, the behavior is similar to that in Tables 109 and 110: there isn't much sensitivity to the overflow fragment character.

Table 112 lists some vinyl and ethynyl coupling constants (in alkenes and alkynes, respectively) for which no experimental values have been reported. The first seven rows are single bond fragment labels and the last four label banana bond fragments. Note that the column labels have different meanings for single and banana bond fragments. In single bond fragments they characterize the bond fragment, e.g. CEX with X = H means that the bond fragment is ethynyl CH. In banana bond fragments they characterize the overflow fragment, e.g. X = H means the overflow fragment is CH. The cis or trans and di in parentheses refer to primary vinyl CH bond fragments cis or trans to monosubstituents and in disubstituted ethylenes. Here, too the behavior is similar to Tables 109 and 110, there being little sensitivity to the overflow fragment type.

Some coupling constants for systems having conjugate banana bonds are shown in Table 113. The first column label is the average energy used for the molecule. These are the previous values except for vinyl acetylene,

TABLE 111. CALCULATED ALKYL COUPLING CONSTANTS

	CX	CX	CX	CX
	H	C	2	3
		X=H		
CP	126	126		
CP	123	123	122	
CP	135	136		134
CS	125	125		
CS	121	122	121	
CS	134	134		132
CT	123			
CT	120		119	
CT	133			131
		X=CS		
CP	34.2	34.3		
CP	33.3	33.4	33.0	
CP	36.7	36.8		36.3
CS	33.8	34.0		
CS	32.9	33.0		
CS	36.3	36.5		35.8
CT	33.4			
CT	32.5			
CT	35.9			
		X=CT		
CP	33.8	34.0		
CP	32.9	33.0	32.7	
CP	36.3	36.5		35.8

TABLE 112. CALCULATED VINYL AND ETHYNYL COUPLING CONSTANTS

X=	H	CP	CS	CT
CPVX(CIS)	162			
CPVX(TRANS)	162			
CPVX(DI)	163			
CSVX-H	161	44.5	44.0	43.6
CSVX-C	162	44.7	44.1	
CTVX-H		44.1		
CEX	246	66.7	66.1	65.2
BCPVCSV-X	58.6	58.8		
BCSVCSV-X	57.8			
BCPECSE-X	175	175		
BCSVCSV-X	173			

TABLE 113. VINYL AND ETHYNYL COUPLING CONSTANTS IN SOME CONJUGATED SYSTEMS

	E	CH	CC	BANANA
BUTADIENE	13.567	162	57.7	57.9
		161(CSVH)		
ISOPRENE	13.567	163	57.2	57.9
		162(CSVH)		57.1
BUTADIYNE	12.297	246	120	172
VINYL ACETYLENE	12.932	234	82.9	166
		171		60.5
		168(CSVH)		

where an average of the ethylene and acetylene values was used. The remaining column labels characterize the bond fragment. The CSVH in parentheses distinguishes the secondary vinyl CH bond fragment from that of the primary vinyl CH. In vinyl acetylene, the first of the three CH bond fragment entries is for the ethynyl CH bond. The CC bond fragments in the first two rows (butadiene and isoprene) are those for vinyl carbon-vinyl carbon single bonds. The CC bond fragments in the last two rows (butadiyne and vinyl acetylene) are for ethynyl carbon-ethynyl carbon and ethynyl carbon-vinyl carbon bond fragments, respectively. The banana bond fragment entries for isoprene are for the primary vinyl-secondary vinyl and primary vinyl-tertiary vinyl cases, respectively, while those for vinyl acetylene are for triple and double bonds, respectively.

Even in conjugated systems, we see that the greatest sensitivities are to the average energy and bond fragment character: the effects of conjugation are small.

BENT BONDING

Introduction

Early LMO (16,17) and related (30,31) works have shown that orbital centroids do not point directly along the bond skeleton, i.e., that bonds are 'bent.' The concept is normally applied to only slightly bent bonds, and not to banana bonds, where the bending is largely due to the availability of several electron pairs for bonding between the same two atoms. It will be shown here that this slight bending occurs because of the LMO delocalization onto the *geminal* fragment *near* (relative to the bond fragment) hybrids and hence is an inherent property of the solutions to the LCAO-MO-SCF equations (87).

Bent Bonds and Geminal Fragments

All non-banana carbon hybrids have centroids lying directly along the bond skeketon. We consider these to be unit vectors along the bond skeleton that are centered on their associated carbon atoms and point away from them. Consider a LMO whose bond fragment hybrid is associated with carbon atom Q. Let h, and a,b,c, be the coefficients of its bond fragment and three geminal fragment near hybrids, respectively, on atom Q. We define vectors $\underline{h}$, and $\underline{a},\underline{b},\underline{c}$ as being proportional to their associated *hybrid* centroid unit vectors with proportionality constants h and a,b,c, respectively. Thus $\underline{h}$ and $\underline{a},\underline{b},\underline{c}$ have magnitudes equal to the magnitudes of the coefficients h and a,b,c of the LMO bond and geminal fragments on atom Q. The vectors $\underline{a},\underline{b},\underline{c}$ may have the same or opposite directions as their associated centroid vectors (according as a,b,c, are positive or negative).

The bending angle A of the bond fragment on atom Q is defined to be the angle between $\underline{h}$ and $\underline{k}$, where

$$\underline{k} = \underline{h} + \underline{a} + \underline{b} + \underline{c}. \tag{72}$$

Thus

$$A = \arccos\ (\underline{k}\cdot\underline{h}/kh). \tag{73}$$

Equations 72 and 73 show the connection between bent bonding and geminal near hybrid delocalization. The larger and more unsymmetric the latter (relative to the bond fragment), the greater is the deviation from the bond skeleton.

Table 114 lists some values of A for the bond fragments having CH overflow fragments that were encountered is this work. All angles have been rounded to the nearest half degree. It is sufficient to specify the character of carbon atom Q (row labels) and the character of the other atom of the bond fragment (column labels). Table 115 lists the sensitivity of the bending angle to overflow fragment (column labels) changes in primary CH bond fragments. Deviations from the angle observed for the CH overflow fragment case are typical of all bond fragments.

TABLE 114. ORBITAL DEVIATIONS FROM THE BOND SKELETON IN DEGREES

	H	CP	CS	CT	CSV	CTV	CE
CP	2.0	0.0	0.5	0.5	1.0	1.0	0.0
CS	2.0	1.5	1.0		2.0		1.5
CT	0.0	1.5			1.0		1.5
CPV	4.0						
CSV	3.0	3.5	3.5	3.5	3.0	2.0	3.5
CTV		2.5			2.0		
CE	0.0	0.0	0.5	0.5	1.5		0.0

TABLE 115. PRIMARY CH ORBITAL DEVIATIONS FROM THE BOND SKELETON IN DEGREES

	H	C	2	3	H*	2*	3*	VH*
BEND	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.5

CONJUGATION AND HYPERCONJUGATION

Traditionally, conjugation has been reserved for molecules having alternating double bonds (56,57,59,111,112), these being common and having unique, often spectacular properties which are readily accessible to theoretical and experimental analysis. Presumably recognizing that the phenomenon involved the interaction of bonds separated by one bond region (next neighbor bonds), Mulliken (113,114) generalized the concept to other systems, calling it hyperconjugation. Since then, it has been widely appreciated in organic chemistry (79) that hyperconjugation and conjugation arise from the same fundamental factor: delocalization of electrons.

Recalling the perturbation theory results given earlier in Table 35, it follows that interactions among the bond fragments (considered as two-center localized orbitals) lead to vicinal fragment coefficients in close agreement with the vicinal fragment coefficients of the actual LMO's. If one makes the reasonable assumption that these interactions are a measure of hyperconjugation, then one expects hyperconjugation effects to be manifest in the following two ways: (1) by variations in the bond fragment coefficients that are induced by changing the vicinal group, and (2) by variations in the vicinal group coefficients that are induced by changing the bond fragment. The former hyperconjugation effect amounts to changing the overflow fragment in most cases. The latter has already been shown to account for hindered rotation origins (18,19,69,70).

Since a given overflow fragment type was found to introduce similar coefficient variations in most bond fragments (see Tables 40 and 46), it is reasonable to think that it will also produce similar variations in bond (fragment) properties, other things being equal. This can be seen in Tables 106-8, where *each hybridization type* displays a characteristic bond energy, around which similar deviations occur, depending on the overflow fragments. It is interesting that *in this context* the *hybridization* effects are typically two to three times larger than the *hyperconjugation* effects, since this is a controversial topic (46,79,115).

EMPIRICAL OBSERVATION OF LOCALIZED BONDS

The November 22, 1971, issue of Physical Review Letters reported the results of some conceptually simple and fundamentally important experiments (116): The Compton X-ray scattering technique was used to directly observe localized bonding in some hydrocarbons. This 'direct' observation is the outstanding contribution of these experiments, for previous experimental evidence for 'observables' in the localized representation has been indirect, e.g. the usual notions of bond energies, moments, etc.

It can be shown (117) that the cross section for Compton scattering by atoms or molecules (in atomic units) is

$$\sigma = 2\pi(\underline{\epsilon}\cdot\underline{\epsilon}')^2 \, \omega'/\omega \; (d\ell/c^4) \; J(\ell) \tag{74}$$

where the primes refer to the outgoing rays, the $\underline{\epsilon}$'s are polarization directions, ℓ is the reduced wavelength, or distance from the Compton peak (118,119), and

$$J(\ell) = \tfrac{1}{2}\Sigma \int I_L(p)dp/p \tag{75}$$

is the 'Compton profile.' The quantity $I_L(p)$ is the radial momentum density for orbital L, and the sum in Equation 75 is over the occupied MO's and the integration from $|\ell|$ to infinity.

Generally, it is impossible to measure the individual I; however, by subtracting out the contributions of inner shell electrons and judiciously choosing pilot systems, Eisenbarger and Marra (116) were able to observe them. Methane gave the CH bond Compton profile, and values for single and double CC bonds (no triple bonds were studied) followed from their experimental ethane and ethylene profiles, respectively, by assuming a constant CH value. Using these numbers, they were able to calculate values agreeing with experiment within experimental accuracy (1-5%) for several other hydrocarbons, thus providing strong proof both for the validity of Equation 75 and the *existence and transferability of 'bond' J*, and hence localized bonding itself.

Prior to this experiment, but still quite recently, a comparative study of some hydrocarbon LMO's in the momentum representation was reported which used *ab initio* minimal basis LCAO-SCF-MO theory (24,118). There, too, a good deal of transferability was observed, not only for Compton profiles, but for momentum density contours and expectation values also. In fact, the theoretical results concluded that hydrocarbon Compton profiles can be well represented by using only three values, one for inner shells, another for all CH bonds, and still another for all CC bonds. It should be pointed out, however, that their building block total profile calculation for benzene, which presumably tests the last assumption, gave generally poorer agreement with the SCF results than did their similar cyclopropane calculation. Especially in view of the fact that Compton profiles are not one of the more sensitive properties to errors in the wave function (119), it may be that too much transferability is being assigned. For example, the highly bent ethylene banana bonds (50 degrees above and below the bond axis) would be expected to *increase* the Compton profiles at $\ell = 0$ (which is the inverse momentum expectation value) from its ethane CC bond value (0.412). In fact, division of the ethane value by the sine of 50° does give a value (about 0.54) rather close to the ethylene double bond value (0.516).

CANONICAL AND VIRTUAL ORBITALS

Introduction

These orbitals have several properties interesting enough to call for some way of determining them from the localized orbitals. Chief among these are that they approximate the selection rules for electronic transitions (44) and provide estimates of the lower excited states of the electronic spectrum (34). To determine them, all that is actually needed is the knowledge that the CMO's diagonalize the Fock matrix (14); but this implies that they are symmetry orbitals (14), i.e., carrier functions (82) for the irreducible representations of the molecule's point group. This can be exploited in many cases to shorten their computation.

Virtual Orbitals

The virtual, or unoccupied, MO's (VMO's) are those produced in any closed-shell LCAO-SCF-MO calculation having more basis functions than electron pairs. They can be used, in canonical form, to approximately describe the electronic spectrum and, in any form, to calculate the so-called polarizabilities useful in the applications of perturbation theory to MO wave functions (87-93). It is therefore desirable to compute them as simply as possible as well as having some way of casting them in canonical form. The latter will be given in the next section.

The simplest way to calculate VMO's from LMO's (87) makes use of the notion of antibonding (100). Let c and c' be bond fragment coefficients for hybrids h and h', respectively, in some LMO λ. The INDO antibonding virtual localized orbital is defined

$$\lambda' = (c'h - ch')/(c^2 + c'^2)^{1/2} \tag{76}$$

and, in the paraffins, are in one-to-one correspondence with the occupied LMO's. The λ' are mutually orthogonal, but only approximately orthogonal to the occupied space. To make them so orthogonal, some process, e.g. Gram-Schmidt orthogonalization (120), should be used which doesn't change the occupied space, as this is the one accurately modeled. When this has been done, one has a set of virtual LMO's (VLMO's).

Canonical Orbitals

In the present context, one should also determine CMO's for the occupied and virtual spaces without altering the former. Thus, let the λ's be LMO's or VLMO's and let

$$\lambda_i = \sum_\mu T_{i_\mu} f_\mu \tag{77}$$

be their expansions in symmetry orbitals. Using standard projection operators (82) P_μ for each irreducible representation, one can project the set

$$\bar{\mu}_i = P_\mu \lambda_i = T_{i_\mu} f_\mu \tag{78}$$

from each λ, and by Gram-Schmidt orthogonalization (120), obtain a set of N_μ linearly independent symmetry MO's μ within the space in question. Since the Fock operator depends only on the occupied space (6), it is known and its matrix elements, $F(\mu;ij)$ in the μ basis can be calculated. The CMO's of symmetry μ are the eigenfunctions of this N_μ by N_μ matrix, and repeating the process for all symmetries produces all of the CMO's.

When a given symmetry occurs only once, N_μ is unity and the μ_i is the CMO. At the other extreme, when there is no symmetry, there are no short cuts and the full Fock matrix in the occupied and/or virtual spaces must be diagonalized. In this situation, one may consider another option, especially for smaller molecules, namely, diagonalizing the Fock matrix in the atomic basis and simultaneously obtaining the occupied and virtual CMO's.

MODEL MOLECULES

Perhaps the most important consequence of this work is that it specifically describes what must be done to obtain truly transferable localized molecular orbitals when one has a set of transferable bond lengths and bond angles. Thus, one is *provided with a prescription (as opposed to a set of equations) for assembling model molecules*. Ultimately, this would be done with a computer. Starting from minimal input data, the entire molecule could be assembled from internal access information and tables. Options could be provided to furnish the user with canonical molecular orbitals, virtual molecular orbitals, and any number of molecular properties. This latter has already been done for diatomic molecules by A. C. Wahl *et al.* (121).

There are less accurate ways to calculate model localized orbitals beginning from SMO's or PMO's such as were given in Table 35. They are based upon the fact that *both* sets of orbitals have coefficients in close agreement with the LMO's, except for the geminal fragments. One could therefore replace the SMO and PMO geminal fragment coefficients with model values to obtain representations of the LMO's.

However, to obtain the SMO's one must have the canonical MO's, and to obtain the PMO's one must essentially model the bond fragment coefficients (to serve as unperturbed functions). As a result, neither method offers a technical advantage to the one which would use the computer catalog.

APPENDIX: INTERPRETATIONS OF LMO'S

For any single determinant, closed-shell, MO wave function, the electron repulsion energy is (6)

$$R = D + C - X, \tag{79}$$

where D is the 'self-energy'

$$D = \Sigma\,[i^2|i^2], \tag{80}$$

C is the Coulombic repulsion energy

$$C = 2\Sigma\,\Sigma'\,[i^2|j^2], \tag{81}$$

and X is the exchange repulsion energy

$$X = \Sigma\,\Sigma'\,[ij|ij]. \tag{82}$$

All sums are over the occupied MO's and the primes mean that the $i = j$ terms are omitted from the sum. The LMO's are those which simultaneously maximize D and minimize C and X, of course leaving R invariant. Maximization of D means that the LMO's are those which, on the average, are the most highly concentrated MO's possible energy-wise. Minimization of C means that they are also the MO's whose average long-range, or Coulombic, interactions are as small as possible. Finally, minimization of X means that their short-range, or exchange interactions are likewise as small as possible (on the average). Succinctly, energy localization accomplishes three things: concentration of the MO's, long-range separation of different MO's, and short-range separation of different MO's (22).

If it were possible to reduce X to zero, one would have instead of Equation 79

$$R = D + C, \tag{83}$$

which is the repulsion energy for a Hartree product wave function (122). The Hartree product for a closed-shell takes the Pauli principle into account by doubly occupying each MO, but does not include that part of the principle which requires total antisymmetry of the wave function. Thus, each electron can be identified with a specific MO and is not exchanged. Since it is generally impossible to reduce X to zero, one doesn't realize this situation, but the LMO's are those MO's for which R most nearly approaches the Hartree form, i.e., *they are proper quantum mechanical orbitals which identify with specific electrons as closely as possible*.

Another interpretation of localized bonding follows from some works done more than twenty years ago which dealt with electron probability distributions and their maxima in atoms (123-125). Single-determinant orbital wave functions were made and the analytical form of their square determined after performing the spin integrations. This was then maximized with respect to *all* spatial coordinates and the resulting centroids determined. By considering the

$$1s^2\ 2s\ 2px\ 2py\ 2pz$$

atomic state of carbon, tetrahedral valence hybrids and inner shells were predicted when all AO's were allowed to mix, and trigonal hybrids obtained when one of the p AO's was witheld. Thus, the *basis functions* which, when perturbed, may be regarded as giving rise to the LMO's, are those whose centroids maximize the atomic spatial electron probability distribution, and *it is very likely that LMO centroids similarly maximize the molecular spatial electron probability distribution*.

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