Theoret. Chim. Acta (Berl.) 37, 177—216 (1975)

Commentationes

Localized Charge Distributions

VII. Transferable Localized Molecular Orbitals for Acyclic Hydrocarbons

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Received July 16, 1974

A localized molecular orbital has been found to extend slightly and regularly into regions away from the chemical bond which contains most of its charge cloud. This was made the basis for a method of transferring localized orbitals among similar molecules. Each localized orbital induces a set of so-called molecule invariant fragments consisting of one bond fragment and collections of geminal fragments, vicinal fragments, and third and fourth neighbor fragments. Localized orbital expansion coefficients in a hybrid basis can be calculated for these molecule invariant fragments without solving any equations or performing any laborious computations.

The present work is an application to acylic hydrocarbons. The results are based on the analysis of 33 INDO-SCF molecular orbital wavefunctions in the localized representation. Computational methods for obtaining close approximations to localized orbitals are also discussed. The application of a suggested pseudo-eigenvalue localization method and its accompanying self-consistent iteration process are found to not converge.

Key words: Localized charge distributions – Acyclic hydrocarbons

1. Introduction

This work combines two 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. It – like all others – is a subjective representation, as has been known for many years [14], but is nonetheless rigorous and has proved exceedingly useful for studying phenomena which do not involve electronic excitations. The present applications will be to the electron distributions in acyclic hydrocarbons, with emphasis on the inherent delocalization and transferability of the localized orbitals which describe the electronic motion. Using INDO overcomes the economic and technical problems (computer storage and time, multicenter integrals, etc.) encountered in *ab initio* methods, which would restrict the study to just a few molecules, at the expense of having a more phenomenological description.

Model geometries are employed [15], in keeping with the model localized orbitals we shall obtain. The orbitals will be described in a basis set of hybrid functions which provide perfectly localized first approximations to them, and hence display their behavior very effectively.

Unlike some studies which concern themselves with the examination of properties [16–19], the present investigation will concentrate on the wave functions themselves. Also unlike some other studies, the present approach does not consider localized orbitals to be perfectly confined to one or two centers [20–24] and examines transferability in much greater detail. The former obtains because of the rigorous approach used and differs from the simple ideas of 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.

The major effort will be the analysis of the localized orbitals for the thirty-three acyclic hycrocarbons studied, and the extension of the results to cases not treated explicitly. The orbitals will be partitioned into fragments that are molecule-independent, and each group will be classified and discussed separately, revealing their behavior and the ways in which each transfers. Methods for obtaining the unoccupied and canonical symmetry molecular orbitals will also be given.

2. Geometry and Hybridization

2.1. Introduction

Directed valence theory [25, 26] is well-suited for exploiting the intimate connection between molecular geometry and hybridization in organic chemistry. Thus, when carbon atoms are called tetrahedral (alkyl), trigonal (vinyl), or linear (ethynyl), the nomenclature describes the geometric arrangement of the near neighbors and, partially, the hybridization. The latter is only partially specified for three reasons:

1. The relative status of the sigma and pi orbitals is arbitrary.
2. The *s*-character [27] of linear carbon hybrids is arbitrary.
3. The orientation of triple bonds is not defined, i.e. they may be rotated freely about the bond axis.

A dividend from the present analysis is that these hybridization ambiguities can be settled by reference to the localized orbitals (LMO's) that will be presented later. In Case 1, the LMO's mix the sigma and pi symmetries in specific proportions. In Case 2, best fit with LMO's obtains if the *s*-character is assigned the value 0.4779 (it is 0.5000 for pure *sp* hybrids). In Case 3, the orientation can be defined by maximizing overlaps between hybrids and LMO's.

2.2. Bond Skeleton and Numbering of Atoms and Hybrids Basis Functions

Figure 1 depicts the molecules for which we have explicitly calculated LMO's. The atoms are labeled C_i, C_j, ..., H_k, H_l, ... The numbers next to each atom label the (hybrid) AO's contributed by that atom. E.g. in the first molecule, propane, the (tetrahedral) hybrids on the carbon atom C_2 carry the identification numbers 5, 6, 7, 8, and the hydrogen 1*s* 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 described 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 [15]. Bondlengths representing averaged experimental values are assigned automatically by the program, making it especially convenient. These values are basically those adopted in organic chemistry models.

2.3. Pair Equivalent Hybrids in Mutually Perpendicular Planes

These consist of 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

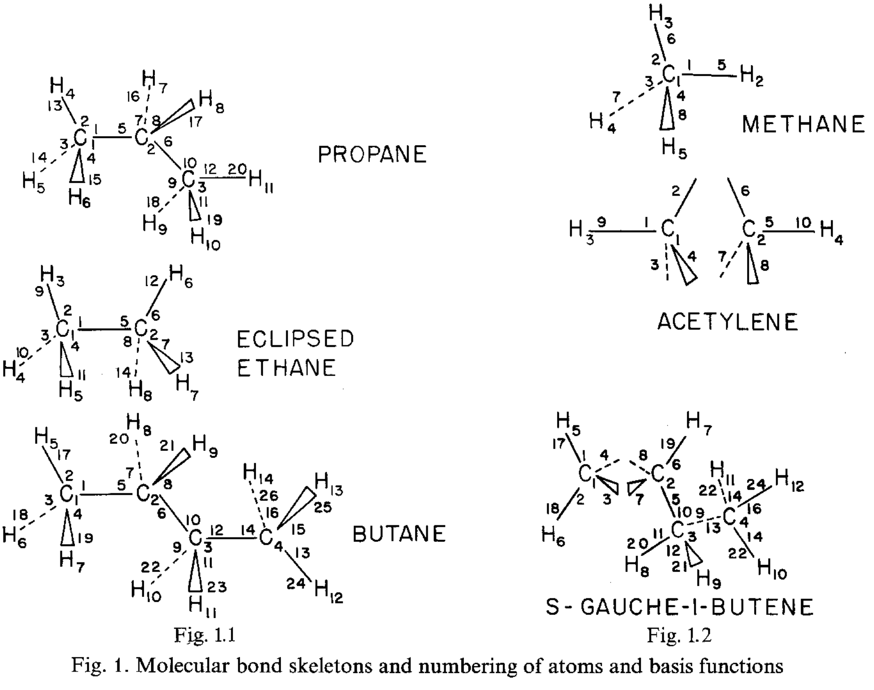

Fig. 1.1

Fig. 1.2

Fig. 1. Molecular bond skeletons and numbering of atoms and basis functions

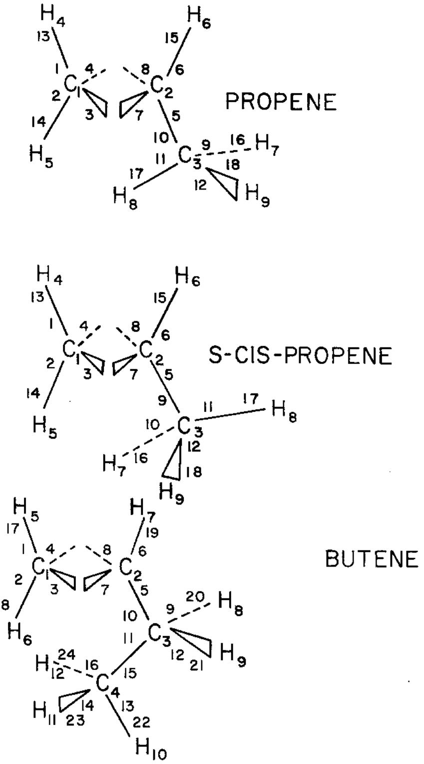

Fig. 1.3

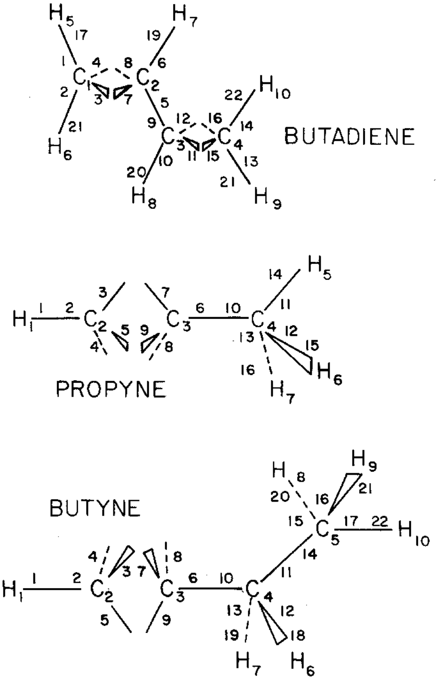

Fig. 1.4

positive x and y axes, respectively, in a right-handed system, then

$$g(\pm) = (s)\cos Q + \sin Q\,[(z)\cos A \pm (x)\sin A]\,, \tag{1}$$

$$\mathrm{g}(\pm) = (s)\cos R + \sin R\,[(z)\cos B \pm (y)\sin B]\,, \tag{2}$$

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)

$$\langle g(+)|g(-)\rangle = 0\,, \tag{3}$$

$$\langle h(+)|h(-)\rangle = 0\,, \tag{4}$$

$$\langle h(\pm)|g(\pm)\rangle = 0 = \cos Q \cdot \cos R + \sin Q \cdot \sin R \cdot \cos A \cdot \cos B\,, \tag{5}$$

there is one free parameter and hence one additional constraint may be imposed. The explicit relations that result from Eqs. (3)–(5) for the parameters Q, R, A, B are conveniently displayed as

$$(\sin Q \cdot \sin A)^2 = \tfrac{1}{2}\,, \tag{6}$$

$$(\sin R \cdot \sin B)^2 = \tfrac{1}{1}\,, \tag{7}$$

$$\cos^2 Q + \cos^2 R = \tfrac{1}{2}\,, \tag{8}$$

$$\cot^2 A + \cot^2 B = 1\,. \tag{9}$$

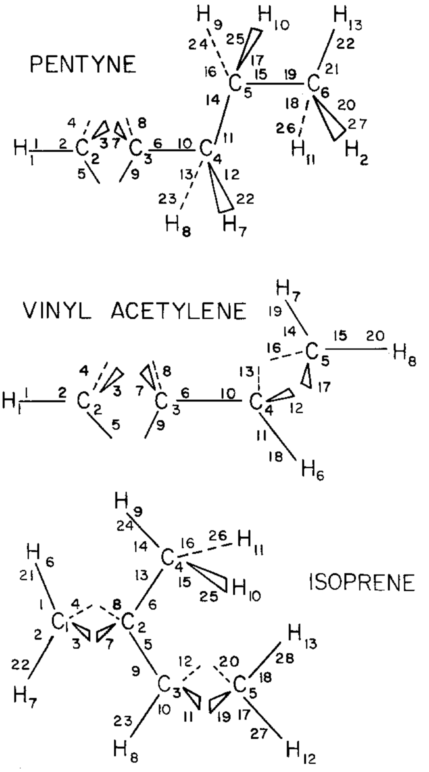

Fig. 1.5

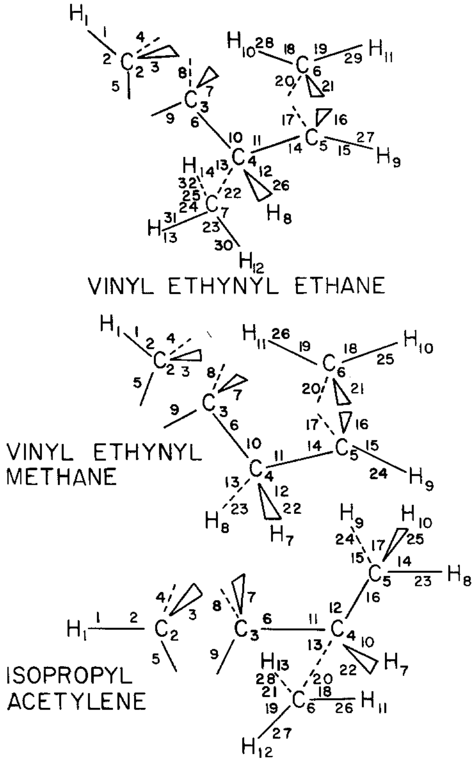

Fig. 1.6

Equations (6) and (7) relate the *s* character and angular dependence in the *same* hybrid, Eq. (8) connects relative *s* characters and Eq. (9) connects relative angles. It is straightforward to adjust the two hybrid pairs to specific situations with these equations, in particular to the two cases we are interested in: tetrahedral carbon and trigonal carbon.

2.3.1. Tetrahedral Carbon (Four Single Bonds)

These are obtained by using the additional constraint to fix the angle between all centroids at 109.5° (the tetrahedral value), i.e. by setting

$$A = B \tag{10}$$

so that from Eq. (9)

$$\cos A = \sqrt{3}/3 \,. \tag{11}$$

The remaining parameters follow from Eqs. (6) and (7), so

$$g(\pm) = 0.5(s) + 0.5(z) \pm 0.7071(x)\,, \tag{12}$$

$$h(\pm) = 0.5(s) - 0.5(z) \mp 0.7071(y)\,. \tag{13}$$

These are the well-known sp^3 hybrids.

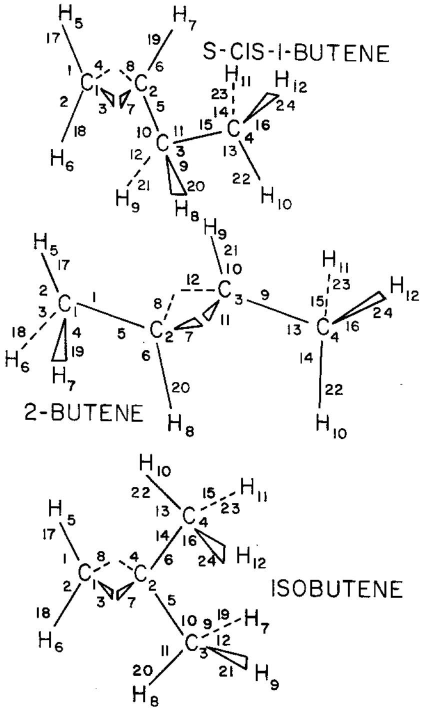

Fig. 1.7

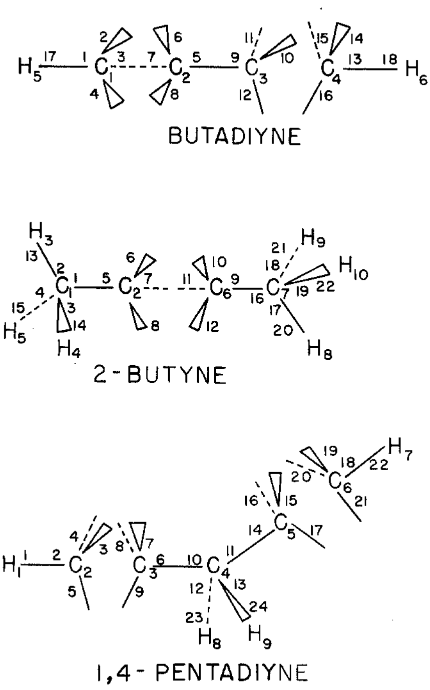

Fig. 1.8

2.3.2. 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

$$A = 60° \tag{14}$$

which implies that

$$B = 51°, \tag{15}$$

giving

$$g(\pm) = 0.5773(s) + 0.4082(z) \pm 0.7071(x) \tag{16}$$

and

$$h(\pm) = 0.4082(s) - 0.5773(z) \mp 0.7071(y). \tag{17}$$

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 exact coplanarity with their vicinal bond neighbors.

2.4. Ethynyl Carbon (Single Bond and Triple Bond)

2.4.1. Construction of the Hybrids

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

$$\langle p | p(i) \rangle = 0 \tag{18}$$

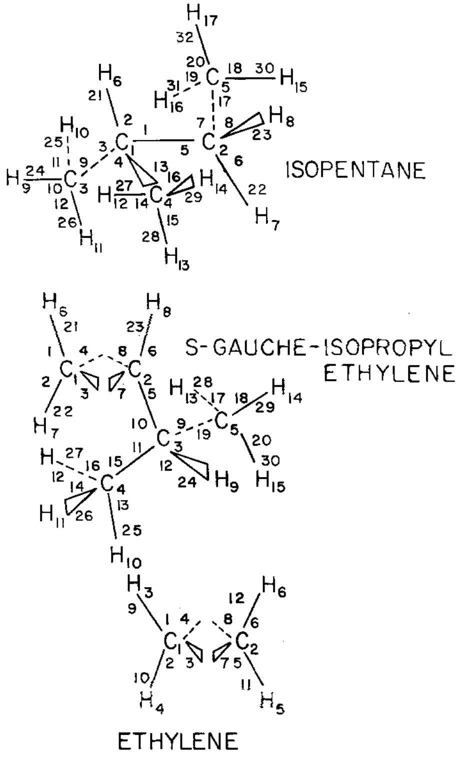

Fig. 1.9

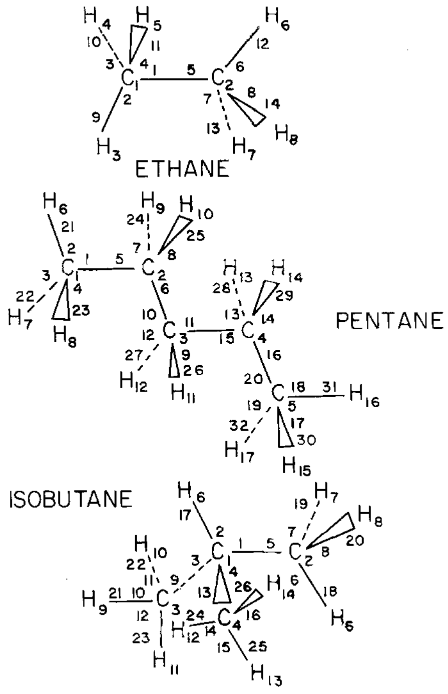

Fig. 1.10

and

$$\langle p(i) | p(j) \rangle = -\tfrac{1}{2}, \qquad i \neq j \tag{19}$$

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

$$l = (s)\cos Q - (p)\sin Q\,, \tag{20}$$

$$r = (s)\sin Q + (p)\cos Q\,. \tag{21}$$

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

$$t(i) = (r + p(i)\sqrt{2})\sqrt{3}/3\,. \tag{22}$$

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

$$l = 0.6736(s) - 0.7391(p) \tag{23}$$

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.

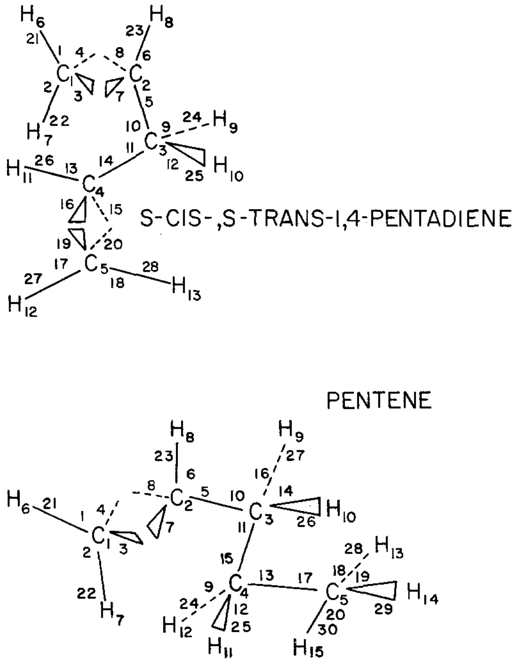

Fig. 1.11

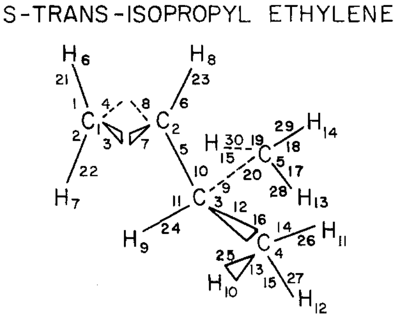

Fig. 1.12

The expression for l implies the expression

$$t(i) = 0.4267(s) + 0.3889(p) + 0.5773\, p(i) \tag{24}$$

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°.

2.4.2. 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

$$L(i) = a(i) \cdot (x) + b(i) \cdot (y)\,, \qquad i = 1, 2, 3\,. \tag{25}$$

The pair of Eqs. (18) and (19) can be expressed as

$$p(i) = -(x) \sin(W + (i-1)\,\pi/3) + (y) \cos(W + (i-1)\,\pi/3) \tag{26}$$

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

$$d/dW[\langle L(i)|p(i)\rangle]=0 \tag{27}$$

which yields an angle $W(i)$ given by

$$\tan(W(i)) = -a(i)/b(i)\,. \tag{28}$$

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

$$W=\sum_i W(i)\,\langle L(i)|p(i)\rangle \Big/ \sum_i \langle L(i)|p(i)\rangle\,. \tag{29}$$

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 Eq. (26).

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.

3. Energy Localized MO's

3.1. Introduction

Energy localized MO's (LMO's) exploit the invariance of the MO equations to unitary transformations, as was pointed out by Fock [14]. The LMO's were themselves proposed later by Lennard-Jones and Pople [28], 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 analogues to the bonds and lone pairs of chemical intuition, as had been hoped all along.

3.2. Localization Equations

At first, the formal discussion of localized orbitals was confined to equivalent MO's, those which carry the regular representation 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)

$$D=\sum_u [u^2|u^2] \tag{30}$$

over all occupied MO's, where

$$[u|v]=\int\!\!\int d^3x\,d^3z\,u(x)\,v(z)/|x-z|\,. \tag{31}$$

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"

$$[u^2-v^2|uv]=0 \tag{32}$$

as the central features for the LMO determinations. This was done by series of successive 2 × 2 transformations rather like the Jacobi diagonalization method. 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 [29].

3.3. 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 [30–32] which used the Mulliken approximation for electron repulsion integrals; and all valence electron localizations using CNDO [33] and INDO [34].

One might wonder what differences obtain between the last two approximations. It has been shown [34] 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.

3.4. 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 [30], 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".

Table 1. 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
3	6984	6984	6980	104	54	76
4	140	140	157	104	54	76
5	8	57	84	7069	7070	7069
6	172	173	176	104	54	76
7	172	173	176	104	54	76
8	-462	-461	-486	104	54	76
9	-123	-123	-140	-5	-54	-79
10	7115	7115	7114	-5	-54	-79
11	-123	-123	-140	-5	-54	-79
12	-158	-159	-159	-5	-54	-79
13	-158	-159	-159	-5	-54	-79
14	441	441	464	-5	-54	-79

We adopt the following procedure:

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 detail of this approach have been given elsewhere [30]. The starting localized MO's (SMO's) obtained in this way turn out to be close approximations to the exact LMO's. This is shown in Table 1 for ethane, which lists the coefficients of the two (CH and CC) orbitals in the hybrid basis. The hybrid basis orbitals are the row labels and are taken from the previous Fig. 1, while here and elsewhere the actual coefficients are obtained from those in the tables by multiplying times 10^{-4}. The degree of approximation is typical.

3.5. 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 [36–38] with energy localization. These authors applied the perturbation theory of Coulson and Longuet-Higgins [39–42] to some simple paraffins by using a hybrid basis analagous 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 1, 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" which will be applied later.
2. The PMO's anticipate some of the dependences on relative bond orientations, types and distances [36–38] that play a great role in the analysis.

3.6. *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 [43], which is closely related)

$$(F+L)\,|n\rangle = \gamma_{nn}|n\rangle\,, \qquad n=1,\ldots,N \tag{33}$$

where F is the Fock operator,

$$L=\sum_{i\neq k}^{N}\sum^{N}|i\rangle\,(C_{ik}-\gamma_{ik})\,\langle k|\,, \tag{34}$$

with

$$\gamma_{ik} = \langle i | F | k \rangle \tag{35}$$

and

$$C_{ik} = |\langle ii - kk | ik \rangle| . \tag{36}$$

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 except for ethane, all attempts at iterative solution of Eq. (34) failed: the C_{ik}, though small initially (for propane the largest were around 0.0025 a.u.), did not become successively smaller.

3.7. The LCAO *Expansions*

The complete LCAO LMO's for each molecule are presented in Table 2. The expansion coefficients are given in the previously described hybrid basis with units of $(\text{a.u.})^{-3/2} \cdot 10^4$. Expansions in a Slater orbital basis will be provided upon request. The rows are labeled by the numbers assigned the hybrids in Fig. 1. The LMO's are also labeled by numbers and these form the column headings. The detailed discussion of these LMO's will be given later in terms of molecule-independent (MI) coefficients.

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 a first order method of energy localization [35] toward the end of the work, the usual Edmiston-Ruedenberg scheme was used. This normally took fifteen minutes or less on an IBM 360/50. but needed more than thirty minutes for some of the larger or triply bonded molecules.

4. Molecule Invariant LMO Fragments

4.1. Local Delocalization and LMO *Fragments*

It is clear from the LCAO expansions in the hybrid basis (Table 2) 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 [36–38], 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 [30–32], and the origins of rotation barriers [44–47] as well as the systematic interpretation of bond dipole moments and energies [18] 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

Table 2. LMO expansion coefficients

METHANE

	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

ETHANE

	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

ECLIPSED ETHANE

	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

ETHYLENE

	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

ACETYLENE

	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

PROPANE

	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

PROPENE

	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

S-CIS-PROPENE

	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	265	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	126	258	98	129	258	-14	-297	-129	7133
18	-18	263	-3	101	-393	-2	224	7092	-123

PROPYNE

	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

BUTANE

	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

ISOBUTANE

	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	105
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	-142
11	496	-148	-37	174	-68	-16	176	-13	-141	-149	66	144	-6977
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	-331
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	-162	-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	-14
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

BUTENE

	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	175	-36	-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

S-GAUCHE-1-BUTENE

	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	-112	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	-23	-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

BUTADIENE

	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	-375	-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	7002	-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	-505
21	7077	0	298	-85	0	24	-82	-85	521	109	281
22	-271	-10	-522	17	10	-3	31	17	-271	19	-7050

S-CIS-BUTENE

	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	-423	-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

ISOBUTENE

	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

2-BUTENE

	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	42	-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	525	-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	126	-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	-2
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

BUTYNE

	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	-59	216	-27	7066	274	-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	-25	89	286	-112	223	264
7	26	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	-6958	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	-46	-14	-10
16	-159	16	456	-133	6998	-158	-135	-32	-84	-14	-10
17	483	-31	-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

2-BUTYNE

	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	138	-344	-22	-64
18	18	-137	36	-64	120	-344	138	6964	462	-22	36
19	344	-137	-64	36	120	462	6964	137	-16	-22	36
20	465	-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

BUTADIYNE

	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

VINYL ACETYLENE

	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	-7015	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	-252	-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

PENTANE

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	-68	339	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	-126	-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	56	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	-35	-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	-435	-145	-8	-20	-121	3	-151	8	-12	-3	-10	7118	-11	-2	13	132

ISOPENTANE

	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	45	-98	-98	-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	98	-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	91	150	23
12	-16	-11	165	-161	-138	463	-12	29	-27	6990	-136	-15	7	7	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	6997	-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	1	-5	59	7067	90	-107	13
18	-6972	46	-491	-138	29	60	150	-176	4	16	-9	6	172	-164	-65	-179
19	-131	-9	172	27	81	-12	138	-166	-10	-38	-37	11	91	-6991	-15	463
20	-136	-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	-19
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	-69
28	13	129	-138	17	-21	-439	-9	-1	7119	2	-4	-130	21	-11	-138	-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

S-TRANS-ISOPROPYL ETHYLENE

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	311	6	-20	-7001	-6	-325	-223	-48	-20	385	590	-96	-48	-96	385
2	7014	0	14	-273	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	505	-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

S-GAUCHE-ISOPROPYL ETHYLENE

	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	45	-5	-566	48
2	-325	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	-7254	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	152	-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	-231	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	-42	-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	38	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	161	-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	-5	-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

PENTENE

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
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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	-120	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	-87	106
12	192	-71	131	-488	-6	-168	117	-431	137	-6937	-185	-166	-28	-21	-6
13	-65	-90	-11	-65	-8	60	87	-60	7033	-107	314	-107	8	-179	-8
14	-35	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	27	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	5	-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	15	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	103	59	-163	-20	-73	131	-73	-135	15	135

ISOPRENE

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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	-299	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	-15	-7074	22	82
28	-9	-68	21	-526	7046	280	68	-9	-21	7	-42	272	-1	-30

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

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
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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

PENTYNE

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
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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
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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	167	-15	20	-76	126	18	-162	134	7131	-444	76

VINYL ETHYNYL ETHANE

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2	8	350	-9	-2	-8	-11	-7230	37	349	-376	-11	-28	37	28	-379	35
3	79	284	7	-13	-73	-102	7	609	-43	63	54	37	-314	191	-7118	-108
4	0	284	58	-13	58	-56	-19	-312	7053	12	-33	-3	-90	-60	23	606
5	-24	302	-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	-6936	-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	109	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

ISOPROPYL ACETYLENE

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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	-723	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	-99	-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	-491	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

1,4-PENTADIYNE

	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	-45	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

VINYL ETHYNYL METHANE

	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	-7033
25	-9	-7015	-133	-9	-303	-273	-34	34	19	0	-129	-112	-523
26	0	780	-73	0	503	7072	85	-85	1	132	-71	-56	294

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 catalogued 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 were not explicitly covered by this work, close estimates (to within a few percent) were 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.

4.2. 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 2) 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 2), 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.

4.3. 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<) denoted by CA;
(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 classified according to their "geminal character"

(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), denoted by CQ.

Finally, the carbon hybrids will be characterized by what kind of bond lies in the coplanar position(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. CMH = single bond between methanic carbon and hydrogen.
2. CPH = single bond between primary alkyl carbon and hydrogen.
3. CSH = single bond between secondary alkyl carbon and hydrogen.
4. CTH = single bond between tertiary alkyl carbon and hydrogen.
5. CPVH = single bond between primary vinyl carbon and hydrogen.
6. CSVH = single bond between secondary vinyl carbon and hydrogen.
7. CEH = single bond between primary ethynyl carbon and hydrogen.
8. CPCP = single bond between two primary alkyl carbons.
9. CPCS = single bond between primary and secondary alkyl carbons.
10. CPCT = single bond between primary and tertiary alkyl carbons.
11. CPCQ = single bond between primary and quaternary alkyl carbons.
12. CPCSV = single bond between primary alkyl and secondary vinyl carbons.
13. CPCTV = single bond between primary alkyl and tertiary vinyl carbons.
14. CPCE = single bond between primary alkyl and secondary ethynyl carbons.
15. CSCS = single bond between two secondary alkyl carbons.
16. CSCT = single bond between secondary and tertiary alkyl carbons.
17. CSCQ = single bond between secondary and quaternary alkyl carbons.
18. CSCSV = single bond between secondary alkyl and secondary vinyl carbons.
19. CSCTV = single bond between secondary alkyl and tertiary vinyl carbons.
20. CSCE = single bond between secondary alkyl and secondary ethynyl carbons.
21. CTCT = single bond between two tertiary alkyl carbons.
22. CTCQ = single bond between tertiary and quaternary alkyl carbons.
23. CTCSV = single bond between tertiary alkyl and secondary vinyl carbons.
24. CTCTV = single bond between tertiary alkyl and tertiary vinyl carbons.
25. CTCE = single bond between tertiary alkyl and secondary ethynyl carbons.
26. CQCQ = single bond between two quaternary alkyl carbons.
27. CQCSV = single bond between quaternary alkyl and secondary vinyl carbons.

28. CQCTV = single bond between quaternary alkyl and tertiary vinyl carbons.
29. CQCE = single bond betwee quaternary alkyl and secondary ethynyl carbons.
30. CSVCSV = single bond between two secondary vinyl carbons.
31. CSVCTV = single bond between secondary and tertiary vinyl carbons.
32. CSVCE = single bond between secondary vinyl and secondary ethynyl carbons.
33. CTVCTV = single bond between two tertiary vinyl carbons.
34. CTVCE = single bond between tertiary vinyl and secondary ethynyl carbons.
35. CECE = single bond between two secondary ethynyl carbons.
36. BCPVCPV = one of the double banana bonds between two primary vinyl carbons.
37. BCPVCSV = one of the double banana bonds between primary and secondary vinyl carbons.
38. BCPVCTV = one of the double banana bonds between primary and tertiary vinyl carbons.
39. BCSVCSV = one of the double banana bonds between two secondary vinyl carbons.
40. BCSVCTV = one of the double banana bonds between secondary and tertiary vinyl carbons.
41. BCTVCTV = one of the double banana bonds between two tertiary vinyl carbons.
42. BCPECPE = one of the triple banana bonds between two primary ethynyl carbons.
43. BCPECSE = one of the triple banana bonds between primary and secondary ethynyl carbons.
44. 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 *near* hybrid and the *far* hybrid, according to their position relative to the bond fragment of the LMO.

5. MI Bond Fragment Coefficients

5.1. General Characteristics

All bond fragment hybrid coefficients have values near those of the ethane CPCP bond fragment, 0.7070, and are an order of magnitude greater than those describing any other fragment types. The bond fragment coefficients are also the only ones that always have the same sign. Coefficient deviations from the ethane CPCP value depend mostly on (1) whether the atoms involved are carbon or hydrogen, and (2) the geminal character of the carbon atoms involved. Generally smaller coefficient variations are transmitted in *planes* including the bond fragment and those fragments lying cis or trans to it. We term the latter fragments *conjugate fragments*. The variations induced in these planes are determined by (1) the conjugate fragment nature and orientation (relative to the bond fragment), and (2) a partially steric effect involving *certain* bond region chains which lie beyond the conjugate fragment and in the aforementioned plane. This last effect is only partially steric because it transmits only through the plane.

5.2. *Tabulation*

The bond fragment coefficients for any acyclic hydrocarbon can be calculated from Table 3. We shall illustrate this explicitly for a CTCE bond fragment. Coefficients for other bond fragments are calculated in the same way.

The numbers labeled "Single Bond Fragments" in the table characterize all *single* bond fragments having (1) no conjugate fragments, or (2) CH conjugate fragments in *trans* positions. The tabulated numbers describe the fragment relative to the homopolar CPCP bond fragment in ethane. To pursue our example of CTCE, consider the numbers that appear in the CTX rows and X = CE column. These are -145 and 10. Thus, the CT and CE bond fragment coefficients for any CTCE bond region with a trans CH conjugate fragment are given by,

$$\mathrm{CT} = \mathrm{CP(ethane)} - 145 = 6925$$

and

$$\mathrm{CE} = \mathrm{CP(ethane)} + 10 = 7080\,.$$

Thus, the sp^3 hybrid coefficient is 0.6925 and sp coefficient is 0.7080. In just the same way, the numbers labeled "Banana Bond Fragments" characterize all double and triple bond regions relative to the CPCP bond fragment in ethane.

Conjugate fragment influences on single and double bond fragments are shown in the two blocks appropriately labeled in Table 3. The row label – in the block for single bonds refers to all single bond fragments, i.e. the influence of a given conjugate fragment is independent of the bond fragment. The row label = in the block for double bonds has a similar meaning, but now refers to double bond fragments. The Ω denotes the conjugate fragments. For example, if we wanted the bond fragment coefficients for a CTCE bond with a CC bond in a *trans* position, we would add the entries in the – rows, $\Omega = C$ column to our last set of numbers, i.e.

$$\mathrm{CT} = 6925 - 10 = 6915$$

and

$$\mathrm{CE} = 7080 + 20 = 7100\,.$$

Thus, conjugate effects are simply additive. If there were simultaneously a double banana hybrid in a *cis* position, we would have,

$$\mathrm{CT} = 6915 + 0 = 6915$$

and

$$\mathrm{CE} = 7100 - 15 = 7085$$

for our CTCE bond fragment coefficients.

Conjugate fragment influences on triple bond fragments are slightly different, but are calculated in the same way. As can be seen from the table, there is a greater sensitivity to the type of the conjugate fragment, but *cis* and *trans* conjugate fragments induce the same variations.

Table 3. LMO bond fragment coefficients

SINGLE BOND FRAGMENTS

X =	CP	CS	CT	CQ	CSV	CTV	CE	H	CMH	CPVH
CP	0	-15	-30	-45	-30	-40	-85	-85	-35	-50
X	0	-25	-50	-65	-40	-60	50	45	30	-25
CS		-40	-60	-75	-55	-75	-110	-125		
X		-40	-60	-75	-55	-95	40	50		
CT			-80	-100	-75	-95	-145	-160		
X			-80	-100	-70	-110	10	50		
CQ				-120	-95	-115	-180	-80		
X				-120	-85	-125	-20	-10		
CSV					-65	-80	-130	160		
X					-65	-80	25	-195		
CTV						-105	-155			
X						-105	0			
CE							-30			
X							-30			

CONJUGATE FRAGMENT INFLUENCES ON SINGLE BOND FRAGMENTS

Ω =	VH	C	2	3	H*	VH*	C*	2*	3*
–	0	-10	-15	-15	0	0	0	0	-10
	0	20	-10	-25	0	15	10	-15	-25

BANANA BOND FRAGMENTS

X =	CPV	CSV	CTV
BCPV	-15	-10	-10
X	-15	-60	-105
BCSV		-60	-60
X		-60	-105
BCTV			-105
X			-105

X =	CPE	CSE
BCPE	-10	10
X	-10	-70
BCSE		-50
X		-50

CONJUGATE FRAGMENT INFLUENCES ON DOUBLE BANANA BOND FRAGMENTS

Ω =	VH	C	2	3	H*	VH*	C*	2*	3*
–	0	-25	-25	-15	0	0	0	0	-15
	0	35	-25	-25	0	15	10	-15	-30

CONJUGATE FRAGMENT INFLUENCES ON TRIPLE BANANA BOND FRAGMENTS

Ω,Ω* =	CPH	CSH	CTH	CSVH	CSC	CTC	CQC	2	3
BCSE	0	15	30	-40	-30	-15	0	-40	-15
CE	0	-10	-20	60	50	30	10	10	35

PARTLY STERIC INFLUENCES

CONFORMATION =	CCT	CCC	CCP	CPL	TPL
C	0	20	20	15	15
X	-15	-30	-40	-20	-10

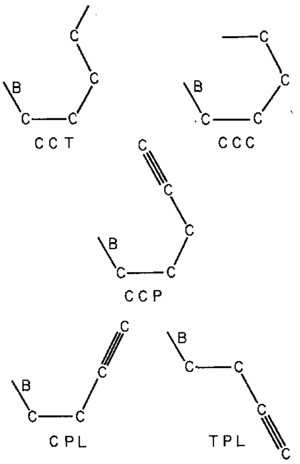

Fig. 2. Conformations transmitting partially steric influences

Conformations for the partially steric influences shown in the table are defined on Fig. 2. The *B* labels the bond fragment. The effects are simply additive and are the same for all bond fragments. For example, suppose the CC conjugate fragment trans to our CTCE bond fragment gives rise to the conformation TPL. We, therefore, take the numbers from column TPL and add them to our last set of coefficients, viz.

$$\mathrm{CT} = 6915 + 15 = 6930$$

and

$$\mathrm{CE} = 7085 - 10 = 7075\,.$$

6. MI Geminal Fragment Coefficients

6.1. General Characteristics

Geminal fragment hybrid coefficient magnitudes are only about 2% as large as those of the bond fragments, and show diverse relative magnitudes and signs. From our experience with bond fragments, we might expect to find classes of CH and CC geminal fragment coefficients that are influenced by the geminal character of their carbon atoms and by the vicinal fragments lying coplanar with the geminal fragment. This is indeed the case. However, a geminal fragment cannot be totally separated from its adjacent bond fragment in the sense that most of the factors which were needed to characterize the bond fragment coefficients have to be repeated to characterize the geminal fragment coefficients. Thus, many combinations of labels are possible, and all are needed to catalog these coefficients.

The greatest geminal fragment coefficient dependences are upon (1) the geminal character of the so-called *pivot* carbon atom (the carbon atom shared by the bond and geminal fragments), and (2) the type and geminal character of the *other* bond fragment and geminal fragment atoms. Superimposed are usually smaller coefficient variations induced by (1) the conjugate fragments, and (2) the fragments lying vicinal and coplanar with the geminal fragment itself. There are also partially steric effects from certain bond region chains which are coplanar with the geminal fragment and lie beyond the *conjugate* fragment. However, we find these to be important only when the geminal fragment is primary vinyl CH.

6.2. *Tabulation*

As we have pointed out, there are many factors to influence the geminal fragment coefficients, and these can lead to a variety of diverse situations. Thus, to make our tabulation compact, we have used slightly different methods for the cases when the pivot carbon is (1) alkyl, (2) vinyl, (3) ethynyl.

6.2.1. Alkyl Pivot Carbon

All alkyl carbon geminal fragment coefficients can be calculated from Table 4. Reference coefficients for secondary pivot carbons are shown in the first four columns and first eight rows of the block labeled "Alkyl Carbon Reference Coefficients". For this case, the row labels describe secondary geminal fragments having either (1) CH fragments in trans vicinal positions, or (2) no coplanar vicinal fragments. The column labels describe the adjacent bond fragments, which have either (1) CH conjugate fragments in trans positions, or (2) no conjugate fragments. For example, a CSCP geminal fragment (with a CH fragment lying *trans*) adjacent to a CSCSV bond fragment (with trans CH conjugate fragments) has a coefficient of -115 for the sp^3 pivot carbon hybrid and 60 for the primary carbon sp^3 hybrid.

The remaining column labels describe what happens to the secondary geminal fragment coefficients when the *pivot* carbon is changed from secondary to either methyl (M), primary (P), tertiary (T), or quaternary (Q). For example, to obtain coefficients for a CTCP geminal fragment (with CH fragments trans) adjacent to a CTCSV bond fragment (with trans CH conjugate fragments), we must add the third and fourth rows of column T to the third and fourth rows of column CSCSV, i.e.,

$$\mathrm{CT} = -115 + 20 = -95$$

$$\mathrm{CP} = 60 - 5 = 55\,.$$

The block labeled "Far Carbon Atom Influences" describes the coefficient variations which occur when the pivot carbon in the previous block is fixed and the other carbon atoms in the bond or geminal fragment are changed. The first two columns refer to the bond fragment far carbon, and the last two columns refer to the geminal fragment far carbon. In both cases the CA and CV stand for alkyl and vinyl carbons, respectively. The row labels complete the specification of the far carbon atom. For example, the CT rows of the bond fragment CV column label the far atom of the bond fragment as a tertiary vinyl carbon atom (CTV). To illustrate this, suppose we ask what happens to our geminal CTCP coefficients when the geminal far carbon becomes a secondary alkyl and the bond far carbon

Table 4. Alkyl carbon LMO geminal fragment coefficients

PIVOT ALKYL CARBON REFERENCE COEFFICIENTS

	CSH	CSCP	CSCSV	CSCE	H	P	T	Q
CS	170	140	75	160	-75	-35	40	
H	-135	-25	-25	0	35	20	-5	
CS	-85	-60	-115	-50		-25	20	40
CP	0	65	60	95		10	-5	-10
CS	-25	-15	-200	-25		-25	20	40
CSV	25	90	80	110		10	-5	-10
CS	-150	-115	-160	-125		-25	20	40
CE	0	115	105	140		10	-5	-10

FAR CARBON ATOM INFLUENCES

	BOND		GEMINAL	
	CA	CV	CA	CV
CS	-15		-20	
	0		-5	
CT	-30	-10	-40	-30
	0	0	-10	0
CQ	-45		-60	
	0		-15	

			– Ω –						
PIVOT	BOND	GEMINAL	C	2	3	H*	C*	2*	3*
CP	H	CA	-40	-100	-40	-135	-70	-35	-45
			-10	-25	-10	-40	-30	-5	5
CA[a]	≠CV	≠CV	0	0	0	0	-35	0	0
			-10	-10	10	0	5	30	30
CA	CV	≠CV	0	0	0	-90	0	0	0
			0	0	0	0	0	0	0
CA	≠CV	CV	-40	-100	-40	-135	-70	-35	-45
			-10	-25	-10	-40	-30	-5	5
CA[b]	CV	CV	0	0	0	90	20	20	0
			0	0	0	0	-10	0	0

[a] Except case in first row
[b] Cannot be CP

					–ω–				
PIVOT	BOND	GEMINAL	C	2	3	H*	C*	2*	3*
CA	≠CV	ALL	60	60	0	0	-25	10	0
			-10	-10	10	0	-5	20	30
CA	CV	ALL	40	120	0	150	40	35	0
			-10	-5	0	-10	-10	5	0

becomes a tertiary vinyl. The changes are described by adding the first two rows of column three (the variations induced by the geminal far atom change) and the second two rows of column two (the variations induced by the bond far atom change) to our previous coefficients, i.e.,

$$\mathrm{CT} = -95 - 20 - 10 = -125$$
$$\mathrm{CS} = 55 - 5 + 0 = 50\,.$$

The block labeled "Ω" describes what happens when (1) conjugate fragments are introduced or (2) the trans CH conjugate fragments are changed. The first column label characterizes the pivot atom. The next two column labels characterize the far atoms of the bond and geminal fragments, respectively. Remaining column labels classify the conjugate fragment Ω. The row labels CP, CA, CV and H refer to primary alkyl carbons, all alkyl carbons, all vinyl carbons, and hydrogen, respectively. The notation $\neq$ CV means that the atom in question may not be a vinyl carbon. As an example, suppose our CTCS geminal fragment adjacent to a CTCTV bond fragment now has a CH bond lying cis. The row groups 5 and 6 of the block characterize this combination of bond and geminal fragment far carbons. Thus we proceed to column H* to obtain our coefficients

$$\mathrm{CT} = -125 - 90 = -215$$
$$\mathrm{CS} = 50 + 0 = 50\,.$$

The only remaining influences on alkyl carbon geminal fragment coefficients arise from vicinal fragments lying coplanar with the geminal fragment itself. These are labeled by ω and appear as such in the table. The method of classification is the same as for the Ω (conjugate fragment) influences, but here the only far atom dependence is a CV or $\neq$ CV in the bond fragment. For example, if a CC single bond lay *cis* to our CTCS geminal fragment, the coefficients would be calculated from the C* column of rows 3 and 4, i.e.

$$\mathrm{CT} = -215 + 40 = -175$$
$$\mathrm{CS} = 50 - 10 = 40\,.$$

6.2.2. Vinyl Pivot Carbon

These coefficients are given in Table 5. Since the tabulation is very similar to the one just discussed, we shall concentrate on the differences between the two schemes. First of all, notice that the character of the pivot carbon is incompletely specified in the first 10 rows and the first 5 columns of the block labeled "Vinyl Carbon Reference Coefficients". This is done because, taken together, the row and column labels always completely specify the pivot carbon. For example, taken together the labels for the first 2 rows (geminal fragment) and the first column (bond fragment) can only describe a primary vinyl CH (CPVH) geminal fragment adjacent to a primary vinyl CH (CPVH) bond fragment. That is, the

Table 5. Vinyl carbon LMO geminal fragment coefficients

PIVOT VINYL CARBON REFERENCE COEFFICIENTS

	CVH	CVCP	CVCSV	CVCTV	CVCE	BCPVCPV	BCSVCPV	BCTVCPV
CV	290	275	240	275	290	340	375	
H	-255	-175	-155	-165	-150	15	-10	
CV	80	105	75	65	115		200	220
CP	-150	-65	-50	-50	-40		90	75
CV	75	95	-100	-110	-65		175	170
CSV	-60	-15	-30	-30	-20		125	120
CV	85	105	-90	-100	-55		185	180
CTV	-60	-15	-30	-30	-20		135	130
CV	25	35	-10	-20	25		145	85
CE	-110	-65	-75	-75	-65		90	40
BCPV	-240					-15		
CPV	-110					-15		
BCSV	-235	-220	-200	-210	-230		50	
CPV	-95	-55	-50	-50	-30		-60	
BCTV		-200	-180	-190	-210			115
CPV		-45	-40	-40	-20			-105

FAR CARBON ATOM INFLUENCES

	CH		CC		BCV	
	BOND	GEMINAL	BOND	GEMINAL	BOND	GEMINAL
CS	-10	20	-15	-20	-15	20
	-10	0	0	0	-10	5
CT	-20	40	-30	-40	-30	40
	-20	0	0	0	-20	10
CQ	-30	60	-45	-60	-45	60
	-30	0	0	0	-30	15
CSV	-25	35	30	-20	-20	-20
	-10	0	-15	-20	-5	-5
CTV	-50	70	60	-40	-40	-40
	-20	0	-30	-40	-10	-10

PARTLY STERIC EFFECTS FOR PRIMARY VINYL CH GEMINAL FRAGMENTS

	CCT	CCC	CCP	CPL	TPL
CPV	45	45	45	25	0
H	-30	-30	-30	-20	-15

- Ω -

PIVOT	BOND	GEMINAL	C	2	3	H*	C*	2*	3*
CPV	H	H	-10				30		
			-15				-30		
CSV	H	C	-30	-30	0	0	0	0	0
			-15	-15	0	0	0	0	0
CSV	C	H	15	15	-10	15	15	15	10
			0	0	0	0	0	0	0
CTV	C	C	-30	-30	0	0	-15	-30	0
			-15	-15	0	0	-15	-15	0
CPV	H	BCV	-20				25		
			-20				0		
CV	H,C	BCV	0	0	0	0	0	0	0
			0	0	0	0	0	0	0
CV	BCV	H	0	0	0	0	0	0	0
			0	0	0	0	0	0	0
CV	BCV	C	-60	-60	0	-30	-60	-60	0
			-30	-30	0	-10	-30	-30	0
CV	BCV	BCV	0	0	0	0	0	0	0
			0	0	0	0	0	0	0

- ω -

PIVOT	BOND	GEMINAL	C	2	3	H*	C*	2*	3*
CSV[a]	H	C	-10	-10	20	0	-10	-10	20
			0	0	0	0	0	0	0
CSV	C	H	40	40	0	0	0	0	0
			-10	-10	30	0	0	0	30
CTV	C	C	-10	-10	20	0	-10	-10	20
			0	0	0	0	0	0	0
CPV	H	BCV	0	0	0	0	0	0	0
			0	0	0	0	0	0	0
CSV	H	BCV	10	10	10	10	10	10	10
			-10	-10	20	-10	-10	-10	20
CV	C	BCV	40	40	0	0	40	40	0
			-10	-10	30	0	-10	-10	30
CPV	BCV	H	20				-35		
			-5				0		
CV[b]	BCV	ALL	0	0	0	0	0	0	0
			0	0	0	0	0	0	0

---

[a] The CPV (pivot), H(bond), H(geminal) is covered by the first row of block Ω

[b] Except for the case in the preceding row.

doubly bonded vinyl pivot carbon is singly bonded to 2 hydrogens and thus must be a primary vinyl carbon. Similarly, the first and second pairs of row labels combine with the second column label to describe secondary (CSV) and tertiary (CTV) vinyl carbons, respectively. On the other hand, the pivot carbon is completely characterized in the last three pairs of rows and last three colums in the block: This also serves to characterize it when these labels are combined with those of the first five columns and last three pairs of rows, respectively. For example, a vinyl CH geminal fragment (the CVH rows in the block) adjacent to a banana bond fragment between two primary vinyl carbon atoms (the BCPVCPV column in the block) can only be a primary vinyl CH fragment (CPVH).

The coefficient variations induced by the far carbon are shown in the block labeled "Far Carbon Atom Influences". There are two far carbons to consider, the far carbon of the bond fragment and the far carbon of the geminal fragment. The two cases are distinguished by the "Bond" and "Geminal" in the second row of column labels. Furthermore, the influence of the far carbon is different depending on whether the *adjacent* fragment (bond or geminal) containing the pivot atom is a CH, single CC, or banana CC. The first row of column labels classifies this. Finally, the influence of far alkyl carbons and far vinyl carbons differs. This is described by the row labels.

We shall now consider several examples. First, suppose we have a CSVCP geminal fragment adjacent to a CSVH bond fragment. The coefficients describing these are,

$$\mathrm{CSV} = 80$$

$$\mathrm{CP} = -150$$

as taken from the reference coefficient block. If the far carbon of the geminal fragment is changed to CS, the new coefficients are calculated by adding the numbers in the first two rows (since the new far carbon is CS) of Column 4 (since the far carbon of a geminal CC fragment has been changed) in the far carbon influences block, i.e.,

$$\mathrm{CSV} = 80 - 20 = 60$$

$$\mathrm{CS} = -150 + 0 = -150\,.$$

Now suppose we have a CTVCP geminal fragment adjacent to a CTVCSV bond fragment so that

$$\mathrm{CTV} = 75$$

$$\mathrm{CP} = -50\,.$$

If the CSV of the bond fragment becomes CTV, we find the coefficients to be

$$\mathrm{CTV} = 75 + 60 = 135$$

$$\mathrm{CP} = -50 - 30 = -80$$

from rows 9 and 10, Column 3 of the far atom influences. Next, suppose that a CTVCS geminal fragment is adjacent to a BCTVCSV bond fragment. From the set of reference coefficients we find for a CTVCP geminal fragment adjacent to

Table 6. Ethynyl carbon LMO geminal fragment coefficients

PIVOT ETHYNYL CARBON REFERENCE COEFFICIENTS

	CEH	CECP	CECSV	CECE	BCPECE	BCSECE		BCECE
BCE	5	-10	140	-5	-10	20	CE	360
CPE	-335	-290	-290	-250	-10	-15	H	-30
BCE	5	-50	120	-25	-10	20	CE	265
CSE	-335	-330	-210	-270	25	20	CP	40
							CE	170
							CSV	0
							CE	210
							CE	70

– Ω –

PIVOT	BOND	GEMINAL	C	2	3	H*	C*	2*	3*
CE	BCE	H	30	-10	15	0	30	-10	15
			10	0	0	0	10	0	0
CE	BCE	C	-70	140	0	0	-70	140	0
			-40	70	0	0	-40	70	0
CE	H,C,BCE	BCE	0	0	0	0	0	0	0
			0	0	0	0	0	0	0

FAR CARBON ATOM INFLUENCES

	BOND		GEMINAL	
	CA	CV	CA	CV
CS	-30		25	
	0		15	
CT	-60	-15	50	20
	0	0	30	0
CQ	-90		75	
	0		45	

– ω –

PIVOT	BOND	GEMINAL	C	2	3	H*	C*	2*	3*
CE	H	BCE	-20	0	-15	0	-20	0	-15
			-10	0	0	0	-10	0	0
CE	C	BCE	130	-210	70	0	130	-210	70
			0	0	40	0	0	0	40
CE	BCE	H,C,BCE	0	0	0	0	0	0	0
			0	0	0	0	0	0	0

a BCTVCPV bond fragment

$$\mathrm{CTV} = 220$$
$$\mathrm{CP} = 75\,.$$

By using rows 7 and 8 of Column 5 in the far atom influences, we find the effect of changing CPV to CSV in the bond fragment to be

$$\mathrm{CTV} = 200$$
$$\mathrm{CP} = 70\,.$$

Finally, we find the desired coefficients from rows 1 and 2, Column 4, in the far atom block

$$\mathrm{CTV} = 180$$
$$\mathrm{CS} = 70\,.$$

The primary vinyl CH geminal fragments are the only class for which significant partially steric influences are observed. These are listed in the block of the same name. The column labels of this block locate the coplanar bond chain relative to the *bond fragment*. The bond chain orientations are shown on the previous Fig. 2. For example, if a CPVH geminal fragment is adjacent to a CPVH bond fragment having CCT coplanar chains, its coefficients are

$$\mathrm{CPV} = 290 + 45 = 335$$
$$\mathrm{H} = -255 - 30 = -285\,.$$

The remaining 2 blocks of the table describe the influence of conjugate fragments, Ω, and the fragments lying vicinal and coplanar with the geminal fragment, ω. Apart from the different sensitivities as manifest by the greater number of rows in each block (relative to the alkyl pivot carbon case), the tabulation is the same as given for alkyl pivot carbons.

6.2.3. Ethynyl Pivot Carbon

The ethynyl pivot carbon reference coefficients are divided into 2 classes, (1) banana geminal fragments adjacent to single-bond and banana bond fragments, and (2) single-bond geminal fragments adjacent to banana bond fragments. These appear in the first and second blocks, respectively of Table 6. The row labels always characterize the geminal fragments and the column labels always characterize the bond fragments. Note that the character of the pivot carbon is usually incompletely specified. The reasons for this are as discussed in the vinyl pivot carbon section.

The remaining blocks are directly comparable to those given for alkyl pivot carbons. This being so, reference should be made to the alkyl pivot carbon section for examples which illustrate their application.

7. Vicinal Fragment Coefficients

7.1. Vicinal Groups and General Characteristics

As a class, vicinal fragment coefficients differ from those of geminal fragments in two ways. (1) Their nodal properties and magnitudes are much less varied, and (2) they are usually larger in magnitude. The latter is noteworthy since the vicinal positions are *farther* removed from the bond fragment, where most of the charge is concentrated.

The term "vicinal group" refers to the collection of vicinal fragments whose near hybrids (relative to the bond fragment) share the same carbon atom. Members of vicinal groups are classified as (1) *conjugate fragments*, those vicinal and coplanar with the bond fragment, or (2) *gauche fragments*, those vicinal and *noncoplanar* with the bond fragment. The character of the conjugate fragment will also be used to characterize the vicinal group itself. If the conjugate fragment is a *trans* primary alkyl CH fragment, then the vicinal group is a *trans* primary alkyl CH vicinal group. Note that this definition incorporates the relative orientation of the bond fragment and the vicinal group.

All vicinal fragment coefficients are largely determined by (1) the character of the vicinal group (or conjugate fragment character), and (2) the degree of unsaturation in the bond region *joining* the bond fragment and the vicinal group. Smaller coefficient variations accompany changes in the bond fragment atoms. The two coefficients of a given vicinal fragment have similar magnitudes, but opposite signs. In a particular vicinal group, the sign of the near (relative to the bond fragment) hybrid coefficient in the conjugate fragment is always the opposite of that in either (adjacent) gauche fragment. If the vicinal group character is *trans*, the coefficient of the near hybrid in the conjugate fragment is always negative and has a magnitude several times larger than those of the gauche fragments. In passing (from the *trans*) to the *cis* vicinal group, regular changes occur in *all* vicinal group coefficients. (1) The conjugate fragment coefficient magnitudes *decrease* by about 25%, (2) the *gauche* fragment coefficient magnitudes *increase* by 30–50% (and as a result generally become more than half as large as those of the conjugate fragment), and (3) *all* coefficient signs are reversed. In previous applications, these facts were found to be important for understanding the origins of hindered rotation [44–47].

7.2. Tabulation

Fragment coefficients are given in Tables 7 and 8 for all vicinal groups having *trans* character. Table 7 lists alkyl groups and Table 8 lists vinyl and ethynyl groups. Overall, there are three possibilities, corresponding to the vicinal group and bond fragment being joined by a single, double or triple bond region. These are designated by C–C, C=C and C≡C and consist of three, two and one fragment members, respectively. The C–C can occur for both the alkyl and vinyl groups, while C=C and C≡C necessarily occur for the vinyl and ethynyl groups, respectively. The dependences on the bond fragment type which occur in the C–C and C=C blocks are recorded by the column labels. The groups of rows specify the different vicinal groups, with the conjugate fragment given first. In

Table 7. Alkyl carbon LMO vicinal group coefficients

ALKYL CARBON VICINAL GROUP COEFFICIENTS

C–C

	CAH	CACA	CACV	CACE	CVH	CVC	BCVCV	BCECE	CIS	GC
CS	-440	-480	-465	-470	-400	-420	-490	-490	-90	20
H	430	430	415	415	390	390	480	490	-90	-15
CS	175	170	170	160	140	150	190	180	90	0
H	-160	-150	-150	-140	-130	-130	-180	-180	90	0
CS	110	125	125	115	95	90	130	120	90	0
C	-110	-110	-100	-95	-95	-85	-120	-120	90	0
CT	-320	-340	-300	-330	-265	-285	-335	-315	-90	0
CA	330	330	295	315	305	305	365	375	-90	0
CT	150	155	145	135	120	115	170	160	90	10
H	-150	-140	-140	-130	-125	-115	-160	-160	90	0
CT	90	105	105	95	70	65	120	110	90	10
C	-110	-110	-110	-100	-90	-80	-110	-110	90	0
CT	-310	-350	-310	-340	-270	-290	-340	-340	-30	15
CV	325	335	305	315	310	310	370	380	-60	-20
CT	150	155	145	135	120	115	170	160	50	0
H	-150	-140	-140	-130	-125	-115	-160	-160	30	0
CT	90	105	105	95	70	65	120	110	50	0
C	-110	-110	-110	-110	-90	-80	-110	-110	30	0
CT	-295	-310	-290	-300	-270	-275	-300	-300	-90	20
CE	300	290	275	280	290	290	320	330	-90	-15
CT	150	155	145	135	120	115	170	160	90	10
H	-150	-140	-140	-130	-125	-115	-160	-160	90	0
CT	90	105	105	95	70	65	120	110	90	10
C	-110	-110	-110	-110	-90	-80	-110	-110	90	0

the $C\equiv C$ block, all bond fragments have the same dependence and since each vicinal group has one member, the tabulation is quite simple. The fragment coefficients in each block are always given in the order (1) near hybrid, (2) far hybrid.

Consider the situation where a secondary CH vicinal group lies *trans* to a bond fragment between secondary and tertiary alkyl carbons. This case is covered by the CSH, CSH, CSC rows of the CACA column. Thus, the *(trans)* conjugate fragment coefficients are

$$\mathrm{CS} = -480$$

$$\mathrm{H} = 430$$

and the two gauche fragment coefficient sets are

$$\mathrm{CS} = 170$$

$$\mathrm{H} = -150$$

Table 8. Vinyl and ethynyl LMO vicinal group coefficients

VINYL CARBON VICINAL GROUP COEFFICIENTS

C–C

	CAH	CACA	CACV	CACE	CVH	CVC	BCVCV	BCECE	CIS	GC
CSV	-430	-475	-475	-455	-430	-455	-465	-455	-165	110
H	430	435	435	420	430	435	475	475	-130	-100
BCSV	130	130	130	130	130	130	160	160	75	-15
CV	-100	-100	-100	-100	-100	-100	-130	-140	90	-10
BCSV	-550	-595	-595	-575	-530	-575	-685	-630	-80	20
CV	540	530	530	515	540	540	660	650	-105	-30
BCSV	320	335	325	325	320	320	400	375	40	0
CV	-310	-310	-310	-300	-310	-310	-400	-385	50	-20
CSV	120	110	110	110	110	110	155	100	140	-35
H	-130	-110	-110	-110	-110	-110	-160	-140	120	40
BCE	-675	-735	-735	-715	-655	-715	-720	-750	-105	
CE	630	630	630	615	630	630	690	740	-95	
BCE	240	250	240	240	235	235	270	250	130	
CE	-230	-230	-230	-220	-230	-230	-255	-250	115	

C = C

	CVH	CVC	GC
CPV	-555	-575	30
H	525	515	-20
CPV	335	335	-100
H	-300	-285	80
CSV	-425	-435	30
CA	415	405	-10
CSV	300	300	-85
H	-300	-285	80

	CVH	CVC	GC
CSV	-380	-390	20
CV	385	375	-5
CSV	300	300	-85
H	-300	-285	80
CSV	-400	-410	30
CE	380	370	-10
CSV	300	300	-85
H	-320	-305	80

ETHYNYL CARBON VICINAL GROUPS

C ≡ C

	CEH	CECA	CECV	CECE
ALL BOND FRAGMENTS	-340	-265	-265	-250
	345	275	275	250

and

$$CS = 125$$

$$C = -110$$

for the CSH and CSC fragments, respectively.

Now, suppose we want the coefficients for a *primary* CH vicinal group lying trans to the bond fragment between secondary and tertiary alkyl carbons. These are obtained from the GC column. The numbers shown there are (1) subtracted from the row entries when the near carbon of the vicinal group *in the table* is bonded to *more* carbon atoms, and (2) added to the row entries when the near carbon is bonded to fewer carbon atoms. That is, the procedure is dictated by the "geminal character" (GC) of the near carbon. In our case the near carbon we are considering is primary, whereas the near carbon shown in the table is secondary, so we subtract the numbers in the VF column from our previous numbers, giving

$$\mathrm{CP} = -480 - 20 = -500$$

$$\mathrm{H} = 430 + 15 = 445$$

and

$$\mathrm{CP} = 170 - 0 = 170$$

$$\mathrm{H} = -150 - 0 = -150$$

for the primary CH group conjugate and gauche coefficients, respectively. Note that the CSC gauche fragment is not relevant to this calculation because there are no CPC vicinal fragments. To illustrate the other case, suppose a tertiary CH conjugate fragment lies *trans* to the same bond fragment. This time we have (since the near carbon of the vicinal group in the table is bonded to fewer carbon atoms),

$$\mathrm{CT} = -480 + 20 = -460$$

$$\mathrm{H} = 430 - 15 = 415$$

and

$$\mathrm{CT} = 125 - 0 = 125$$

$$\mathrm{C} = -110 - 0 = -110$$

for the *trans* and gauche fragment coefficients. Note that here the CSH gauche fragment coefficients are irrelevant.

The usage of the GC column is slightly different when the near carbon of the vicinal group is a vinyl carbon and the vicinal group and the bond fragment are joined by a single bond region (Table 8). Suppose we take a secondary vinyl CH group *trans* to a CSVCS bond fragment as an example. (The CSV carbon of the bond fragment is nearest to the vicinal group.) The coefficients are obtained from the C–C block, rows CSVH and BCSVCV, column CVC. They are,

$$\mathrm{CSV} = -455$$

$$\mathrm{H} = 435$$

for the conjugate fragment, and

$$\mathrm{BCSV} = 130$$

$$\mathrm{CV} = -100$$

for *both* gauche fragments. The necessarily different usage of the GC column can be appreciated by two observations: (1) a CPVH vicinal group cannot be joined to any bond fragment by a *single* bond region, and (2) tertiary vinyl CH fragments don't exist. Thus, the numbers in the GC column describe the coefficient changes that occur in passing from a CSVH vicinal group to a CTVC vicinal group. For example, the coefficients for a CTVCP vicinal group *trans* to a CSVCS bond fragment are calculated from those of the previous CSVH case as

$$\mathrm{CTV} = -455 + 110 = -345$$

$$\mathrm{CP} = 435 - 100 = 335$$

and

$$\mathrm{BCTV} = 130 - 15 = 115$$

$$\mathrm{CV} = -100 - 10 = -110\,.$$

Cis vicinal fragments in the CC blocks are obtained from the *trans* coefficients and the column labeled "*Cis*". For example, suppose we return to the situation where the secondary CH vicinal group lies *trans* to a bond fragment between secondary and tertiary alkyl carbons. We get the cis vicinal group coefficients by taking the numbers in the *Cis* column, adding them to the *magnitudes* of the *trans* group coefficients, and then reversing the signs relative to the original coefficients. Thus,

$$\mathrm{CS} = (480 - 90) = 390$$

$$\mathrm{H} = -(430 - 90) = -340$$

for the *cis* conjugate fragment and

$$\mathrm{CS} = -(170 + 90) = -260$$

$$\mathrm{H} = (150 + 90) = 240$$

and

$$\mathrm{CS} = -(170 + 90) = -260$$

$$\mathrm{C} = (110 + 90) = 200$$

for the two corresponding gauche fragments of the *cis* CSH vicinal group.

Cis fragments are explicitly listed in the C=C block because both vicinal fragments are necessarily coplanar with the bond fragment. The *trans* fragment will be used to characterize the vicinal group, and therefore its coefficients are always listed first. Consider a CSVCTV vicinal fragment trans to a CPVH bond fragment. This case is covered by the CSVCV and CSVH rows of the CVH column. The *trans* fragment coefficients are

$$\mathrm{CSV} = -380$$

$$\mathrm{CTV} = 385$$

and the *cis* fragment coefficients are

$$\mathrm{CSV} = 300$$

$$\mathrm{H} = -300\,.$$

8. Third and Fourth Neighbor Fragment Coefficients

8.1. Third Neighbor Groups

Third neighbor groups are the fragments common to a far carbon of the vicinal fragment. Four cases are observed, two for conjugate fragment far carbons, and two for gauche fragment far carbons. The former, termed T and C, correspond to situations where the conjugate and bond fragments lie *trans* or *cis*, respectively. The latter, termed S and S′, correspond to situations where the dihedral angle between the bond and conjugate fragments is about 110° and 55°, respectively. The bond region skeletons defining these are shown on Fig. 3. On the figure, the bond fragment is labeled B. F labels the third neighbor fragment lying in the plane defined by two bond regions. The first bond region is the one connecting the third neighbor group to the near vicinal carbon (bond region *r* on the figure) and the second is the one connecting the vicinal group to the near carbon of the bond fragment (bond region *r*′ on the figure). In the case of S and S′, there is asymmetry about this plane. The third neighbor fragment on the same side of the plane as the bond fragment is called the CX(+) third neighbor fragment, while the one on the other side is called the CX(−) third neighbor fragment.

The coefficients for the third neighbor fragments are listed in Table 9. There are four divisions within the table corresponding to the four observed cases. The column headings in each division describe the F fragment dependences. F* means that the F fragment lies *cis* to the previously defined bond region *r*′. The F fragment dependence in the T and C sections differs from that in the S and S′ sections.

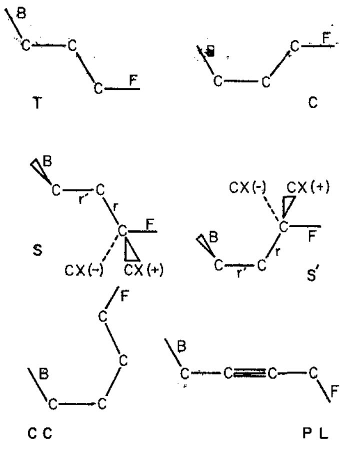

Fig. 3. Third and fourth neighbor fragment orientations. B labels the bond fragment. The fragments *F*, *r*, and *r*′ are discussed in the text

Table 9. Third and fourth neighbor LMO group coefficients

THIRD NEIGHBOR GROUP COEFFICIENTS

-T-

F =	H	C	2	3	H*	C*	2*	3*
F	130 -130	110 -110	150 -165	200 -200	-25 45	0 25	-40 80	-90 115
CH	-15 0	-5 20	10 0		80 -80	70 -70	90 -90	140 -140
CC,2,3	0 0	0 10	-85 80	-30 30	60 -60	50 -60	60 -70	80 -90

-C-

F =	H	C	2	3	H*	C*	2*	3*
F	-100 110	-100 110	-100 110	-100 110	-65 40	-65 40	-65 40	-65 40
CH	-40 20	-40 20	-40 20		-40 45	-15 30	-15 30	
CC,2,3	-5 30	-5 30	-5 30	10 -10	-40 45	-15 30	-5 30	10 -10

-S-

F =	H	C	CVY	2	3	H*	C*	CVY*	2*	3*
F	-50 70	-60 70	80 -70	-60 70	-85 95	-10 -10	-10 -10	10 -10	-10 -10	-10 -10
C X(+)	-40 40	-30 0	-20 30	-30 0	30 -50	0 -15	0 -25	0 10	0 -25	0 -10
C X(-)	20 0	20 0	-20 30	20 0	0 25	-80 110	-80 110	0 10	-80 110	-105 135

-S'-

		F	F*			F	F*
BCVCV BOND FRAGMENTS	F	-80 80	10 -10	OTHER BOND FRAGMENTS	F	-40 10	10 -10
	C X(+)	-45 5	0 -20		C X(+)	-30 30	30 -30
	C X(-)	15 0	80 -90		C X(-)	-60 90	70 -50

FOURTH NEIGHBOR GROUP COEFFICIENTS

	-CC-					-PL-	
F =	CX	CVX	CX*	VVX*	F =	CX	CX*
F	-180 150	-170 155	-190 160	-180 190	F	65 -135	-60 90
C Y	25 -15	-190 200	10 0	-180 80	C Y	-35 70	50 -80

The vinyl carbon single bond F fragments in the S section (Columns CVY and CVY*) behave differently from the other single bond F fragments (Columns H, C, H*, and C*). In the S′ section there is a bond fragment dependence only. That is, the heading BCVCV Bond Fragments means that the numbers to the immediate right apply when the bond fragment is a double banana bond, and the heading Other Bond Fragments precedes the numbers that apply in all other cases. The row labels characterize the F fragment and those fragments geminal to it. The order of tabulation is near hybrid, far hybrid. Thus, the row labels CH and CC, 2, 3 in the T and C sections characterize all carbon-hydrogen fragments and singly, doubly and triply bonded carbon-carbon fragments, respectively. The row labels CX(+) and CX(−) in the S and S′ sections mean that only the orientation of the fragments relative to the plane defined by r and r' is important, i.e. we needn't specify CH(+), CH(−), CC(+), etc.

8.2. Fourth Neighbor Groups

Fourth neighbor groups consist of the fragments common to far carbons of third neighbor groups. Only two cases are found to have coefficients large enough to warrant classification. The first, CC, occurs when all bond regions between the bond fragment and the fourth neighbor fragment lie coplanar and *cis*. The second, PL, occurs when the near carbon of the *third* neighbor fragment is an ethynyl carbon. Both are shown on Fig. 3. The B labels the bond fragment and the F labels the fourth neighbor fragment coplanar to B.

Coefficients for fourth neighbor fragments are likewise listed in Table 9. The column labels characterize the F fragment and the row labels distinguish the F fragment from the other fourth neighbor fragments. The order of tabulation is near hybrid, far hybrid. F* means that F lies *cis* to the conjugate fragment. Other than the geometric dependence which defines the fourth neighbor group itself, there is virtual insensitivity. In particular there is no dependence on the far atom of F (X in the column labels) or the far atom of its neighbor fragments (Y in the row labels). However, differences are observed in the CC section according to whether the near carbon of F is alkyl or ethynyl (Columns CX and CX*) or whether it is vinyl (Columns CVX and CVX*).

9. Examples of Model LMO's

Sample LMO's obtained from molecular fragment coefficients are compared with exact LMO's in Table 10. The row labels define the atomic basis functions as in the previous Tables 1 and 2. The first of the two sets of column labels specifies the molecule from which the exact LMO was taken. Two columns of coefficients are given below the molecule label and these contain the exact LMO and the corresponding model LMO. The exact LMO is always given first and the number above it is the same as its column label in the previous Table 2. The model LMO's are headed by the label M. For example, the first column in Table 10 contains LMO Number 4 in butane (from the previous Table 2) and the second column contains its molecular fragment model.

Overall agreement is excellent and significantly better than shown for the SMO's and PMO's in Table 1. Deviations between exact and model coefficients are less than 1% as large as the bond fragment coefficients. This is typical of the modelling scheme. If higher accuracy is needed, a more detailed model can be used. This would be preferred for constructing model geometry, model LMO molecules via a computer program. However, the present model is accurate enough for most purposes and describes the situation in a way that reveals the important influences.

Table 10. Comparison of accurate and model LMO's

	BUTANE		ISOBUTANE		BUTENE		BUTADIENE		BUTYNE		VINYL ACETYLENE	
	12	M	4	M	5	M	4	M	10	M	3	M
1	7069	7066	7019	7021	384	380	399	400	-24	-20	-35	-30
2	173	150	175	180	326	325	309	340	388	390	352	350
3	86	90	-40	-40	7062	7061	7034	7035	-35	-15	20	-15
4	86	90	-40	-40	-56	-60	-9	-60	-35	-15	7037	7041
5	7040	7036	7039	7041	210	220	112	115	7127	7131	-75	-15
6	-82	-80	72	75	382	375	370	375	223	235	310	310
7	140	140	144	145	7005	7011	6984	6985	52	20	19	20
8	140	140	144	145	47	50	53	50	52	20	7010	7011
9	140	145	61	60	-485	-490	95	95	6969	6971	9	20
10	53	60	-496	-500	82	95	152	155	13	40	66	70
11	140	145	174	170	125	130	403	400	-313	-315	-246	-240
12	-346	-340	162	170	191	190	-687	-685	154	170	-413	-415
13	148	130	61	60	-77	-80	98	0	159	170	546	550
14	334	330	-496	-500	-38	-45	-9	0	382	375	-34	0
15	-18	-15	162	170	-119	-120	-409	-400	-14	-15	-47	0
16	-18	-15	174	170	27	15	664	660	-14	-15	-548	-545
17	-20	-25	-34	-30	1	5	0	10	161	130	434	435
18	-11	-15	-16	-5	10	10	10	0	-182	-160	260	260
19	-11	-15	-24	-25	-15	-10	-7	-10	-186	-160	12	0
20	-29	-25	-24	-25	473	480	-160	-160	18	20	60	0
21	-29	-25	442	445	-177	-180	-85	10	18	20		
22	-145	-140	-150	-150	79	80	17	0	-154	-130		
23	-145	-140	-138	-150	3	5						
24	-134	-130	442	445	6	0						
25	20	20	-138	-150								
26	20	20	-150	-150								

	BUTANE		ISOBUTANE		BUTENE		BUTYNE		BUTENE		BUTYNE	
	4	M	7	M	2	M	11	M	12	M	1	M
1	-144	-150	-69	-65	7004	7011	6874	6786	-561	-575	352	345
2	6971	6976	6905	6911	280	280	7228	7231	331	335	-349	-340
3	139	135	-69	-65	-267	-265	8	5	-62	-60	-285	-290
4	139	135	-69	-65	-267	-265	8	5	-62	-60	-285	-290
5	-9	0	-3	-5	-423	-425	-18	-15	7014	7016	-292	-290
6	-322	-320	-465	-460	299	300	-264	-265	314	295	7108	7111
7	145	140	176	175	-131	-120	-334	-335	-235	-240	-36	-40
8	145	140	176	175	-131	-120	-334	-335	-235	-240	-37	-40
9	-6	-5	-3	-5	70	70	-345	-345	186	195	82	90
10	343	330	176	175	417	415	279	275	7016	7016	6956	6961
11	-6	-5	176	175	0	0	12	0	-114	-115	-68	-50
12	105	110	-465	-460	70	70	23	0	186	195	160	160
13	-47	0	-3	-5	52	0	23	0	-453	-440	160	160
14	-111	-110	176	175	-2	0	-18	0	156	150	94	95
15	11	0	-465	-460	26	25	10	0	62	60	159	160
16	11	0	176	175	-2	0	10	0	156	150	159	160
17	7138	7136	7122	7121	7074	7066	-24	0	504	515	-483	-490
18	-132	-125	441	445	-274	-270	-24	0	-290	-285	2	0
19	-131	-125	-161	-160	-295	-300	-24	0	-187	-185	2	0
20	-156	-150	-161	-160	-78	-70	-13	0	-23	-25	-135	-140
21	-156	-150	-161	-160	-78	-70	-12	0	-23	-25	-135	-140
22	21	20	-161	-160	-38	0	35	0	411	405	432	430
23	21	20	441	445	7	0			-136	-130		
24	59	0	-161	-160	7	0			-136	-130		
25	-14	0	441	445								
26	-14	0	-161	-160								

10. Canonical and Virtual Orbitals

10.1. 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 and provide estimates of the lower excited states of the electronic spectrum. To determine them, all that is actually needed is the knowledge that the CMO's diagonalize the Fock matrix; but this implies that they are symmetry orbitals, i.e., carrier functions for the irreducible representations of the molecule's point group. This can be exploited in many cases to shorten their computation.

10.2. 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 [36–42]. 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 makes use of the notion of antibonding. 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

$$\lambda' = (c'h - ch')/(c^2 + c'^2)^{1/2} \tag{36}$$

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 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).

10.3. 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

$$\lambda_i = \sum_{\mu} T_{i_\mu} f_\mu \tag{37}$$

be their expansions in symmetry orbitals. Using standard projection operators [48] P_μ for each irreducible representation, one can project the set

$$\mu_i = P_\mu \lambda_i = T_{i_\mu} f_\mu \tag{38}$$

from each λ, and by Gram-Schmidt orthogonalization, 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, 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.

Acknowledgement. The authors are particularly grateful to the Ames Laboratory for supplying the computer time that made this work possible. A preliminary description of this work was given in W. England, Ph. D. Thesis, Iowa State University, Ames, Iowa, 1973. One of us (M.S.G.) was supported in part by a grant from Research Corporation.

References

1. Kekulé, A.: Ann. Chem. **137**, 129 (1866)
2. Japp, F. R.: Trans. Chem. Soc. (London) **73**, 97 (1898)
3. Lewis, G. N.: Valence and the structure of atoms and molecules. New York: The Chemical Catalog Co. 1923
4. Langmuir, I.: J. Am. Chem. Soc. **38**, 2221 (1961)
5. Edmiston, C., Ruedenberg, K.: Rev. Mod. Phys. **35**, 457 (1963)
6. Edmiston, C., Ruedenberg, K.: J. Chem. Phys. **43**, S97 (1965)
7. Edmiston, C., Ruedenberg, K.: In: Löwdin, P. O. (Ed.): Quantum theory of atoms, molecules and the solid state. New York: Academic Press 1966
8. Ruedenberg, K.: In: Sinanoğlu, O. (Ed.): Modern quantum chemistry, Vol. 1. New York: Academic Press 1965
9. Pople, J. A., Santry, D. P., Segal, G. C.: J. Chem. Phys. **43**, S129 (1965)
10. Pople, J. A., Segal, G. A.: J. Chem. Phys. **43**, S136 (1965)
11. Pople, J. A., Segal, G. A.: J. Chem. Phys. **44**, 3289 (1966)
12. Pople, J. A., Beveridge, D. L., Dobosh, P. A.: J. Chem. Phys. **47**, 2026 (1967)
13. Pople, J. A., Beveridge, D. L.: Approximate molecular orbital theory. New York: McGraw-Hill 1970
14. Fock, V.: Z. Physik **61**, 126 (1930)
15. Gordon, M. S., Pople, J. A.: MBLD: Standard geometric models and cartesian coordinates of molecules. Quantum Chemistry Program Exchange Newsletter **24**, 28 (1969)
16. Rothenberg, S.: J. Chem. Phys. **51**, 3389 (1969)
17. Rothenberg, S.: J. Amer. Chem. Soc. **93**, 68 (1971)
18. England, W., Gordon, M. S.: J. Am. Chem. Soc. **94**, 5168 (1972)
19. Epstein, I. R.: J. Chem. Phys. **53**, 4425 (1970)
20. Sovers, O., Karplus, M.: J. Chem. Phys. **44**, 3033 (1966)
21. Veillard, A., Del Re, G.: Theoret. Chim. Acta (Berl.) **2**, 55 (1964)
22. Del Re, G., Esposito, U., Carpentieri, M.: Theoret. Chim. Acta (Berl.) **6**, 36 (1966)
23. McWeeny, R., Del Re, G.: Theoret. Chim. Acta (Berl.) **10**, 13 (1968)
24. Magnasco, V., Musso, G. F.: Chem. Phys. Letters **9**, 433 (1971)
25. Pauling, L.: J. Am. Chem. Soc. **53**, 1367 (1931)
26. Slater, J. C.: Phys. Rev. **37**, 481 (1931)
27. Coulson, C. A.: Valence, 2nd ed. London: Oxford University Press 1961
28. Lennard-Jones, J. E., Pople, J. A.: Proc. Roy. Soc. (London) A **198**, 166 (1950)
29. England, W.: Intern. J. Quantum. Chem. **5**, 683 (1971)
30. England, W., Ruedenberg, K.: Theoret. Chim. Acta (Berl.) **22**, 196 (1971)
31. England, W., Salmon, L. S., Ruedenberg, K.: Fortschr. Chem. Forsch. **23**, 31 (1971)
32. England, W., Ruedenberg, K.: J. Am. Chem. Soc. **95**, 8769 (1973)
33. Trindle, C., Sinanoğlu, O.: J. Chem. Phys. **49**, 65 (1968)
34. England, W., Gordon, M. S.: J. Am. Chem. Soc. **91**, 6864 (1969)
35. England, W.: J. Chem. Phys. **58**, 5182 (1973)
36. Pople, J. A., Santry, D. P.: Mol. Phys. **7**, 269 (1963)
37. Pople, J. A., Santry, D. P.: Mol. Phys. **9**, 301 (1965)
38. Pople, J. A., Santry, D. P.: Mol. Phys. **9**, 311 (1965)
39. Coulson, C. A., Longuet-Higgins, H. C.: Proc. Roy. Soc. (London) A **191**, 39 (1947)
40. Coulson, C. A., Longuet-Higgins, H. C.: Proc. Roy. Soc. (London) A **192**, 16 (1947)
41. Coulson, C. A., Longuet-Higgins, H. C.: Proc. Roy. Soc. (London) A **193**, 447 (1948)
42. Coulson, C. A., Longuet-Higgins, H. C.: Proc. Roy. Soc. (London) A **195**, 188 (1948)
43. Gilbert, T. L.: In: Löwdin, P. O., Pullman, B. (Eds.): Molecular orbitals in chemistry, physics, and biology. New York: Academic Press 1964

44. England, W., Gordon, M. S.: J. Am. Chem. Soc. **93**, 4649 (1971)
45. England, W., Gordon, M. S.: J. Am. Chem. Soc. **94**, 4818 (1972)
46. Gordon, M. S., England, W.: Chem. Phys. Letters **15**, 59 (1972)
47. Gordon, M. S., England, W.: J. Am. Chem. Soc. **95**, 1753 (1973)
48. Hamermesh, M.: Group theory. Reading, Mass.: Addison-Wesley 1962

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