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(20) This energetic observation does not provide direct evidence on the question of the importance of through-bond interaction of substituent and reaction site by admixture with the skeletal valence orbitals shown in Figures 1 and 2. If this coupling is important, it is comparable in the two series considered here, but the analysis of this paper (based on total energies and Mulliken charges) would detect such coupling only if it produced enhanced charge transfer between substituent and reaction site; no charge transfer was observed. Energetically important interaction which does not involve such transfer, e.g., exchange or polarization perturbation, would escape detection in this simple analysis. A self-consistent perturbation theory of substitution (SeCPeTS) under development in this laboratory should allow us to resolve this difficulty.
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Bonding in Acyclic Hydrocarbons. An FSGO Analysis and Computational Procedure

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Abstract: The FSGO method is used to study the nature of bonding orbitals in acyclic hydrocarbons. For a given local chemical environment, a bonding orbital's exponent and center are shown to depend linearly on bond length. Variations between different chemical environments are displayed and analyzed. The near-transferability of bond orbitals and chemical environments from molecule to molecule is demonstrated. Predictions for dipole moments and for certain bond lengths and stretching force constants in acetylene, ethylene, propene, ethane, propane, isobutane, butadiyne, vinylacetylene, propyne, 1,3-butadiene, butatriene, and allene are presented, and are shown to successfully monitor differences in similar chemical bonds. A procedure for determining orbital exponents and locations for FSGO wave functions, without explicit energy optimizations, is proposed. Calculations at fixed geometries, as reported for propyne, vinylacetylene, *cis*-1,3-butadiene, *trans*-1,3-butadiene, and isobutane, illustrate the speed of the proposed method, and demonstrate that the resulting wave functions are comparable in accuracy to explicitly optimized FSGO wave functions. Theoretical equilibrium geometries are computed for allene, propyne, *trans*-2-butene, *cis*-1-butene, and isoprene, to show the capabilities of the method. All calculations are ab initio in the sense that all integrals are evaluated and there is no recourse to experimental data.

I. Introduction

In 1967 Frost proposed[1] a quantum mechanical scheme, the floating spherical Gaussian orbital (FSGO) method, for generating crude ab initio molecular wave functions. This method avoids the LCAO approach and instead uses an absolutely minimal basis set of Gaussian core, lone pair, and bonding orbitals. A number of investigators have since performed FSGO calculations on hydrocarbons. Their results demonstrate that accurate predictions can be made for molecular geometries,[2-7] conformational preferences,[2-8] orbital energy orderings,[6,9] ESCA chemical shifts,[10] charge densities,[11,12] dipole moments,[6,12] and polarizabilities and suscep-

Figure 1. Exponent α for CH orbital in ethylene as a function of C–H bond length R in bohr.
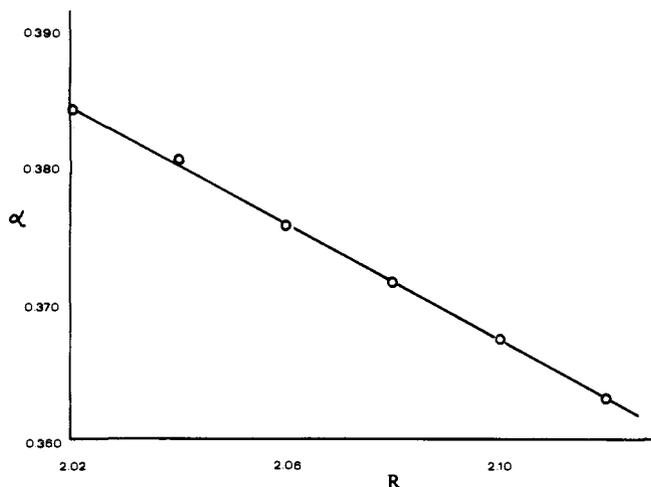
Figure 2. Multiplier m for CH orbital in ethylene as a function of C–H bond length R in bohr.

tibilities.[13] Although some of these studies have touched on the nature of individual FSGO chemical bonds, by and large their emphasis has been elsewhere. At the same time, the one-to-one correspondence between FSGOs and bonds, in conjunction with the variety of bonding patterns associated with acyclic hydrocarbons, suggest that an analysis of the patterns of FSGO bonding might be most fruitful. In the following we report the results of such a study. Initially, we sought to (1) establish the effects of different chemical environments and bond lengths on bond orbitals, and to (2) assess the accuracy of FSGO predictions of bond-oriented properties for various types of bonds; these issues are addressed in sections II and III, respectively.

As an outgrowth of these studies on bonding patterns, we have developed a computational method for generating ab initio FSGO wave functions for large molecules which is competitive with standard semiempirical schemes. A direct application of Frost's method to large systems is not practical, owing to the time-consuming nonlinear optimization process ordinarily employed to determine orbital exponents and locations. One alternative was proposed by Christoffersen and co-workers,[14] who modified Frost's approach by introducing variational flexibility through a linear optimization procedure. By determining FSGO wave functions for molecular fragments, and using these orbitals as basis functions for SCF calculations on larger molecules, they successfully performed ab initio calculations on some very large systems. Their molecular fragment method does, however, employ a larger than absolutely minimal basis set. For example, a calculation on acetylcholine required[15] 54 basis functions and a subsequent SCF calculation to determine the occupied molecular orbitals, whereas Frost's original model would have employed only 38 occupied Gaussians. In contrast, our porposed procedure involves a simulated (rather than explicit) optimization of orbital exponents and locations, avoids an SCF calculation, and therefore retains the simplicity of the Frost-type wave functions. It is based on the observed near-transferability of bond orbitals and chemical environments. The method is ab initio in the sense that all integrals are evaluated and there is no recourse to experimental data; at the same time, it reflects the philosophy enunciated by Pople[16] of employing theoretical information obtained from calculations on small molecules to aid in calculations in larger systems. This technique is described in section IV, and illustrative results are presented in sections V and VI.

All of our calculations were performed with a modified version of a previously described[6] computer program, and
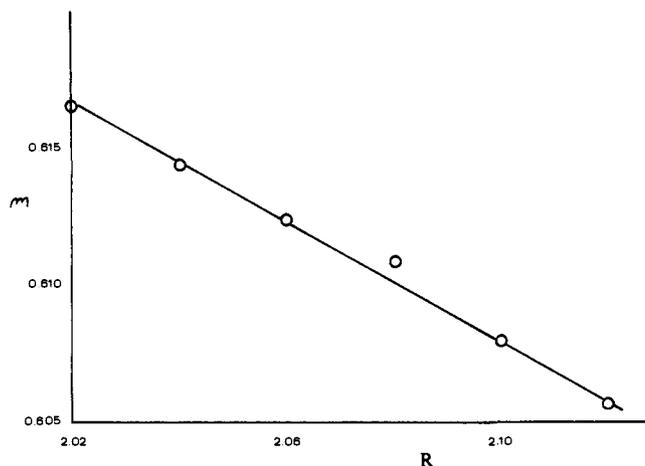
detailed values for wave functions are available from the authors.

II. Patterns of Bonding

A Gaussian orbital ϕ_i is defined by $\phi_i = (2\alpha_i/\pi)^{3/4} \exp[-\alpha_i(r - R_i)^2]$, where α_i is the orbital exponent and R_i is the vector denoting the orbital center. Except for highly strained systems, bond orbitals are located on or nearly on bond axes,[6] so that an orbital in an A–B bond may be described by its exponent and its multiplier m_i, m_i = distance from A to orbital center/bond length. Presumably, the key factors governing the nature of bond orbitals are the bond length and the local chemical environment. The environment of a bond may be specified by the immediate bonding pattern. In acyclic hydrocarbons, for example, there are six basic C–H bond environments: $-CH_3$, $-CH_2-$, $=CH_2$, $>CH-$, $=CH-$, and $\equiv CH$. These bond types can be studied by conducting FSGO calculations on the respective prototype molecules ethane, propane, ethylene, isobutane, propene, and acetylene. We have performed calculations on each of these species, at several different C–H bond lengths, to determine the functional dependence of α and m on R(C–H). Results for α(R) and m(R) for the C–H bond in $=CH_2$ are presented in Figures 1 and 2. Both relationships are extraordinarily close to linear over an extended range of C–H bond lengths. These results are typical of those from other bond types, in that in all cases a linear relationship was found. The slopes and intercepts which define these lines are summarized in Table I. Analogous calculations were performed for carbon–carbon bonds, where ten different environments may be defined: $>C-C<$ (ethane), $=\dot{C}-C<$ (propene), $\equiv C-C<$ (propyne), $=\dot{C}-\dot{C}=$ (1,3-butadiene), $=\dot{C}-C\equiv$ (vinylacetylene), $\equiv C-C\equiv$ (butadiyne), $>C=C<$ (ethylene), $>C=C=$ (allene), $=C=C=$ (butatriene), and $-C\equiv C-$ (acetylene). The exponent relations for these bonds were also linear functions of R, and are included in Table I. C–C multipliers were observed to depend on the presence or absence of adjacent multiple bonds and on the degree of substitution on each carbon, but to be essentially independent of bond length.

Figure 3 displays all the C–H α(R) functions; there are three groups of lines, each with a slope of approximately -0.20. The negative slope indicates that as the bond length increases the bonding orbital grows more diffuse—hardly a surprising result! The universal value for the slope was, however, unexpected. The three line groups may be delineated by the coordination number of the bonding carbon (2, 3, or 4) or, using the vocabulary of atomic orbital hybridization, by carbon sp, sp^2, and sp^3 orbitals. In agreement with conventional analyses, the

Table I. Orbital Exponents and Multipliers

Bond	Type	Molecule	Exponent Slope	Exponent Intercept	Multiplier[a] Slope	Multiplier[a] Intercept
C–H	–CH_3	Ethane	−0.2030	0.7780	−0.1019	0.8215
	–CH_2–	Propane	−0.2350	0.8469	−0.1415	0.9162
	>C–H	Isobutane	−0.2199	0.8160	−0.0641	0.7681
	=CH_2	Ethylene	−0.2193	0.8277	−0.1095	0.8358
	≡CH	Acetylene	−0.1911	0.7892	−0.1552	0.9102
	=Ċ–H	Propylene	−0.2527	0.8971	−0.0945	0.8151
C–C	>C–C<	Ethane	−0.1763	0.8700		0.5000
	=Ċ–C<	Propylene	−0.1847	0.9019		0.4981
	≡C–C<	Propyne	−0.1603	0.8391		0.4702
	=Ċ–Ċ=	1,3-Butadiene	−0.1987	0.9525		0.5000
	≡C–Ċ=	Vinylacetylene	−0.2126	1.0036		0.4740
	≡C–C≡	Butadiyne	−0.2284	1.0570		0.5000
C=C	>C=C<	Ethylene	−0.1605	0.7208		0.5000
	>C=C=	Allene	−0.1572	0.7196		0.4742
	=C=C=	Butatriene	−0.0515	0.4557		0.5000
C≡C	–C≡C–	Acetylene	−0.1677	0.7016		0.5000

[a] C–H multipliers defined from carbon; carbon–carbon multipliers defined from left atom in bond type.
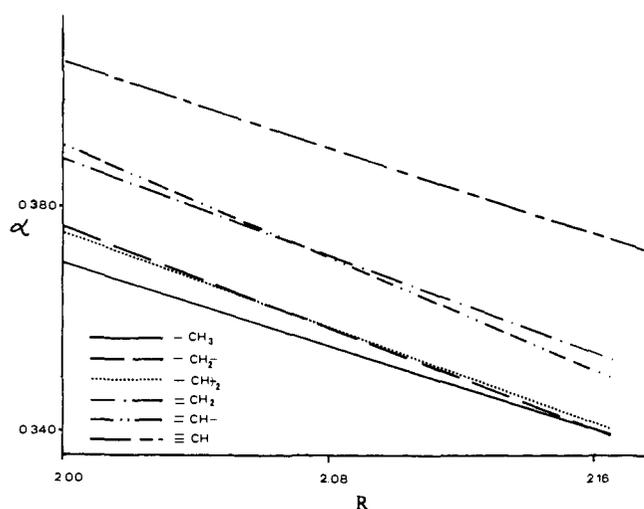

**Figure 3.** C–H exponents as a function of bond length.
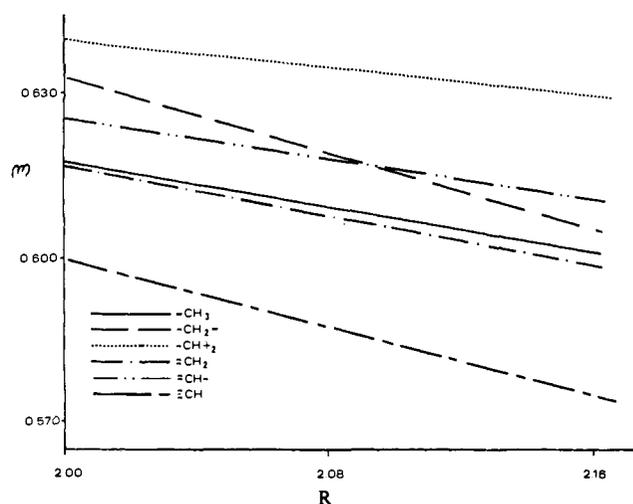
Figure 4. C–H multipliers as a function of bond length.

>C–H (sp³) orbital is the most diffuse, and the ≡C–H (sp) orbital is the most compact.

The $m(R)$ relations for C–H bonds are shown in Figure 4. Note that the C–H orbitals are located closer to the H than to the C. There are four groups of lines in Figure 4. In order of proximity to the carbon nucleus the groups are H–C≡; –CH_3 and =CH_2; C=CH–C and C–CH_2–C; CH(C)₃. This pattern does not correlate with atomic hybrid orbitals. Instead, as the degree of multiple bonding and/or the number of hydrogens associated with a given carbon increases, that carbon exerts a stronger "pull" on its bonding electrons. As shown in section VII, this can be interpreted via effective electronegativities. Variations in carbon–carbon multipliers can be similarly understood.

Exponent–distance relations for carbon–carbon single bonds are in accord with arguments suggesting that sp–sp bonds are the most compact and sp³–sp³ bonds are the most diffuse.

The utility of these relations is predicated on the transferability, or near transferability, of these exponent and multiplier relations from the prototype bonds used to generate the data in Table I to other bonds in other molecules. As a test of this transferability, in Table II we compare the predictions of the linear equations with explicitly optimized exponents and multipliers for various bonds. There is a high degree of agreement; on the average, exponents are predicted to within 0.5%, and multipliers to within 1%. Triple bonds and cumu-

lated double bonds are observed to perturb nearby bonding orbitals somewhat, but we believe that this is due to the energetically poor FSGO description of multiple bonding. Nearby single bond orbitals adjust their exponents and multipliers to aid in the multiple bonding, and consequently are less effective in describing their own bonds. For that reason, the predicted C–H multipliers for propyne (–CH_3), butatriene (=CH_2), and allene (=CH_2), as examples, may more truly reflect the actual bonding structure than the energy optimized multipliers.

The apparent transferability of the local chemical environments suggests that the equations in Table I could be used in larger hydrocarbons to eliminate or reduce the expensive and time-consuming nonlinear optimization process associated with the FSGO method. Indeed, such a simulated optimization process has been developed, and is discussed in sections IV–VI.

III. Bond-Oriented Properties

The most direct bond-oriented property is equilibrium bond length, and in Table III FSGO bond lengths for our 16 prototype bonds are tabulated. Some of these have been reported previously, but all values for isobutane, 1,3-butadiene, vinylacetylene, butadiyne, and butatriene are from the current study. For comparison, we have included experimental values and theoretical values from the semiempirical CNDO method and from the ab initio STO-3G method. In most cases the FSGO predictions are superior to the CNDO and are only

Table II. Transferability of Local Chemical Environments[a]

Bond	Environment	Molecule	α(pre)	α(exp)	m(pre)	m(exp)
C–H	–CH$_3$	Propane	0.348	0.347	0.606	0.605
		Propene	0.350	0.351	0.607	0.599
		Propyne	0.354	0.361	0.609	0.588
		Isobutane	0.360	0.358	0.611	0.608
		trans-2-Butene	0.360	0.360	0.611	0.607
	=CH$_2$	Propene	0.371	0.370	0.610	0.610
		Vinylacetylene	0.371	0.371	0.610	0.600
		Butatriene	0.375	0.376	0,612	0.588
		1,3-Butadiene	0.380	0.379	0.614	0.613
		Allene	0.375	0.372	0.612	0.587
	≡C–H	Propyne	0.400	0.397	0.594	0.593
		Butadiyne	0.400	0.404	0.594	0.584
		Vinylacetylene	0.400	0.402	0.594	0.594
	=CH–	1,3-Butadiene	0.386	0.382	0.624	0.624
		trans-2-Butene	0.381	0.381	0.622	0.617
		Vinylacetylene	0.384	0.390	0.623	0.605
C–C	>C–C<	Propane	0.368	0.369		
		Isobutane	0.357	0.362	0.515	0.517
	=Ċ–C<	*trans*-2-Butene	0.367	0.367	0.498	0.498
C=C	>C=C<	Propene	0.311	0.310		
		trans-2-Butene	0.322	0.322	0.511	0.507
		Butadiene	0.315	0.316	0.511	0.507
		Vinylacetylene	0.311	0.314	0.511	0.503
	=C=C<	Butatriene	0.321	0.325	0.498	0.498
C≡C	–C≡C–	Propyne	0.318	0.318		
		Butadiyne	0.315	0.318	0.514	0.483
		Vinylacetylene	0.319	0.320	0.514	0.501

[a] α(pre) and m(pre) are determined from the relations in Table I; α(exp) and m(exp) are determined from explicit energy optimizations.

Table III. Equilibrium Bond Lengths

Bond	Environment	Molecule	CNDO[a]	FSGO	STO-3G[b]	Expt[b]
C–H	≡C–H	Acetylene	1.093	1.079	1.065	1.064
	=CH$_2$	Ethylene	1.110	1.101	1.079	1.085
	=CH–	Propene		1.108	1.085	1.090
	–CH$_3$	Ethane	1.117	1.120	1.085	1.095
	–CH$_2$–	Propane		1.125	1.089	1.096
	CH(C)$_3$	Isobutane		1.133	1.098[g]	1.108[g]
C–C	≡C–C≡	Butadiyne		1.462	1.408[h]	1.379[d]
	=Ċ–C≡	Vinylacetylene		1.484	1.459[h]	1.431[e]
	≡C–C<	Propyne		1.491	1.484[c]	1.459[c]
	=Ċ–Ċ=	1,3-Butadiene		1.488	1.488[h]	1.483[d]
	=Ċ–C<	Propene		1.497	1,520	1.501
	>C–C<	Ethane	1.476	1.501	1.538	1.534
C=C	=C=C=	Butatriene		1.350	1.257[h]	1.283[f]
	>C=C=	Allene		1.340	1.288[c]	1.308[c]
	>C=C<	Ethylene	1.320	1.351	1.305	1.339
C≡C	–C≡C–	Acetylene	1.198	1.214	1.168	1.206

[a] G. A. Segal, *J. Chem. Phys.*, **47**, 1876 (1967); all values are in ångstroms. [b] C. E. Blom, P. J. Singerhand, and C. Altona, *Mol. Phys.*, **31**, 1359 (1976). [c] I. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 5339 (1971). [d] Z. B. Maksic and M. Randic, *ibid.*, **92**, 424 (1970), [e] T. Fukuyama, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jpn.*, **42**, 379 (1969). [f] A. Almennigen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **15**, 1557 (1961). [g] G. Kean and S. Fliszar, *Can. J. Chem.*, **52**, 2272 (1974). [h] W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 6941 (1975).

slightly inferior to the STO-3G values. FSGO C–H bond lengths are longer than experimental values, whereas the STO-3G predictions are shorter, Within a given bond type, the experimental trend of variation in bond length with respect to local environment is generally reproduced—thus the method is capable of successfully differentiating between environments, The FSGO C–C single bond is too "tight"; it does stretch or shrink in the correct direction as the environment is changed, but not by a sufficiently large amount.

Stretching force constants are reported in Table IV. The experimental values in parentheses have not been corrected for anharmonicity, and are presumably 1–10% too small. The FSGO values were determined by polynomial fits using some five or seven bond lengths; in a few cases, such as the C–H bond

in propane, there is an appreciable (5%) uncertainty in the FSGO result. Here again, the FSGO values are slightly inferior to the STO-3G results, but much more accurate than the CNDO/2 predictions. Trends within C–H bonds, ranging from acetylene as the stiffest to isobutane as the most flexible, are well reproduced. FSGO C–H stretching constants are ~1.6 times as large as experimental values. Trends in C–C force constants are less satisfactory, although, in the absence of experimental values corrected for anharmonicity, the experimental trend is uncertain. Judging from ethane, FSGO C–C force constants are 2,5 times experimental values, and this unreasonably large degree of stiffness explains the previously mentioned tightness of the C–C bond.

Dipole moments are often interpreted in terms of bond

Table IV. Stretching Force Constants

Bond	Environment	Molecule	CNDO	FSGO	STO-3G[a]	Expt[b,c]
C–H	≡C–H	Acetylene	15.03[d]	9.99	8.2	6.34
	=CH₂	Ethylene	13.71[d]	8.91	7.6	5.64
	=CH–	Propene		8.29		(5.00)
	–CH₃	Ethane	13.84[d]	8.04	7.3	5.31
	–CH₂–	Propane		8.23		4.95
	⋗C–H	Isobutane		8.03		(4.59)
C–C	≡C–C≡	Butadiyne		11.75		(10.31)[f]
	=C–C≡	Vinylacetylene		10.72		(7.19)[g]
	≡C–C⋖	Propyne		9.55	6.8	(5.3)[a]
	=C–C=	1,3-Butadiene		11.05		
	=C–C⋖	Propene		11.34		(5.86)
	⋗C–C⋖	Ethane	12.26[d]	11.50	6.5	4.57
C=C	=C=C=	Butatriene		24.90		
	⋗C=C=	Allene	26.7[e]	16.82		(9.7)[e]
	⋗C=C⋖	Ethylene	22.99[d]	16.25	14.4	9.39
C≡C	–C≡C–	Acetylene	34.62[d]	25.89	25.8	16.3

[a] M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970); all values are in units of 10⁻¹¹ dyn/cm. [b] C. E. Blom, P. J. Slingerhand, and C. Altona, *Mol. Phys.*, **31**, 1359 (1976). [c] Values in parentheses are not corrected for anharmonicity. [d] K. Kuzmutza and P. Pulay, *Theor. Chim. Acta*, **37**, 67 (1975). [e] H. Fisher and H. Kollman, *ibid.*, **13**, 213 (1969). [f] K. Ramaswamy and K. Srinivasan, *Aust. J. Chem.*, **22**, 1123 (1969). [g] E. M. Popov, I. P. Yakovlev, G. A. Kogan, and V. V. Zhogena, *Teor. Eksp. Khim.*, **3**, 533 (1967).

Table V. Dipole Moments (D)

Molecule	CNDO[b]	FSGO	STO-3G[b]	Expt[a]
Propane	0.00	0.03	0.03	0.084
Isobutane	0.00[c]	0.09	(0.11)[e]	0.132
Propylene	0.36	0.27	0.24	0.366
Vinylacetylene		0.42	(0.45)[e]	(0.4; 0.223)[d]
Propyne	0.43	0.97	0.50	0.781
cis-Butadiene		0.06	(0.10)[e]	

[a] R. D. Nelson, D. R. Lide, and A. A. Maryott, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, 10 (1967). [b] W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 2191 (1970). [c] J. A. Pople and M. Gordon, *ibid.*, **89**, 4253 (1967). [d] C. Hirose, *Bull. Chem. Soc. Jpn.*, **43**, 3695 (1970). [e] 4-31G value from W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 6941 (1975).

contributions; hence we have reported FSGO dipole moments in Table V, The results are excellent. In accord with earlier observations, the floating nature of the Gaussian orbitals acts to balance the calculation and allows the correct amount of electron flow to occur. We have been unable, however, to partition the dipole moment of Table V into bond components.

Taken as a whole, the results of this section solidify the position of the FSGO method as the simplest ab initio procedure, intermediate in character between standard semiempirical schemes and minimal basis set ab initio LCAO methods. Variations in bonds due to different local chemical environments are successfully monitored. Using Tables III–V, the accuracy to be expected from calculations on larger hydrocarbons can be estimated,

IV. Simulated Optimization

We suggest that the bond orbital analyses conducted on small prototype hydrocarbons can be used to determine approximate wave functions for other hydrocarbons. Compact expressions for α and m for carbon–hydrogen and carbon–carbon bonding orbitals are presented in Table VI. The thrust of our approach is to use these relations to determine orbital exponents and locations. A computer program has been developed which, for a given input nuclear geometry of an acyclic hydrocarbon, automatically determines the molecular Lewis structure, classifies all bonds with respect to type, order, and environment, and generates the simulated optimization FSGO

wave function. The energy (and other properties) associated with this wave function may then be calculated with the proper evaluation of all nonnegligible one- and two-electron integrals.

The relations in Table VI allow for the unambiguous assignment of exponents and multipliers for all standard bonding orbitals in acyclic hydrocarbons. If a particular orbital is "nonstandard", its exponent and location can be determined by an explicit energy minimization, while retaining the simulated optimization for the rest of the molecule, Likewise, if a surprising or questionable result is obtained in a given calculation, any orbital or group of orbitals can be explicitly optimized. In this manner the systematic "improvability" generally associated with ab initio methods is retained.

In the following we present results of simulated optimization FSGO calculations, including comparisons to both explicitly optimized FSGO wave functions and associated properties, and to other theoretical and experimental structures, dipole moments, and energies.

V. Calculations at Fixed Geometries

Using nuclear geometries previously employed for explicitly optimized FSGO calculations, simulated optimization FSGO calculations were conducted for isobutane, *cis*- and *trans*-1,3-butadiene, vinylacetylene, and propyne. Some of the results are summarized in Table VII. The two sets of orbital exponents and locations usually agreed to within 1%, although a slightly larger deviation was observed for the C–H methyl orbitals in propyne and the C–H methylene orbitals in vinylacetylene. The dipole moments also compare favorably; the largest discrepancy occurs for propyne (see section VI) where the simulated optimization dipole moment of 0.56 D is in better agreement with the STO-3G value[17] of 0.50 D than is the explicitly optimized FSGO value[6] of 0.97 D. The total energies associated with the simulated optimization FSGO wave functions agree to within 0.005 hartree with the explicitly optimized energies. We also find that the two procedures yield identical orbital energy orderings, with an average orbital energy deviation of only 0.007 hartree, Energy differences are also consistent; the two procedures predict the trans isomer of 1,3-butadiene to be more stable than the cis by 0.0026 (simulated optimization) and 0.0024 hartree (explicit optimization),[12]

The FSGO wave functions generated according to Table VI are thus quite similar to the wave functions which would have

Table VI. Simulated Optimization Relations[a-c]

Bond	Environments	Exponent		Multiplier	
		Slope	Intercept	Slope	Intercept
C–H	$-CH_3, -CH_2-, \mathord{+}_3CH$	−0.2030	0.7780		
C–H	$=CH_2, =CH-$	−0.2193	0.8277		
C–H	$\equiv CH$	−0.1911	0.7892	−0.1552	0.9102
C–H	$-CH_3, =CH_2$			−0.1054	0.8292
C–H	$=CH-, -CH_2-$			−0.0987	0.8079
C–H	$\mathord{+}_3CH$			−0.0641	0.7861
C–C	$\mathord{+}_3C-C\mathord{+}_3$	−0.1763	0.8700		
C–C	$=\dot{C}-C\mathord{+}_3$	−0.1847	0.9019		
C–C	$\equiv C-C\mathord{+}_3, =\dot{C}-\dot{C}=$	−0.2081	0.9757		
C–C	$\equiv C-\dot{C}=$	−0.2126	1.0036		
C–C	$\equiv C-C\equiv$	−0.2284	1.0565		
C=C	$>C=C<$	−0.1605	0.7208		
C=C	$>C=C=$	−0.1572	0.7196		
C=C	$=C=C=$	−0.0515	0.4557		
C≡C	$-C\equiv C-$	−0.1677	0.7016		

[a] These relations were used to generate the simulated optimization FSGO wave functions and results described in this paper. They are based on the data of Table I; similar exponent lines or multiplier lines have been combined. [b] Exponents and multipliers are expressed as linear functions of the bond length in bohrs. [c] To determine the locations of carbon-carbon orbitals, C–C, C=C, and C≡C bonds are regarded as derivatives of ethane, ethene, and acetylene. The replacement of –H by –C shifts the multiplier 0.010 away from the carbon at which substitution has occurred. The replacement of 2(–H) by =C and of 3(–H) by ≡C shifts the multiplier 0.002 and 0.030, respectively, toward the carbon at which substitution has occurred. Multiplier shifts are assumed to be additive.

Table VII. Comparison of Explicit and Simulated Orbital Optimizations

Molecule	Explicit optimization[a]			Simulated optimization		
	E^b	μ^c	t^d	E	μ	t
Propyne	−97.696	0.97		−97.692	0.56	0.1
Vinylacetylene	−129.524	0.42	84.3	−129.520	0.27	0.4
cis-1,3-Butadiene	−130.671	0.06	59.6	−130.667	0.26	0.3
trans-1,3-Butadiene	−130.695	0	60.4	−130.693	0	0.3
Isobutane	−133.014	0.04	133.6	−133.013	0.04	0.4

[a] Explicit optimization on propyne from ref 6; *cis*- and *trans*-1,3-butadiene from ref 12; vinylacetylene and isobutane from current work. [b] Energy in hartrees. [c] Dipole moment in debyes. [d] CPU time in minutes for a double precision calculation on an IBM-360-44 computer with high-speed registers.

Table VIII. Allene[a]

	FSGO-explicit opt	FSGO-simulated opt	Exptl[b]
E	−97.652	−97.646	
R(C–H)	1.09	1.09	1.09
R(C=C)	1.34	1.34	1.31
∠HCH	126°	121°	118°

[a] Energies in hartrees; bond lengths in ångstroms. [b] A. G. Maki and R. A. Toth, *J. Mol. Spectrosc.*, **17**, 136 (1965).

Table IX. Propyne[a]

	FSGO-explicit opt	FSGO-simulated opt	Exptl[b]
E	−97.696	−97.692	
R(C–H)	1.08	1.08	1.06
R(C≡C)	1.21	1.21	1.21
R(C–C)	1.49	1.50	1.46
R(C–H)$_{CH_3}$	1.11	1.11	1.10
∠HCH	113°	112°	109°

[a] Energies in hartrees; bond lengths in ångstroms. [b] C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

been obtained by an energy minimization, and similar numerical values should be obtained for most expectation values. The two "t" columns of Table VII display the required amount of computer time. One observes that for these systems the simulated optimization technique is faster by a factor of 200–300; for larger molecules the differential would be greater.

VI. Structural Predictions

One of the major applications of the FSGO method has been the determination of molecular geometries. Accordingly, we have further tested our technique by calculating theoretical equilibrium structures for the molecules allene, propyne, *trans*-2-butene, *cis*-1-butene, and isoprene.

Earlier FSGO calculations[6] on allene and propyne were somewhat disappointing, in that the H–C–H angles were too large. In allene the predicted angle was 126°, 8° larger than experiment; in propyne there was a 4° error. Both of these deviations can be at least partially attributed to the energeti-

cally poor FSGO description of triple bonds and cumulated double bonds. Since appropriate combinations of the C–H orbitals possess the correct symmetry to assist in the multiple bonding, during the energy optimization they move too close to their respective carbon atoms, and therefore describe their own bonds less effectively. The simulated optimization procedure should avoid this difficulty, and one might expect improved geometries. These expectations are borne out in Tables VIII and IX, where we note that the bond length predictions are quite similar, but that the H–C–H angles in allene and propyne are improved by 5 and 1°, respectively. Note further that the energy difference between the two C_3H_4 isomers is essentially unchanged, 0.044 hartree as compared to 0.046 hartree.

trans-2-Butene and *cis*-1-butene (the conformer in which the dihedral angle between the $C_1=C_2$ and C_3-C_4 bond is zero) are among the C_4 hydrocarbons studied by Hehre and

Table X. *trans*-2-Butene

	Bond[a]	R(FSGO)	R(exp)[b]	Angle	Angle (FSGO), deg	Angle (exp), deg
	C_1-C_2	1.496	1.508 ± 0.002	C_2C_1H	110.4	109.0 ± 5.0
	$C_2=C_3$	1.342	1.347 ± 0.003	$C_1C_2C_3$	125.5	123.8 ± 0.4
$E = -131.8660$ hartrees $\mu = 0$ D	C_2-H_4	1.110	1.15 ± 0.14	$C_3C_2H_4$	118.8	121.5 ± 4.0
	C_1-H_3	1.110	1.10 ± 0.04			
	C_1-H_1	1.119	1.10 ± 0.04			
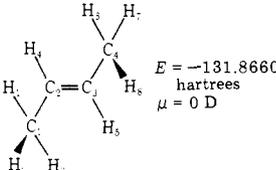
[a] Bond lengths are in ångstroms. [b] Reference 19.

Table XI. *cis*-1-Butene

	Bond[b]	R(FSGO)	R(exp)[a]	Angle	Angle (FSGO), deg	Angle (exp),[a] deg
	$C_1=C_2$	1.338	1.335	$C_1-C_2-C_3$	125.4	126.0
	C_2-C_3	1.511	1.501	$H_1-C_1-C_2$	121.2	119.8
$E = -131.8597$ hartrees	C_3-C_4	1.496	1.530	$H_2-C_1-C_2$	121.2	119.8
$\mu = 0.14$ D	C_1-H	1.104	1.092	$H_3-C_2-C_1$	120.5	119.0
$\mu(exp)^a = 0.41$ D	C_2-H	1.096	1.091	$H_4-C_3-C_2$	107.0	109.0
	C_3-H	1.128	1.093	$H_7-C_4-C_3$	109.9	111.3
	C_4-H	1.116	1.095			
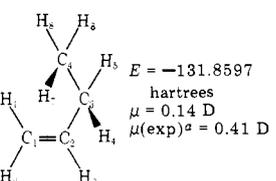
[a] S. Kondo, E. Hirota, and Y. Morino, *J. Mol. Spectrosc.*, **28**, 471 (1968). [b] Bond lengths in ångstroms.

Pople[18] using LCAO methods. These authors employed standard bond lengths and angles except for CCC angles which were optimized. They found that at the STO-3G and 4-31G levels, respectively, the *trans*-2-butene isomer was the more stable by 0.0079 and 0.0056 hartree. We have conducted simulated optimization FSGO calculations with geometry optimization on these species. Results are presented in Tables X and XI. The FSGO total energies are on the order of 132 hartrees, approximately 85% of the Hartree–Fock energies. Nevertheless, the energy difference between the isomers is predicted to be 0.0063 hartree, in excellent agreement with Hehre and Pople's results.[18] The computed geometry for *trans*-2-butene compares quite favorably with the experimental geometry reported by Almennigen et al.;[19] bond angles are of comparable quality to those obtained using standard bond lengths by PCILO calculations.[20] Similar comments apply to the structural predictions for *cis*-1-butene. In this latter molecule the FSGO dipole moment of 0.14 D is, however, only in moderate agreement with the experimental value of 0.44 D.

The isoprene molecule is a key building block in organic chemistry, forming the basis for many polymers and for the terpene class of natural products. There has been little in the way of previous theoretical experience with this molecule, and we have consequently studied it with the simulated optimization FSGO method. Results are presented in Table XII. Theoretical and experimental dipole moments agree well. An experimental structure for the molecule has been reported,[21] but the authors of that study were forced to assume several values, and the data were insufficient to accurately determine other geometric parameters. The uncertainties associated with their work are probably several times larger than the deviations given in Table XII. Dodziuk[22] has used an empirical force field to predict a structure for isoprene, and her results are presumably resonably accurate. As compared to these results, the FSGO structural predictions are excellent. Preliminary calculations showed, in agreement with Dodziuk, that the conformer with H_3 in the $C_3-C_4-H_2$ plane was the most stable. FSGO correctly predicts the lengthening of the $C_3=C_4$ bond as compared to the $C_1=C_2$ bond, and the respective absolute bond lengths agree well with Dodziuk's values. The C_3-C_5 bond is correctly predicted to be larger than the C_2-C_3 bond, but by an insufficient amount (see section III). Out of eight comparative bond angles, only two differ by more than 1°. The

Table XII. Isoprene
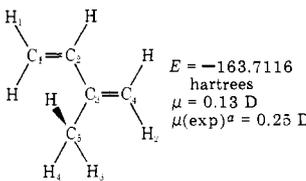
$E = -163.7116$ hartrees
$\mu = 0.13$ D
$\mu(exp)^a = 0.25$ D

Bond[b]	R(FSGO)	R(empirical)[c]	R(exp)[d]
$C_1=C_2$	1.348	1.348	1.338 ± 0.005
C_2-C_3	1.494	1.487	1.470 ± 0.005
C_3-C_5	1.498	1.518	1.510 ± 0.007
$C_3=C_4$	1.356	1.352	1.338 ± 0.005
C_1-H	1.100		1.068 ± 0.01
C_2-H	1.094		1.068 ± 0.01
C_4-H	1.102		1.068 ± 0.01
C_5-H	1.107 (H_3)		1.122 ± 0.01
	1.118 (H_4)		1.122 ± 0.01

Angle	Angle (FSGO), deg	Angle (empirical),[c] deg	Angle (exp),[d] deg
$H-C_1-H$	117.7	118.6	(115.5)
$H_1-C_1-C_2$	121.2	121.3	
C_1-C_2-H	121.8	118.1	
$C_1-C_2-C_3$	119.9	125.1	122.4
$C_2-C_3-C_5$	120.2	119.5	120.1
$C_2-C_3-C_4$	119.9	120.6	120.1
$C_3-C_4-H_2$	121.2	121.1	
$H-C_4-H$	117.6	118.3	(115.5)
$C_3-C_5-H_3$	109.1		(110.5)

[a] D. R. Lide, Jr., and M. Jen, *J. Chem. Phys.*, **40**, 252 (1964). [b] Bond lengths in ångstroms. [c] Reference 22. [d] Reference 21.

largest deviation occurs for the $C_1C_2C_3$ angle, for which the FSGO value is slightly closer to the experimental value than is the empirical result.

Based on these calculations, the simulated optimization FSGO technique can be used with some confidence to predict geometries of hydrocarbons.

VII. Discussion

Using the simulated optimization technique, Frost's FSGO

CH₃—CH₃
2.30

CH₃—CH₂—CH₃
2.27 2.31

TRANS CH₂=CH—CH=CH₂
2.25 2,28

CH₂=CH₂
2.29

CH₃—CH=CH₂
2.34 2.26 2.28

CH≡C—C≡CH
2.40 2,48

CH≡CH
2.36

CH—(CH₃)₃
2.18 2.29

CH₃—CH=CH—CH₃
2.30 2.22

CH₃—C≡CH
2.39 2.28 2.34

CH₂=CH—C≡CH
2.33 2.31 2.36 2,36

CH₂=C=C=CH₂
2.39 2,38

CH₂=C=CH₂
2.28 2.16

cis CH₂=CH—CH=CH₂
2.26 2.25
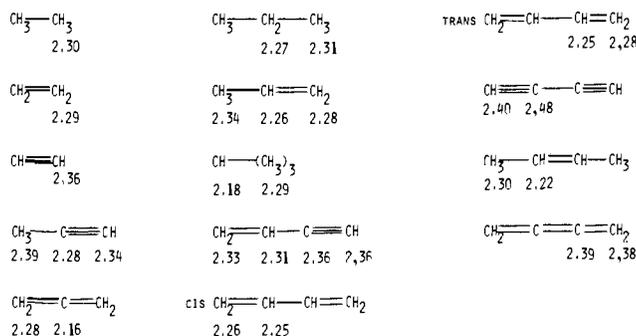
Figure 5, Electronegatives of carbon in different environments.

method can be extended to large molecules. Results of comparable quality to those of explicitly optimized FSGO wave functions can be obtained. The procedure allows for the very rapid determination of wave functions, energies, and other properties without ignoring integrals or using experimental parameters.

The key to the method's success is the transferability of bond orbital exponent and multiplier equations between similar local chemical environments. The use of bond-oriented rather than atom-oriented basis functions makes the analysis of transferability much simpler and more direct. In fact, the results of this paper may be regarded as a testimony to the extent to which chemical bonds actually are transferable. Of course, there will be some molecules in which a given bond or region will not be transferable, If unusual results are obtained (or are expected), that bond or region can be explicitly optimized. In fact, the entire simulated optimization procedure could be used to provide a good starting point for an explicit optimization, so that an energy optimized wave function could be obtained with a minimum of calculation.

Logical extensions of the simulated optimization procedure include (a) the analysis of bonding patterns of common heteroatoms and their inclusion into the program, (b) the treatment of resonant molecules, and (c) the generation of wave functions of higher accuracy. In regard to (b), some work has been done,[12] but a fully successful treatment will require a slightly increased basis set. One procedure for generating improved wave functions as in (c) would be to employ combinations of Gaussian functions for core, lone pair, and bonding orbitals, Some authors have considered this possibility,[23,24] but the explicit optimization of individual component Gaussians presents serious computational problems that would not be associated with a simulated optimization method.

The bonding patterns of the prototype hydrocarbons may be profitably analyzed. Since FSGO wave functions are quantum mechanically valid analogues of Lewis electron dot structures, they may be interpreted in terms of classical chemical concepts. Blustin,[25] for example, has proposed an interesting "packing orbital" analysis, In earlier work, we have demonstrated the utility of a classical charge decomposition procedure,[11] in which a bonding orbital's electrons are apportioned to the bond nuclei through the orbital multiplier, and have further shown[26] that orbital multipliers may be used to define electronegativity differences.

Unlike most Mulliken population analyses of LCAO wave functions, our FSGO charge decomposition procedure yields negatively charged hydrogens, This may be due to the lack of hydrogen core functions in the basis set; however, we note that it is in harmony with the observation that in most aspects of organic chemistry a hydrogen is more electron withdrawing than an alkyl carbon. Within a sequence of molecules, the acidity of various hydrogens is presumably related to their respective charges, Table XIII summarizes data on C–H multipliers, hydrogenic charges, and acidities. The comparisons

Table XIII, FSGO Hydrogenic Charges and Acidities

Molecule	Environment	Multiplier	Charge	pK$_a$[a,b]
Acetylene	≡C–H	0.594	−0.189	25[c]
Methane	CH₄	0.596	−0.192	39
Propylene	–CH₃	0.599	−0.199	36.5
Ethylene	=CH₂	0.610	−0.221	37
Propane	–CH₃	0.605	−0.210	41
Ethane	–CH₃	0,606	−0.213	40.5
Propane	–CH₂–	0.614	−0.228	43
Propylene	C=CH–C	0.616	−0.233	
Isobutane	C(–)₃CH	0.634	−0.269	41.5

[a] These are solution values, which may differ somewhat from gas-phase values. [b] R. E. Dessy, W. Kitching, I. Psurras, R. Salinger, A. Chen, and T. Chevers, *J. Am. Chem. Soc.*, **88**, 460 (1966). [c] D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, N.Y., 1965, p 19.

are conceptually satisfactory; as the orbital center moves "closer" to the H, the acidity decreases. In a more speculative vein, the stability of carbocations (R⁺) might be associated with the electronic structure of the RH compound; the carbon in RH with the smallest positive (most negative) charge might be most willing to give up an H⁻. From that perspective, we note that the FSGO carbon charges C=C(+0.275)–C (propene), C–)₃C(+0,311) (isobutane), C–)₂C(0.480) (propane), C–C(+0,638) (ethane), and C(+0.769) (methane) correlate with the observed order of carbocation stability; allyl ≃ tertiary > secondary > primary > methyl. Since the charges of both carbons and hydrogens are determined by the orbital multipliers, these examples illustrate the direct effect of bond orbital locations on chemical activity.

The bond orbital locations, in turn, may be regarded as being determined by the relative electron-attracting powers or electronegativities of the various atoms in a given molecule. If the electronegativity difference between atoms A and B in an A–B bond is defined as being proportional to the deviation of the bond orbital multiplier from 0,5, an electronegativity scale may be generated,[26] Under the assumption that the electronegativity of H is constant in hydrocarbon environments, it becomes possible to evaluate numerically the electronegativities of different carbon atoms in the same or different molecules. A variety of values are presented in Figure 5. When a carbon was bonded to one or more hydrogens, its electronegativity was determined from a C–H multiplier,[26]

$$\epsilon_c = -4,545 m_{C-H} + 5.059$$

In other cases, the multiplier of a carbon–carbon bond[26] (with multiple bonds given precedence) was employed.[27] From Figure 5 we note that for these systems carbon electronegativities range from 2.16 to 2.48; thus, it would be an oversimplification to assign only one electronegativity value to the carbon atom. Moreover, the different chemical natures of the carbons are largely reflected in their varying electronegativities. For instance, centrally located carbons are generally less electronegative than terminal carbons, which is consistent with the fact that electrophilic addition reactions of alkenes and alkynes normally proceed via attack at central carbons. Further, the lower electronegativity of central carbons should aid in the dispersal of the odd electron in free-radical intermediates, so that the FSGO results are also in accord with observed free-radical stabilities,

It is clear that atomic charges and electronegativities, as well as the orbital exponents (sizes) and locations discussed in section II, are constructs, not observables. Nevertheless, they play a major role in understanding and describing molecular structure and properties, and they remain at the heart of quantum chemistry,[28] It is our contention that the FSGO

method establishes a point of contact between ab initio quantum mechanics and these classical concepts, Through an interpretation of nonempirical (although crude) FSGO wave functions, it is possible to quantify these concepts without reference to experiment, and to explore their variation with respect to chemical environment. The numerical predictions for observables presented in section III indicate a reasonable level of accuracy and sensitivity to environment and therefore reinforce the overall analysis of bonding in acyclic hydrocarbons.

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Substituent Effects on Spin Delocalization in Triplet Phenylnitrenes. 1. Para-Substituted Phenylnitrenes

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Abstract: The ESR spectra of 14 triplet 4-substituted phenylnitrenes in methylcyclohexane glasses at 77 K are reported. The zero field parameters have been calculated. E is <0.002 cm^{-1} in all cases and D varies from 0.871 to 1.008 cm^{-1}. All of the para substituents decreased D, i.e., delocalized spin density, except fluorine, where a small increase in D was noted. The results are compared to similar studies on 4-substituted diphenylmethylenes. In five cases, hyperfine splitting was noted; $a_N = 18 \pm 1$ G, indicating that the spin density on nitrogen does not change much. INDO calculations were carried out on eight of the compounds. The dipole–dipole distance, r_{12}, was calculated from D and from INDO spin densities; both gave values in the range 1.08–1.18 Å. The INDO calculations indicate that the total spin density on nitrogen remains essentially constant and that the variation of D is being determined primarily by the spatial extent of that portion of spin that is delocalized. Details of how individual substituents affect the spin density distribution are discussed and some generalizations are given for predicting spin delocalization in para-substituted phenylnitrenes.

Smolinsky and Wasserman were the first to mention the observation of the ESR spectrum of triplet phenylnitrene.[1] The details of their observation were reported in a communication by Smolinsky, Wasserman, and Yager.[2] The nitrene was generated by photolysis of phenyl azide in a Fluorolube glass at 77 K. This was the same procedure that was used previously to generate diphenylmethylene.[3] They reported two broad lines in the spectrum, at 6701 and 1620 G, which were assigned to the $\Delta m = 1$ and $\Delta m = 2$ transitions, respectively.[2] The zero field parameters, D and E, were calculated to be 0.99 and <0.002 cm^{-1}.[4,5] The broad band at 6701 G was assigned to an x,y transition.[4-7]

The ESR spectra of 4-methoxyphenylnitrene and 4-nitrophenylnitrene were reported to exhibit broad peaks at 6618 and 6671 G, respectively.[4] The low-field line was observed only in the 4-methoxy case. Coope, Farmer, Gardner, and McDowell[6] calculated the zero field parameters for all of the nitrenes reported by Smolinsky, Snyder, and Wasserman.[4] They reported D values of 1.00, 0,98, and 0,96 cm^{-1} for phenylnitrene, 4-nitrophenylnitrene, and 4-methoxyphenylnitrene. They suggested that impurities may account for the weak half-field line that was occasionally observed.[6] Moriarty and Rahman reported a D of 0.999 cm^{-1} for phenylnitrene in a phenyl azide glass.[7] Wasserman reviewed the ESR work on nitrenes and included in the review data on the D and E parameters of several nitrenes which had not been reported previously.[8] Also, the D and E values for several nitrenes were recalculated. D values of 1.009, 0.9287, 0.7961, 1.065, and 0.9978 cm^{-1} for 4-chloro-, 4-bromo-, 4-methyl-, 4-nitro-, and 4-methoxyphenylnitrenes and 0.9978 cm^{-1} for phenylnitrene were reported. The value of E in each case was reported to be <0.003, except for 4-methoxyphenylnitrene, where E was given as 0.0039 cm^{-1}.

In studies dealing with the effect of substituents on the re-