structures for the $^1E_3$ state of $C_7H_7^-$ and the $^1A_1$ state of $C_7H_7^+$ are given in Figure 2. The comparison of the two systems is quite difficult in this case, a circumstance due in part to the very large number of structures. The calculation reported here gives the excitation energy $^3A_2$–$^1E_3$ to be 11.4 kcal and $^3A_2$–$^1A_1$ to be 21.2 kcal for the heptagonal negative ion. As far as kinetic processes are concerned either of these is readily accessible from the ground state at normal temperatures.

These calculations on $C_7H_7^+$ and $C_7H_7^-$ show as well as those on the C_5H_5 compounds that the rules used by chemists to judge qualitatively the acceptability of VB structures were designed primarily with the data on stable, singlet substances and that they may work rather poorly when applied to more exotic states.

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Simple *ab Initio* Studies of the Isomers of N_2H_2, Li_2O, C_3H_4, and O_3

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Abstract: The results of a series of FSGO computations including geometry optimizations are reported for the isomers of N_2H_2, Li_2O, C_3H_4, and O_3, and are compared to values obtained from the semiempirical INDO and from conventional *ab initio* procedures. Reasonable FSGO structures are obtained for all of these systems, and some predictions are significantly superior to those of INDO. The FSGO descriptions of cis-trans isomers, highly polarized double bonds, ionic bonds, cumulative double bonds, a double bond in a ring, and a non-Lewis electron structure are examined. Certain kinds of "nonstandard" bonding are shown to be poorly represented, and the energy of double and triple bonds is consistently underestimated. A set of recommended exponents and locations for FSGO bond orbitals is given.

Most of the currently employed methods for determining electronic wave functions initially adopt an atomic orientation and use a linear combination of atomic orbitals to form molecular orbitals. An alternative approach which focuses directly on molecular functions, the floating spherical Gaussian orbital (FSGO) method, has been developed by Frost.[1] This method describes each pair of electrons by a spherical Gaussian orbital, ϕ_i

$$\phi_i = (2\alpha_i/\pi)^{3/4} \exp[-\alpha_i(\mathbf{r} - \mathbf{R}_i)^2] \qquad (1)$$

and approximates the electronic wave function by a Slater determinant of the FSGO's. The exponents α_i and the orbital centers $\mathbf{R}_i$ are determined variationally. Since the calculations require only integrals which can be readily evaluated, FSGO wave functions can be generated for systems of moderate size, and the method is competitive with semiempirical schemes such as CNDO or INDO[2] and with minimum basis set techniques such as STO-3G.[3] In many respects the FSGO method is the simplest *ab initio* procedure yet developed.

FSGO wave functions have the further advantage of being interpretable in terms of classical chemistry, since one can clearly distinguish the location and "size" of the core, bonding, and lone pair orbitals. In fact, the FSGO model can be regarded as a quantum mechanical equivalent of the Lewis electron dot model, and information obtained from calculations on molecules can be related to the highly successful VSEPR theory of Gillespie.[4]

Unfortunately, the FSGO procedure is at best only semiquantitative. The basis set employed is "subminimal" in comparison with conventional minimum basis set calculations; hence, only a rough approximation to the Hartree-Fock result can be obtained. While the method appears to describe simple hydrocarbons reasonably well,[5-9] bond angles and bond lengths for some systems are not predicted accurately.[10,11] It is unclear how much confidence can be placed in numerical results obtained for systems with bonding patterns that have not been previously studied, or for systems which are not adequately described by a single Lewis structure. In the following, we report the results of a series of FSGO computations of the isomers of N_2H_2, Li_2O, C_3H_4, and O_3, and evaluate these results in comparison to values obtained from semiempirical and conventional *ab initio* procedures. These molecules include examples of cis-trans isomerism, highly polarized double bonds, ionic bonds, cumulative double bonds, a double bond in a ring, and a non-Lewis electron structure; they are also species for which semiempirical analyses are often inaccurate. By comparing energies, geometries, and electronic structures of the various isomers, we seek to assess the ability of the FSGO method to deal with these species, and to determine more clearly its applicability as a structural tool in chemistry.

Computational Information

The computations were performed in double precision on an IBM-360-44 computer. The necessary integrals were calculated using formulas given by Frost;[12] the error function related integrals were evaluated using a polynomial approximation developed by Mosier and Shillady.[13] Care was taken to avoid computing integrals which were less than 10^{-13} and to avoid recomputing integrals which had not changed from the previous iteration. Molecular symmetry was not, however, employed in the evaluation of the two-electron integrals.

Table I. FSGO Energies

Molecule	Energy, hartrees
trans-Diimide	−92.977
cis-Diimide	−92.950
1,1-Dihydrodiazine	−92.985 (−92.883)[a]
Lithium oxide (4πe)	−75.272
Lithium oxide (2πe)	−75.449
Propyne	−97.696
Allene	−97.652
Cyclopropene	−98.746
Ozone (open form)	−189.314
Ozone (cyclic form)	−189.656

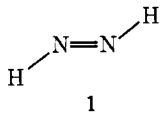
[a] Energy with restricted N=N distance; see text.

Core orbitals were kept on nuclei and their exponents were not varied, but all other orbital locations and exponents, as well as bond lengths and angles, were varied within the constraints of symmetry; bond orbitals were not restricted to bond axes. The constraints suggested by Frost[5] to prevent coalescence of multiple bond orbitals and of lone pair orbitals were enforced.

Three standard minimization routines, PATTERN SEARCH,[14] VAO4A,[15] and STEPIT[16] were employed; STEPIT seemed to be the most useful. Typically, it took 350 iterations to obtain minima for the molecules considered in this paper if reasonably accurate values were supplied as initial guesses. In all cases further minimization might improve the energies slightly, but would be unlikely to make any significant changes in the results. It is dangerous to compare computer programs which have been optimized to different degrees; nevertheless, for the systems we have studied our double precision FSGO calculations took about five times longer than single precision CNDO or INDO results obtained with a slightly modified version of the Dobosh program.[17] This, in turn, is about five times faster than comparable STO-3G calculations.[18]

Detailed information on all wave functions is available from the authors. Computed energies are given in Table I; as in previous FSGO computations,[2,5] these energies are about 85% of the respective Hartree-Fock values.

N_2H_2. In recent years there has been a great deal of interest in the N_2H_2 molecule, for which there are three reasonable structures: *trans*-diimide (**1**), *cis*-diimide (**2**), 1,1-dihydrodiazine (**3**). The trans structure has been established as the ground state of the species,[19] but the use of diimide as a reducing agent for symmetrical double bonds with cis addition[20] suggests the existence of a cis form. In addition, **3** may well be important as a transient species in chemical reactions.[21]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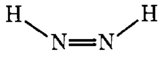
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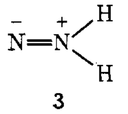
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Both semiempirical and *ab initio* computations for these species are in the literature. Extended Hückel[22] and INDO[23] calculations erroneously predict the cis isomer to be more stable than the trans. Christoffersen[24] has used the FSGO-SCF method (which employs more basis functions than the FSGO approach) to predict the electronic structure and the N=N bond length for structures **1** and **2**. Robin, Hart, and Kuebler,[25] Lehn and Munsch,[26] and Wagniere[27] have reported SCF calculations. Schaad and Kinser[28] have optimized geometries using a minimum basis set SCF approach, with two Gaussians per STO, for **1** and **2**. Wong, Fink, and Allen[29] have optimized geometries for all three isomers using an extensive basis set.

In Table II we compare the relative energies, bond angles, and bond lengths obtained for N_2H_2 from the semiempirical INDO method, the FSGO method, the minimum basis set Schaad and Kinser (SK) calculation, and the large basis set Wong, Fink, and Allen (WFA) values.

Table II. Structures of the Isomers of N_2H_2[a]

	INDO[b]	FSGO	SK[c]	WFA[d]
		trans-Diimide		
E	0	0	0	0
∠N-N-H	109	94.7	104	102.5
r(N=N)	1.23	1.21	1.28	1.20
r(N—H)	1.08	1.01	1.13	1.01
		cis-Diimide		
E	−4.5	17.1	7.5	5.3
∠N-N-H	117	99.4	112	115.5
r(N=N)	1.22	1.22	1.27	1.24
r(N—H)	1.08	1.00	1.13	1.01
		1,1-Dihydrodiazine		
E	22.3	−5.0 (58.9)[e]		7.1
∠N-N-H	125	129 (123)[e]		122
r(N=N)	1.23	1.58 (1.21)[e]		1.28
r(N—H)	1.07	1.00 (0.98)[e]		1.01

[a] Relative energies are in kcal/mol, bond angles are in degrees, bond lengths are in Å. [b] INDO results for *trans*- and *cis*-diimide are from ref 23. Results for 1,1-dihydrodiazine are from M. Zandler, private communication. [c] Minimum basis set results calculated by Schaad and Kinser, ref 28. [d] Extended basis set results computed by Wong, Fink, and Allen, ref 29. [e] See footnote *a*, Table I.

trans-Diimide was chosen as the reference point for the comparison of relative energies. All the *ab initio* methods correctly predict the trans isomer to be more stable than the cis; thus, FSGO appears to be able to distinguish between alternative structures with the same number and type of chemical bonds. FSGO overestimates the energy difference between **1** and **2**; however, the correct value might well be larger than 5.3 kcal.[26,27]

The trend in N-N-H bond angles is predicted correctly by all four methods. The INDO angles for structures **2** and **3** are close to the WFA values, but the angle for structure **1** is too large. FSGO angles for **1** and **2** are much too small. This underestimation of bond angles when one or more lone pair electron orbitals are present is characteristic of the FSGO method.[10,30] When a calculation for *cis*-diimide with a fixed N-N-H angle of 115.5° was performed, the lone pair orbitals contracted and moved farther away from the nitrogen nuclei, supporting an earlier conclusion that FSGO lone pair orbitals are too diffuse and located too near the parent nucleus.[30] N=N distances predicted by the FSGO method for **1** and **2** are in reasonable agreement with WFA, with the correct trend observed going from trans to cis; the minimum basis set results are too long. FSGO N-H bond lengths are in excellent agreement with WFA, while both INDO and SK bond lengths are considerably larger. Exponents for comparable bonds between the cis and trans isomers are almost exactly equal (±<2%); the 1,1-dihydrodiazine lone pair orbitals are slightly more diffuse, and the N-H orbitals are slightly more compact.

Due to the highly polarized double bond of 1,1-dihydrodiazine, two different computations were performed on this isomer. In the first (i) all geometric parameters were varied, and in the second (ii) the N=N bond length was held at the average of the values calculated for **1** and **2**. Computation i predicted a N=N bond length of 1.58 Å, much larger than the WFA value, and an energy of −92.985 hartrees. This energy is *lower* than those calculated for the cis and trans isomers, and indicates that FSGO is not treating the polarized $N{=}NH_2$ double bond properly. An inspection of the orbital locations reveals that the double bond orbitals have overcompensated for the polarization, and moved so near

Table III. Molecular Orbital Structures of N_2H_2[a,b]

trans-Diimide			*cis*-Diimide			1,1-Dihydrodiazine		
MO	FSGO	LCAO–SCF	MO	FSGO	LCAO–SCF	MO	FSGO	LCAO–SCF
$1a_g$	12.902		$1a_1$	12.899		$1a_1$	13.008 (12.880)[c]	
$1b_u$	12.901		$1b_2$	12.903		$2a_1$	12.738 (12.822)	
$2a_g$	1.300	1.41	$2a_1$	1.298	1.37	$3a_1$	1.067 (1.240)	1.32
$2b_u$	0.809	0.93	$2b_2$	0.803	0.94	$4a_1$	0.868 (0.822)	0.94
$3a_g$	0.396	0.66	$3a_1$	0.566	0.76	$1b_2$	0.393 (0.538)	0.76
$3b_u$	0.479	0.65	$4a_1$	0.320	0.56	$5a_1$	0.248 (0.295)	0.57
$1a_u(\pi)$	0.194	0.53	$1b_1(\pi)$	0.189	0.52	$1b_1(\pi)$	0.087 (0.201)	0.52
$4a_g$	0.193	0.40	$3b_2$	0.209	0.40	$2b_2$	0.262 (0.116)	0.37

[a] Energies are the negative of orbital energies. [b] LCAO–SCF results taken from a figure in ref 29. [c] See footnote *a*, Table I.

the nominally positively charged nitrogen (within 0.14 Å) that the molecule takes on the appearance of an N^+ ion and NH_2^-. The species will not dissociate, as the calculated energy of the diazine is lower than the sum of the FSGO energies of the two ions (−92.671 hartrees), but the electronic structure is certainly not reasonable. Effectively, the double bond electrons have become lone pair electrons of the NH_2 nitrogen. This suggests that the FSGO model treats lone pair electrons with less energetic error than double bonds; consequently, the minimization process has forced this transformation to occur. If the N═N bond length is fixed as in computation ii, this transformation cannot occur. In this case the double bond orbitals are located near the middle of the bond (69% of the distance to the NH_2 nitrogen), and reasonable properties are predicted. A moderate lengthening of the N═N bond would improve the relative energies.

These interpretations are supported by the FSGO molecular orbital structures given in Table III. Although a single Gaussian orbital is clearly not a molecular orbital, in that it is not orthogonal to the other orbitals, does not possess the appropriate symmetry, and is not an eigenfunction of the Fock operator, a simple transformation enables one to determine the molecular orbitals of the system. The orbital energies obtained in this manner are generally not quantitatively correct (which is not surprising since the total energy is so poor), but the relative ordering of the molecular orbitals allows one to further assess the quality of the subminimal FSGO basis set.

An examination of Table III reveals that ordering of valence molecular orbitals is generally correct. For *trans*-diimide the $3a_g$ and $3b_u$ FSGO-MO's are reversed. Since the $3a_g$ orbital contains a large σ contribution from the N═N double bond, this implies a relatively poor energetic description of that bond. The $3b_2$ and $1b_1$ (π) orbitals of *cis*-diimide are also reversed, which is again consistent with a poor description of double bonds. It is interesting to note that the FSGO-SCF procedure, which employs extra basis functions in the double bond region, over-corrects this deficiency in the basis set in this instance, and yields a $1b_1$ (π) orbital which is lower in energy than the $4a_1$ orbital.[24] The FSGO molecular orbitals of 1,1-dihydrodiazine, for the optimized N═N bond length, are in substantial disarray, with the $1b_1$ (π) orbital very poorly described, but the restricted bond length MO's are in perfect agreement with the LCAO-SCF results given by Wong, Fink, and Allen.[29]

Thus, the FSGO model treats the "standard" bonding in *cis*- and *trans*-diimide with reasonable accuracy, but will not always successfully describe a structure in which the "type" of orbitals is subject to change without additional constraints.

Li_2O. Generally, triatomic molecules with a central oxygen atom have a nonlinear equilibrium geometry; Li_2O is unusual in that it is an exception to this rule.[31] This departure from a conventional sp^3 hybridization scheme has been attributed to the highly ionic nature of the Li-O bonds;[32] the repulsions between the two positively charged lithium atoms presumably keeps the molecule linear. SCF calculations employing extensive basis sets correctly predict linearity and yield reasonable bond lengths.[33,34] Wagner[34] has noted, however, that "the CNDO and INDO methods incorrectly imply stable bent structures with very acute apex angles and very long Li-O distances." Thus, Li_2O is an excellent example of the breakdown which can occur in semiempirical schemes when unusual molecules or structures are examined. Since FSGO is the simplest *ab initio* method and is timewise competitive with INDO, it presents an attractive computational alternative in this instance. Moreover, Li_2O is a suitable test case for determining how FSGO treats highly ionic structures with respect to both bond angles and lengths.

Table IV. Structure of Lithium Oxide[a]

	INDO	FSGO ($4\pi e$)	Exptl
∠Li-O-Li, deg	50	180	180
r(Li-O)	2.45	1.51	1.60

[a] INDO results from ref 34; experimental values from ref 31.

We have found two different minima in the FSGO potential surface, corresponding to two different singlet states. In the first state the bonding might best be described as distorted sp^3, with the lithium atoms located along the bisector of the FSGO-oxygen nucleus-FSGO angles. All bond orbitals were quite close to the oxygen nucleus, yielding the anticipated $Li^+O^{2-}Li^+$ structure. This structure has four electrons in π orbitals, and clearly is the state determined experimentally. As shown in Table IV, the predicted geometry is quite reasonable. The second state corresponds to an sp bonding situation, where the limitations of the basis set allow only two electrons to be in π orbitals. This structure is also linear, with a very large bond length of 3.06 Å. As indicated in Table I, the FSGO method predicts the second state to be the lower in energy; this is certainly incorrect. The reason for this erroneous prediction can be seen by inspecting the orbital energies in Table V. Although the valence MO's of the $4\pi e$ form of Li_2O are ordered correctly, the higher MO's have positive orbital energies. The $1\pi_u$ pair of MO's, with four electrons, are much too high in energy. This is the same poor description of π electrons noted in N_2H_2; since the second state of Li_2O only has $2\pi e$, its energetic description is presumably more accurate.

Thus for molecules of this type, the FSGO model appears to be able to predict the geometry of certain states to reasonable accuracy, but does not accurately predict the order of the states.

C_3H_4. The C_3H_4 isomers, allene, propyne, and cyclopropene, have been studied by Radom, Lathan, Hehre, and

Table V. Molecular Orbital Structures of Li_2O[a,b]

Li_2O ($2\pi e$)	FSGO	Li_2O ($4\pi e$)	FSGO	LCAO–SCF
$1\sigma_g$	17.827	$1\sigma_g$	16.716	20.2
$1\sigma_u$	1.824	$2\sigma_g$	1.669	2.3
$2\sigma_g$	1.816	$1\sigma_u$	1.683	2.3
$3\sigma_g$	1.560	$3\sigma_g$	0.820	0.95
$1\pi_u$	0.731	$2\sigma_u$	−0.121	0.25
$4\sigma_g$	0.154	$1\pi_u$	−0.165	0.22
$2\sigma_u$	0.148			

[a] Energies are the negative of orbital energies. [b] LCAO–SCF energies are estimated from a figure in ref 34.

Pople.[35] These authors have computed geometries for these molecules using the minimum basis set STO-3G method, and have determined relative energies and dipole moments using larger basis sets. Similar SCF calculations using Gaussian lobe functions have been reported by Peyerimhoff and Buenker.[36]

Previous FSGO calculations of hydrocarbons, including methane, ethane, propane, butane, ethylene, propylene, acetylene, cyclopropane, and cyclobutane, have generally yielded excellent geometries, with bond angles never in error by more than 2°.[5-8] The C_3H_4 series of compounds, however, provides several bonding patterns often encountered in organic chemistry but not previously studied with the FSGO model, such as the CC≡C bonding in propyne, cumulative double bonds in allene, and a cyclic double bond in cyclopropene. We have tested the ability of the FSGO model to describe these features.

The relative energies and geometries of the three isomers are presented in Table VI. All three theoretical methods predict generally good geometries. The average error in predicted carbon–carbon bond lengths is about 2% for all three methods. C–H bond lengths are predicted most accurately by STO-3G (0.5%), next most accurately by FSGO (1.5%), and least accurately by INDO (3%). As one would expect, STO-3G gives accurate bond angle predictions for all three isomers, while INDO is somewhat less accurate, with a 5° error for the H–C–H angle in allene and a 6° error for the H–C–H angle in cyclopropene. What is surprising, however, is the relatively poor prediction of bond angles made by FSGO. The average error is 4°, and the H–C–H angle in allene is 8° too large! Apparently the earlier good angle predictions of FSGO were somewhat fortuitous. We note further that the double bond orbitals in allene are more compact than those of ethylene or propylene. This effect is probably caused by electron repulsions between the cumulative double bonds, and is a likely cause for the large H–C–H bond angle. We have performed two additional calculations on allene in which the double bond orbitals were held 0.3 and 0.6 bohr off the C–C–C axis, respectively, instead of the standard 0.1 bohr. These calculations gave poorer energies (−97.628 and −97.513 hartrees) and only moderately better bond angles (124 and 122°).

Both INDO and FSGO correctly predict that propyne is more stable than allene. At the same time, both methods incorrectly predict cyclopropene (with one less π bond than the other isomers) to be the most stable instead of the least stable isomer. The INDO result is expected, since it is well known that the INDO and CNDO parameterization schemes are biased toward small rings. We suggest that the incorrect FSGO prediction is caused not by a bias toward small rings, but by a poor energetic description of multiple bonds. In related results, Linnett[7] has noted that FSGO incorrectly predicts cyclopropane to be more stable than propene. A better description of multiple bonds is needed before FSGO will accurately predict relative energies.

Table VI. Structures of the Isomers of C_3H_4[a]

	INDO	FSGO	STO-3G	Exptl
	Propyne			
E	0	0	0	0
∠H-C-H, deg	108	113	108	109
r(C≡C)	1.21	1.21	1.17	1.21
r(C—C)	1.44	1.49	1.48	1.46
r(C—H, ethynyl)	1.10	1.08	1.06	1.06
r(C—H, methyl)	1.12	1.10	1.09	1.10
	Allene			
E	19.4	27.6	17.1	2.1
∠H-C-H, deg	113	126	116	118
r(C=C)	1.31	1.34	1.29	1.31
r(C—H)	1.11	1.09	1.08	1.09
	Cyclopropene			
E	−41.5	−31.4	30.0	22.3
∠H—C—H, deg	109	110	112	115
∠C=C—H, deg	154	150	150	150
∠C=C—C, deg	63	63.3	64.7	64.6
r(C=C)	1.34	1.36	1.28	1.30
r(C—C)	1.48	1.52	1.50	1.52
r(C—H, vinyl)	1.10	1.10	1.09	1.09
r(C—H, methylene)	1.12	1.11	1.08	1.07

[a] INDO and FSGO results are from the present study; STO-3G and experimental values are from ref 35.

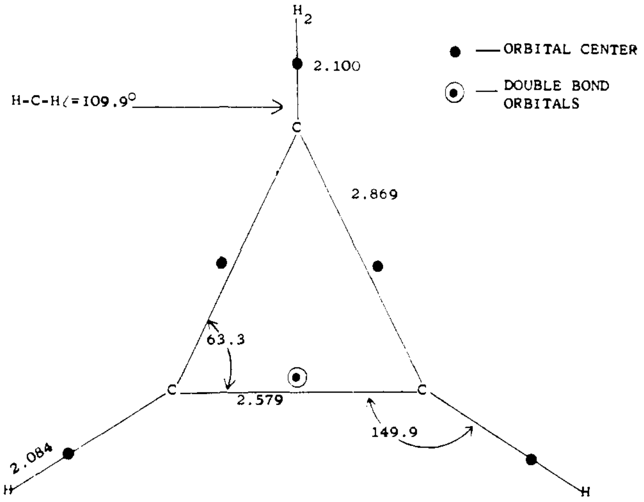


Figure 1. Projection diagram of cyclopropene in the plane of the ring. FSGO predicted bond lengths and bond angles are shown. Core orbitals are not included.

Frost has shown that the FSGO C–C bonding orbitals in cyclopropane form bent bonds, in that they lie outside of the bond axes. This prediction of the FSGO model is clearly related to a relaxation of ring strain process. In studying cyclopropene, we have found (Figure 1) that the C–C orbitals move out of the ring, as expected, but the C=C double bond orbitals move *into* the ring. This can only be regarded as a transfer of π character toward the CH_2 group, and, indeed, is also predicted by conventional *ab initio* techniques.[35] Despite this movement of π charge density, the FSGO model predicts a dipole moment of 0.13 D in the *same* direction as the experimental result of 0.45 D[37] (away from the CH_2), while a 6-31G SCF calculation yields a dipole of 0.54 D in the opposite direction.[35] Equally good dipole moment predictions are made for propyne; all methods predict the methyl end to be positive, with the respective values: INDO, 0.21 D; FSGO, 0.97 D; STO-3G, 0.50 D;[38] exptl, 0.75 D.[39] Of course, calculated dipole moments are strongly dependent upon the nuclear geometries employed, so these computed moments may not necessarily be indica-

Table VII. Molecular Orbital Structures of C_3H_4[a,b]

Propyne			Allene			Cyclopropene		
MO	FSGO	LCAO-SCF	MO	FSGO	LCAO-SCF	MO	FSGO	LCAO-SCF
$1a_1$	9.193	11.250	$1a_1$	9.216	11.279	$1a_1$	9.165	11.254
$2a_1$	9.170	11.248	$1b_2$	9.150	11.241	$1b_2$	9.140	11.252
$3a_1$	9.089	11.227	$2a_1$	9.116	11.241	$2a_1$	9.126	11.240
$4a_1$	0.977	1.059	$3a_1$	0.973	1.079	$3a_1$	1.046	1.169
$5a_1$	0.843	0.959	$2b_2$	0.850	0.963	$4a_1$	0.724	0.828
$6a_1$	0.617	0.715	$4a_1$	0.600	0.711	$2b_2$	0.682	0.764
$7a_1$	0.444	0.616	$3b_2$	0.421	0.624	$5a_1$	0.535	0.683
$1e(\pi)$	0.481	0.586	$1e(\pi)$	0.484	0.614	$1b_1(\pi)$	0.441	0.602
$2e(\pi)$	0.152	0.381	$2e(\pi)$	0.156	0.374	$6a_1$	0.281	0.491
						$3b_2$	0.243	0.419
						$2b_1(\pi)$	0.123	0.352

[a] Energies are the negative of orbital energies. [b] LCAO-SCF results from ref 36.

Table VIII. Structures of the Isomers of O_3

	INDO	FSGO	Exptl[a]
	Ozone (open form)		
E	0	0	0
$\angle$O-O-O, deg	120	122	117
r(O-O)	1.17	1.11	1.28
	Ozone (cyclic form)		
E	−144.5	−215.0	[83-95]
r(O-O)	1.24	1.20	1.41, 1.46

[a] Experimental geometry for open form of ozone from G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand-Reinhold, New York, N.Y., 1966; estimated experimental results for cyclic form from ref 40 and 41 and from W. R. Wadt and W. A. Goddard III, *J. Amer. Chem. Soc.*, **96**, 1689 (1974).

Table IX. Molecular Orbital Structures of O_3[a,b]

Ozone (open form)			Ozone (cyclic form)		
MO	FSGO	LCAO-SCF	MO	FSGO	LCAO-SCF[c]
$1a_1$	17.875	20.890	$1e'$	17.281	20.82
$1b_2$	17.061	20.726	$1a_1'$	17.242	20.82
$2a_1$	17.061	20.726	$1a_1'$	1.878	1.95
$3a_1$	1.879	1.723	$2e'$	1.104	1.30
$2b_2$	1.347	1.426	$1a_2''(\pi)$	0.544	0.92
$4a_1$	0.925	1.111	$3a_1'$	0.449	0.79
$5a_1$	0.521	0.817	$3e'$	0.277	0.73
$3b_2$	0.501	0.781	$1e''(\pi)$	0.072	0.60
$1b_1(\pi)$	0.387	0.760			
$4b_2$	0.096	0.581			
$6a_1$	0.088	0.566			
$1a_2(\pi)$	0.104	0.491			

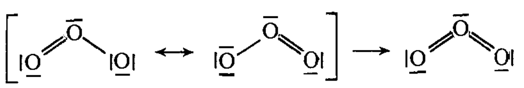
[a] Energies are the negative of orbital energies. [b] LCAO-SCF results from S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.* **47**, 1953 (1967). [c] Estimated from a graph; see footnote *b*.

tive of the validity of the approximate charge distributions.

The molecular orbital structures given in Table VII contain no surprises. The ordering of the orbitals of cyclopropene is in complete agreement with the LCAO-SCF results obtained by Peyerimhoff and Buenker.[36] The $1e(\pi)$ orbitals of both propyne and allene are interchanged with the levels beneath them in the FSGO computations, but both LCAO-SCF and FSGO energy differences between these orbitals are quite small. INDO orbital orderings display the same error. The $1e(\pi)$ orbitals in both molecules possess large contributions from C-H bond FSGO's, so these results are not inconsistent with those obtained for N_2H_2 and Li_2O.

O_3. The most stable form of ozone is known to be an open chain with a bond angle of 117°; however, schemes such as CNDO/2,[40] INDO, MINDO,[40] and even the minimal basis set STO-3G approach[41] incorrectly predict the equilateral triangle form to be most stable. Although based on the C_3H_4 results one would anticipate that FSGO would also predict the cyclic form to be most stable, we thought it appropriate to calculate the FSGO wave functions and geometries since standard electron dot diagrams require two equally important resonance structures for the open form of O_3. The ability of the FSGO model to describe such species is subject to question. One could employ a two-configuration wave function, but this would complicate the FSGO method ; besides, single-configuration wave functions using LCAO-MO procedures yield moderately accurate geometries for O_3.

We have chosen to model the open form of ozone using a structure which nominally possesses two double bonds and to rely on the optimization of orbital locations to reduce the number of electrons near the central oxygen and to extend π character to the "lone pair region" of the end atoms.



The computed structures for the two isomers of ozone are given in Table VIII. As anticipated, the ordering of energies is incorrect, with the ring structure predicted to be most stable. The bond angle for the open form is in error by 5°. Bond lengths in both isomers are too short; the FSGO bond length for singlet O_2 is too short by about the same amount (1.07 Å calculated *vs.* a Hartree-Fock value of 1.23 Å[42]). The difference between the calculated cyclic and open form bond lengths, 0.09 Å, is about what one would expect, but no experimental bond lengths are available for the cyclic form for purposes of comparison. Given the non-Lewis nature of the open form, it is described quite well by the FSGO model. Figure 2 shows that the double bond orbitals have, as expected, moved quite near the end oxygen nuclei. If these electrons are partitioned as per their position, three to each end atom and two (one from each double bond) to the central atom, a picture remarkably like that used by Takahata, Schnuelle, and Parr[43] to predict bond angles and bending force constants emerges.

The FSGO double bond can be transformed into conventional σ and π orbitals by considering, respectively, the sum and the difference of the banana bonds.[5] Unfortunately, the FSGO model requires both σ and π orbitals to be polarized to the same extent; *i.e.*, they are centered at the same point. If this restriction were removed, we anticipate that the σ orbital would move nearer the center of the bond. This separation of the two orbitals should significantly lower the energy of the open form. This failure to allow for different polarizations in the FSGO double bond (which would require more basis functions) could well be the predominant reason for the poor relative energies of the two isomers. In support

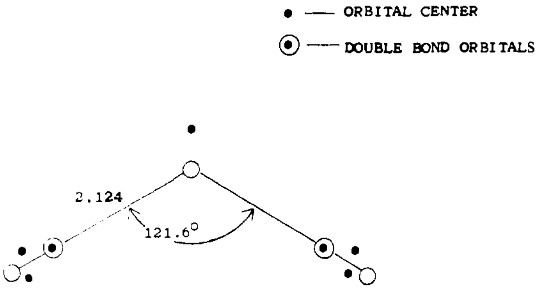


Figure 2. FSGO structure for open form of ozone. Bond lengths and angles are as indicated. Core orbitals are not included.

of this, we note (Table IX) that the FSGO-MO's of the cyclic form of ozone have the same order as the LCAO-SCF orbitals, but that in the open form the $4b_2$ and $6a_1$ orbitals, which primarily consist of the σ portions of the O-O bonds, are too high in energy.

The end atom lone pair electrons of the open form of O_3 are on the "wrong side" (in the bonding region), as are the lone pair electrons of H_2O.[10] The lone pair electrons for the cyclic form are, however, outside of the ring, in accord with chemical intuition. Symmetrically orthogonalized molecular orbitals would yield more realistic pictures of the location of various orbitals, but an accurate description of these functions would require a series of contour diagrams, which we have avoided here for reasons of space.

Discussion

The preceding results illustrate the strengths and weaknesses of the FSGO model. With the exception of the charge transfer double bond in 1,1-dihydrodiazine, the bonding features we have considered are described at least semiquantitatively. Cis-trans isomerization problems and ionic bonding situations are better characterized by FSGO than by CNDO or INDO. Hydrocarbons are generally well-described, but perhaps are not quite as accurately treated as previous calculations[5-9] might suggest. The ozone computations indicate that useful results can be obtained for molecules which have two important resonance structures. The FSGO model is not capable of making accurate energy comparisons between isomers with different numbers of multiple bonds. In general, the FSGO model of singlets is a useful alternative to the often less accurate semiempirical methods or to the more time-consuming *ab initio* LCAO-MO procedures.

The FSGO model could well be applied to larger species (Frost, for example, has studied cyclopentane[44]); however, one encounters serious difficulties due to the large number of nonlinear parameters. The number of parameters to be varied can be reduced by making several simplifications which do not seriously affect structural predictions. It has already been noted, for instance, that core orbitals can be frozen in terms of both size and location without major effects. In the current calculations we have found that in all the nonring structures, bond orbitals are located almost exactly on bond axes. Even in the cases of cyclopropene and cyclic ozone, forcing the bond orbitals to be on the bond axes increases the energy less than 5 kcal. Thus, we concur with the suggestion recently made by Blustin and Linnett[7] that bond orbitals be restricted to bond axes, where their location can be determined by one "orbital multiplier" instead of three Cartesian coordinates.

Along with these simplifications, it would be useful to have a set of recommended orbital exponents and multipliers for various bonds (see ref 6 and 7). These values would provide good starting points for calculations which minimize all parameters; they could also be used in calculations which did not optimize all orbital parameters, but instead emphasized only those orbitals which were of particular interest. In many molecules, for example, one expects that the C-H bond orbitals are not of pivotal importance and little would be lost by using standard exponents and multipliers. A partial list of these bond-orbital parameters, determined from the calculations of Frost and coworkers[5,6,10] and those of Linnett and coworkers[7,8,9] as well as the present results, is given in Table X.

Table X. Some Recommended Orbital Exponents and Multipliers

Orbital	Bond type	Exponent	Multiplier[a]
C—H	Methyl	0.351	0.599
C—H	Methylene	0.360	0.606
C—H	Vinyl	0.373	0.621
C—H	Ethynyl	0.399	0.596
N—H	NH_3	0.414	0.418
N—H	$—NH_2$	0.436	0.485
N—H	=NH	0.455	0.508
C—C	Open chain	0.369	0.500
C—C	C—C=C or C—C≡C	0.383	0.500
C—C	Small ring	0.325	0.500
C=C	Open chain	0.311	0.500
C=C	Small ring	0.296	0.500
C≡C		0.316	0.500
N=N		0.442	0.500
N≡N		0.476	0.500

[a] Multiplier = (distance from heavy atom to center of bond orbital)/bond length.

The poor behavior of lone pair electrons, particularly as they affect bond angles, remains a disturbing aspect of the FSGO model. One could employ additional basis functions to describe the lone pair orbitals; however, Tan and Linnett[45] have shown that a combination of five Gaussians is required for a variationally minimized lone pair orbital before an accurate bond angle is predicted for NH_3. This would certainly be impractical in most FSGO calculations. Since total energy is not accurately predicted in any case, we suggest that an appropriate standard set of nonvariationally determined lone pair exponents and distances might be much more useful for the prediction of molecular properties, and could further reduce the number of parameters to be varied.

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On Additivity Rules in Molecular Thermodynamics

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Abstract: Benson and Buss have shown that molecular heat capacities and entropies can be moderately well estimated as sums of empirical atomic contributions. This additivity approximation is examined from the standpoint of statistical thermodynamics and the atomic parameters are semiquantitatively accounted for. The dominant role of atomic ligancy on the translational part of the entropy is explained. On the level of atomic additivity, molecular vibrations can be likened to the modes of a heteroatomic Einstein crystal. Possibilities for more elaborate atomic parametrization schemes are discussed.

1. Introduction

Heat capacities and entropies of molecular substances in the ideal gaseous state can be estimated to moderate accuracy on the basis of atomic additivity rules. Benson and Buss,[1] in their detailed study of thermodynamic additivity principles, assigned a set of empirical values, reproduced in Table I, for atomic contributions to molar heat capacity $\bar{C}_p°$ and entropy $\bar{S}°$ at 298°K. Within the group of 75 compounds they considered, the atomic additivity assumption for $\bar{C}_p°$ and $\bar{S}°$ was generally good to within ±2 cal/(°K mol). (For symmetrical molecules, $R \ln \sigma$ is subtracted from the sum of atomic entropies.)

In Table I, l stands for the ligancy of an atom: the number of other atoms directly bonded to it. For example, C has a ligancy of 4 in CH_4, 3 in C_2H_4, 2 in C_2H_2, and 1 in CO. It is striking that atomic entropies are predominantly dependent on ligancy whereas heat capacities appear relatively insensitive.

In the scheme developed by Benson and Buss, additivity of atomic properties plays the role of a zeroth-order approximation. The corresponding first- and second-order approximations involve additivity of bond contributions and of group contributions, respectively.[2] Our concern in this paper will, however, be limited to atomic additivity.

It is perhaps remarkable that such additivity principles work at all. The theoretical calculation of thermodynamic properties from molecular parameters and spectroscopic data by the methods of statistical mechanics is, of course, well established.[3] To a high level of approximation, the relevant parameters are just molecular weight, moments of inertia, fundamental vibrational frequencies, and symmetry number (plus, in special situations, electronic contributions, internal rotational barriers, etc.). The molecular weight enters, of course, *via* its logarithm and none of the other parameters is, at first glance, anything with an additive atomic structure. It will be our purpose to account semiquantitatively for the nature of atomic contributions to heat capacity and entropy and to show why additivity approximations work even as well as they do.

2. Heat Capacity

For an n-atomic molecule in the ideal-gas limit

$$\bar{C}_p° = \begin{cases} 4R + \sum_{i=1}^{3n-6} C(\nu_i) & \text{(non-linear)} \\ {}^7\!/_2 R + \sum_{i=1}^{3n-5} C(\nu_i) & \text{(linear)} \end{cases} \tag{1}$$

where the ν_i are fundamental vibrational frequencies. Electronic contributions are assumed to be negligible at the temperature considered. In the harmonic approximation, $C(\nu_i)$ is the Einstein heat-capacity function.

$$C(\nu_i) = \frac{R x_i^2 e^{x_i}}{(e^{x_i} - 1)^2}, \quad x_i = \frac{hc}{kT}\nu_i(\text{cm}^{-1}) \tag{2}$$