Absolutely Minimal Basis Set Descriptions of Resonant Systems

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Abstract: The ability of wave functions constructed from absolutely minimal basis sets to describe resonant molecules is investigated. FSGO calculations are reported on the s-cis and s-trans conformers of 1,3-butadiene, furan, pyrrole, the histamine monocation, pyridine, and benzene. Orbital energies, dipole moments, charge distributions, and orbital locations are presented and discussed. The results suggest that for resonant molecules such as furan, where there is one dominant resonance structure, the variational flexibility associated with orbital optimization allows the FSGO wave functions to describe the resonance. Systems such as pyridine and benzene can only be described by an absolutely minimal basis set if both s and p Gaussians are used.

In conventional usage, the term "minimum basis set" refers to the smallest set of atomic orbitals needed to describe a given molecule. For water, as an example, a minimum basis set consists of seven functions (each of which may be written as a combination of simpler functions or primitives): a 1s, a 2s, and three 2p orbitals centered on the oxygen and a 1s orbital centered on each hydrogen. Similarly, a minimum basis set for a molecule such as butane contains 30 atomic orbitals. These basis sets are not, however, truly minimal, in that the smallest basis set which could be employed to describe an N electron system (if N is even) need contain only $N/2$ basis functions. An absolutely minimal basis set, or Lewis basis,[1] consists of core, bonding, and lone pair basis orbitals instead of atomic orbitals, and therefore requires only 5 and 17 basis functions to respectively describe water and butane. Absolutely minimal basis sets are attractive in that they may be directly associated with classical Lewis structures. In addition, they avoid the basis set imbalance which occurs when LCAO wave functions describe isoelectronic systems with different numbers of nuclei. Since the number of two-electron integrals increases[2] as the number of basis functions to the fourth power, subminimal or absolutely minimal basis sets offer enormous computational advantages when applied to large systems,[3,4] and can allow calculations to be made which would have been impractical with conventional minimal basis sets.

One absolutely minimal basis set scheme, the floating spherical Gaussian orbital (FSGO) method, has been developed by Frost and co-workers[5] and has been applied to a number of chemical systems.[6] The method uses spherical Gaussians to represent core, bonding, and lone pair orbitals and provides variational flexibility through an optimization of the exponents and locations of the Gaussians. Absolute energies are poor, but a number of properties of a variety of systems have been predicted with surprising accuracy.[6-10] No one, however, appears to have yet addressed the question of whether this (or any other) absolutely minimal basis set method can treat chemical systems where resonance occurs. Since most of the traditional explanations of resonance are couched in terms of delocalized combinations of atomic orbitals and, since single Lewis structures do not lend themselves to these arguments, it has been generally assumed that FSGO wave functions cannot usefully describe resonant molecules. This need not be the case. The flexibility associated with the floating nature of the FSGOs could, in at least some cases, allow incorporation of resonance effects into the wave functions. If this is observed, it might be of considerable consequence for future applications of the FSGO method to large systems, and would provide an alternative picture of the resonance phenomenon. In considering this question, we have found it useful to divide molecules of interest into three categories: (i) aliphatic systems such as 1,3-butadiene; (ii) aromatic species with one dominant resonance structure, such as furan, pyrrole, and the histamine monocation; and (iii) molecules with two or more strongly contributing resonance structures, such as ozone, pyridine, and benzene. In the following we present and analyze the results of a series of calculations on these species and categories which are designed to determine the quality and usefulness of the FSGO description of resonant systems.

Our computational procedures have been described previously.[8] Detailed information regarding the various wave functions is available from the authors.

1,3-Butadiene

1,3-Butadiene is the simplest conjugated diene, a class of molecules which is somewhat more stable to hydrogenation than molecules with isolated double bonds. This increased stability has been variously attributed either to the increased s character of the central C–C single bond or to resonance involving a C–C=C–C structure. We have performed FSGO calculations on both the s-cis and s-trans conformers of this molecule at standard geometries.[11] Total and orbital energies for both conformers are presented in Table I, where they are compared to LCAO values. The s-trans conformer is correctly predicted to be the more stable, but, as in previous FSGO conformational studies,[6-8] the energy difference between conformers is overestimated. The predicted electronic structures for both conformers are correct in that, with the exception of the nearly degenerate $6b_u$–$6a_g$ orbital pair, orbital orderings parallel those given by Buenker and Whitten.[11] The FSGO π molecular orbitals ($1b_1$, $1a_2$, $1a_u$, and $1b_g$) are observed to be energetically inferior in comparison to the σ molecular orbitals; this may be due to resonance or may be part of a previously observed[8] FSGO energetic bias against π orbitals. The absolutely minimal basis set is sufficient to monitor differences in comparative orbital energies between the conformers: $\epsilon(3b_u)$ of the trans is more negative than $\epsilon(3b_2)$ of the cis, $\epsilon(5a_g)$ of the trans is less negative than $\epsilon(5a_1)$ of the cis, and so on.

A pictorial representation, in the spirit of a Lewis diagram, is given for the FSGO wave function of the s-trans conformer in Figure 1. Orbital centers for the valence FSGOs are indicated. The patterns of bonding are similar to those previously found in propene[12] and 2-butene.[13] The double bond orbitals are located closer to the terminal carbons (49.3% of the bond length compared to 49.1% in propene), and the C–H orbitals are located essentially on their respective bond axes some 61 or 62% of the bond length away from the carbon atoms. Exponents for C=C, C–C, and C–H bonding orbitals agreed well with values for ethylene and propylene. Figure 1 suggests that a classical charge decomposition, in which bonding electrons

Table I. Orbital Energies for Butadiene

	Cis				Trans			
Method	FSGO		LCAO–SCF[a]		FSGO		LCAO–SCF[a]	
Basis set	15		130 contracted to 30		15		130 contracted to 30	
Energy	−130.6712		−154.7023		−130.6947		−154.7103	
	$1a_1$	−9.1599	$1a_1$	−11.3463	$1a_g$	−9.1613	$1a_g$	−11.3466
	$1b_2$	−9.1554	$1b_2$	−11.3457	$1b_u$	−9.1542	$1b_u$	−11.3459
	$2a_1$	−9.1152	$2b_2$	−11.3045	$2a_g$	−9.1221	$2b_u$	−11.3098
	$2b_2$	−9.0917	$2a_1$	−11.3045	$2b_u$	−0.0926	$2a_g$	−11.3098
	$3a_1$	−1.0063	$3a_1$	−1.1155	$3a_g$	−1.0035	$3a_g$	−1.1089
	$3b_2$	−0.8850	$3b_2$	−1.0109	$3b_u$	−0.9004	$3b_u$	−1.0214
	$4a_1$	−0.7525	$4a_1$	−0.8570	$4a_g$	−0.7321	$4a_g$	−0.8381
	$4b_2$	−0.6252	$4b_2$	−0.7442	$4b_u$	−0.6456	$4b_u$	−0.7751
	$5a_1$	−0.5381	$5a_1$	−0.7073	$5a_g$	−0.4999	$5a_g$	−0.6638
	$6a_1$	−0.4515	$6a_1$	−0.6292	$5b_u$	−0.4916	$5b_u$	−0.6603
	$5b_2$	−0.4326	$5b_2$	−0.6022	$6b_u$	−0.4210	$6a_g$	−0.5942
	$6b_2$	−0.3720	$6b_2$	−0.5370	$6a_g$	−0.3837	$6b_u$	−0.5693
	$7a_1$	−0.3692	$7a_1$	−0.5261	$7a_g$	−0.3619	$7a_g$	−0.5140
	$1b_1$	−0.1966	$1b_1$	−0.4768	$1a_u$	−0.1903	$1a_u$	−0.4765
	$1a_2$	−0.0911	$1a_2$	−0.3541	$1b_g$	−0.1179	$1b_g$	−0.3579

[a] Reference 11; fourth decimal figure on orbital energies cited by M. Krauss, *Natl. Bur. Stand.* (*U.S.*), *Tech. Note*, **No. 438** (1967).

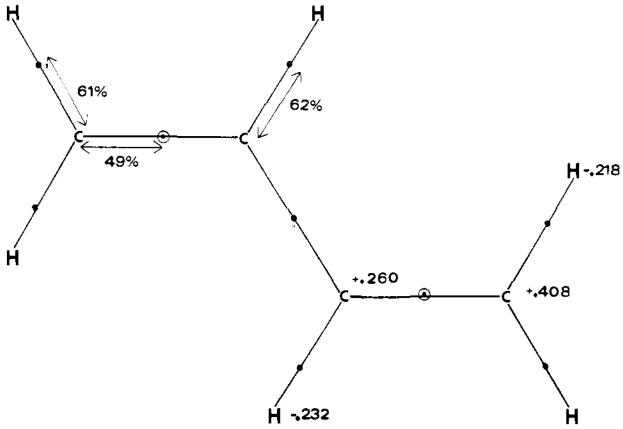


Figure 1. FSGO structure for *s-trans*-1,3-butadiene. Centers of orbitals are indicated; ⊙ denotes a pair of banana bond orbitals. Core orbitals are not included.

are apportioned according to their location (50% of the bond length implies equal sharing, 100% implies total ionic character, etc.), might be profitable. We have previously applied this partitioning procedure to diatomics,[14] and have obtained atomic charges which, although usually reflecting a greater degree of electron transfer than LCAO–Mulliken values do, were in excellent agreement with electron populations derived from zero-flux partitioning surfaces.[15] Moreover, anticipated chemical trends were faithfully reproduced. Calculated charges are included in Figure 1. One notes that the classical decomposition procedure yields negatively charged hydrogens. This is consistent with the observation that alkyl groups are usually more electron donating than hydrogens; the carbon of interest would be assigned ~50% of a C–C electron pair instead of ~40% of a C–H pair. Since the secondary carbons possess smaller positive charges than the primary carbons, they should accept the loss of some C=C electrons more readily, and one would therefore predict that electrophilic addition would proceed via addition of H^+ to a terminal carbon. Lastly, the methylene-like hydrogens are predicted to be slightly less negative (hence more acidic) than the other hydrogens, in agreement with experiment.

In summary, the absolutely minimal basis set gives a chemically viable description of 1,3-butadiene, and there is little evidence that resonance is playing a significant role.

Furan and Pyrrole

Furan and pyrrole are typical examples of a large class of heterocyclic molecules which are aromatic but still possess one dominant resonance structure. Our approach to these systems has been to model the initial FSGO configuration after the dominant structure and subsequently allow variational optimization of FSGO exponents and locations. Experimental geometries were employed. Energies for both species are compared to large basis set LCAO-SCF values in Table II. The FSGO orbital structures are not entirely satisfactory; the π orbital energies ($1b_2$, $2b_2$, and $1a_2$) are overly positive so that the $1b_2$ orbital is misplaced. In addition, there are three pair reversals: the $4b_1$–$6a_1$ and $6b_1$–$8a_1$ orbitals of furan and the $8a_1$–$5b_1$ orbitals of pyrrole. These results are inferior to those obtained from a subminimal but not absolutely minimal basis[16,17] and, insofar as the chemistry of these species is monitored by orbital energetics, the description may be inadequate. Of course, it should be kept in mind that standard semiempirical schemes such as CNDO/2 and INDO yield significantly more "scrambled" orbital orderings for these systems[18] than does the FSGO method.

Diagrammatic representations of FSGO wave functions for furan and pyrrole are given in Figures 2 and 3. The combined σ–π lone pair orbitals in furan are located slightly (0.016 bohr) out of the ring; an absolutely minimum number of s-type Gaussians is maintained in pyrrole by modeling the N–H bond as a highly polarized double bond. In both molecules the C=C double bond orbitals are closer to the β than α carbons. Electrostatic inductive effects would be expected to move these electrons toward the electronegative heteroatoms, so the observed results are presumably due to resonance. The heteroatom π lone pair spreads π character to the heteroatom–carbon bonds, and the C=C orbitals act to add π character to the C_β–C_β bonding region. One measure of the quality of the overall electron distribution is the dipole moment; for furan we calculate a value of 0.654 D, in excellent agreement with the experimental value of 0.661 D. This level of agreement must be somewhat fortuitous, especially since FSGO-SCF[16] [The FSGO-SCF method uses a larger basis set than the FSGO method described here, but does not optimize FSGO orbital locations in each molecule.] and LCAO-SCF[19] dipole moments are 0.320 and 1.29 D, respectively, but it does indicate a geometrically balanced electronic distribution. The FSGO dipole moment for pyrrole is 1.36 D, in good agreement

Table II. Orbital Energies for Furan and Pyrrole

	Furan				Pyrrole			
Method	FSGO		LCAO-SCF[a]		FSGO		LCAO-SCF[b]	
Basis set	18		148 contracted to 70		18		155 contracted to 80	
Energy	−192.9251		−228.5738		−176.0217		−208.7764	
	$1a_1$	−17.1934	$1a_1$	−20.6241	$1a_1$	−12.8186	$1a_1$	−15.6076
	$1b_1$	−9.2013	$1b_1$	−11.3119	$1b_1$	−9.1879	$1b_1$	−11.2667
	$2a_1$	−9.1893	$2a_1$	−11.3119	$2a_1$	−9.1729	$2a_1$	−11.2667
	$3a_1$	−9.1192	$3a_1$	−11.2571	$3a_1$	−9.1301	$3a_1$	−11.2234
	$2b_1$	−9.0768	$2b_1$	−11.2564	$2b_1$	−9.0838	$2b_1$	−11.2224
	$4a_1$	−1.3808	$4a_1$	−1.4734	$4a_1$	−1.1975	$4a_1$	−1.3051
	$5a_1$	−0.9771	$5a_1$	−1.1033	$5a_1$	−0.9473	$5a_1$	−1.0512
	$3b_1$	−0.8886	$3b_1$	−1.0199	$3b_1$	−0.8803	$3b_1$	−0.9884
	$6a_1$	−0.6929	$4b_1$	−0.8115	$6a_1$	−0.6736	$6a_1$	−0.7979
	$4b_1$	−0.6631	$6a_1$	−0.7847	$4b_1$	−0.6524	$4b_1$	−0.7684
	$7a_1$	−0.5568	$7a_1$	−0.7446	$7a_1$	−0.5843	$7a_1$	−0.7394
	$5b_1$	−0.4117	$1b_2$	−0.6351	$5b_1$	−0.4230	$8a_1$	−0.5968
	$8a_1$	−0.3965	$5b_1$	−0.6068	$8a_1$	−0.4127	$5b_1$	−0.5832
	$6b_1$	−0.3881	$6b_1$	−0.5888	$6b_1$	−0.3849	$1b_2$	−0.5705
	$1b_2$	−0.3196	$8a_1$	−0.5697	$9a_1$	−0.3661	$6b_1$	−0.5469
	$9a_1$	−0.2420	$9a_1$	−0.5417	$1b_2$	−0.2938	$9a_1$	−0.5288
	$2b_2$	−0.0986	$2b_2$	−0.4054	$2b_2$	−0.0639	$2b_2$	−0.3490
	$1a_2$	−0.0562	$1a_2$	−0.3330	$1a_2$	−0.0463	$1a_2$	−0.2989

[a] Reference 19. [b] Reference 21.

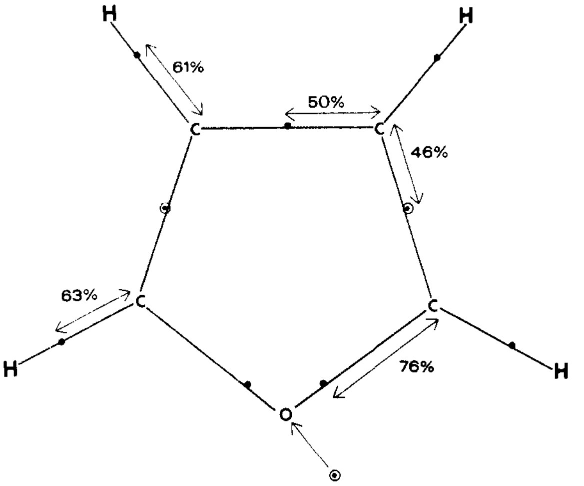


Figure 2. FSGO structure for furan. Centers of orbitals are indicated; ⊙ denotes a pair of banana bond orbitals. Core orbitals are not included.

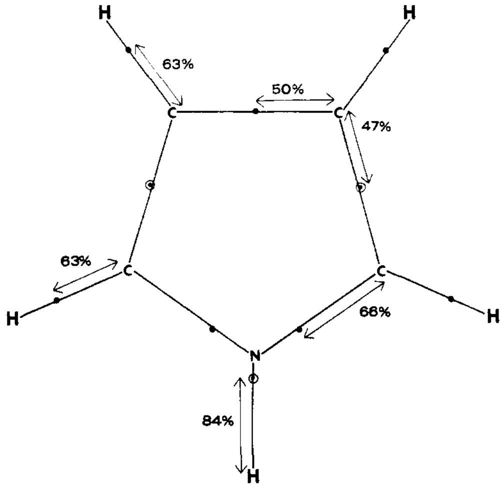


Figure 3. FSGO structure for pyrrole. Centers of orbitals are indicated; ⊙ denotes a pair of banana bond orbitals. Core orbitals are not included.

with the experimental value of 1.74 D; the primary source of error is presumably the description of the N–H bond. The direction of the dipole moment of pyrrole is correctly predicted to be reversed from that of furan, and we further note that this sign reversal is commonly attributed to resonance.[20]

Table III. Charge Patterns in Furan and Pyrrole

	FSGO		LCAO-SCF[a]	
Atom	Furan	Pyrrole	Furan	Pyrrole
N (or O)	−1.029	−1.005	−0.407	−0.373
C_α	+0.940	+0.691	+0.119	+0.010
C_β	+0.055	+0.139	−0.143	−0.170
HN		+0.366		+0.241
H_α	−0.265	−0.257	+0.127	+0.099
H_β	−0.216	−0.253	+0.114	+0.087

[a] Values taken from ref 21. Pyrrole wave function reported by those authors used Gaussian basis functions C,N $9^s5^p \rightarrow 4^s2^p$ (Dunning contractions); H $4^s1^p \rightarrow 3^s1^p$. Wave function for furan is from ref 19, and uses a C,O $9^s5^p \rightarrow 4^s2^p$ (Huzinaga contraction) H $4^s1^p \rightarrow 2^s1^p$ basis set.

Atomic charges for both furan and pyrrole have been determined and are reported in Table III along with Mulliken analysis values computed from two similar LCAO-SCF wave functions.[21] Atomic charge is a construct rather than an observable, and it would be difficult to prove the absolute validity of any set of values. Methods using different definitions of atomic charge often give widely different results, as do the FSGO and Mulliken methods in this instance. Nevertheless, trends in charge values within a given decomposition procedure should be chemically meaningful. Several interesting comparisons can be made: (i) both procedures yield oxygens in furan which are slightly more negative than the nitrogens in pyrrole, (ii) both procedures yield α carbons which are much more positive than β carbons, (iii) both procedures show that the difference in charge between the α and β carbons is much greater in furan than in pyrrole, (iv) both procedures show that the H–N hydrogen in pyrrole is much more acidic (positive) than the other hydrogens. The small discrepancies which do exist between the trends of the FSGO-classical decompositions

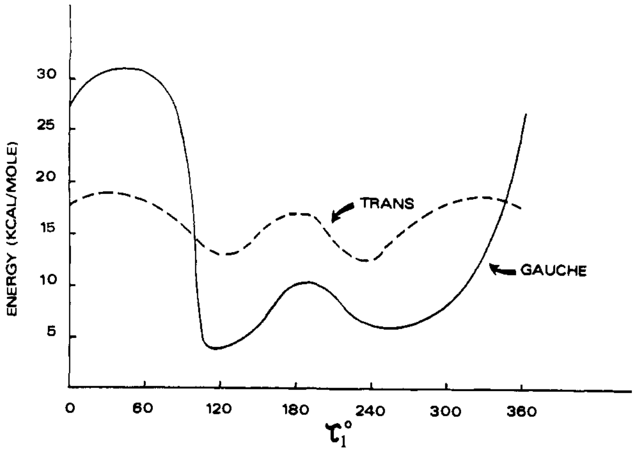


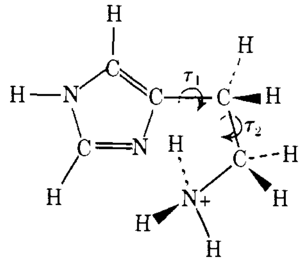
Figure 4. Relative energies in kcal/mol of conformations of the histamine monocation. The zero point is $E = -302.25$ hartree $= 1.8967 \times 10^5$ kcal/mol. See text and ref 26 for detailed description of geometries.

and the LCAO-Mulliken analyses do not appear to be chemically significant. In addition, the calculated charges are consistent with electrophilic attack occurring primarily at the α carbon so that the positive charge of the intermediate is located on the initially less positive β carbon.

We conclude that, as measured by orbital locations, dipole moments, or atomic charges, the effects of resonance are incorporated into the FSGO wave function, but that FSGO orbital energies are less accurate.

Histamine Monocation

The histamine monocation has been the subject of several recent theoretical investigations.[22-29] Since the biological properties of histamine (I) may depend on the conformation of the side chain,[30] interest has centered on determining equilibrium values for the dihedral angles τ_1 and τ_2. Of primary concern are the $\tau_2 = 180°$ trans conformer and the $\tau_2 = 300°$ gauche conformer, in which hydrogen bonding involving one or more of the hydrogens on the protonated nitrogen and lone pair electrons on the nearby ring nitrogen can occur. Since one expects that the values of these dihedral angles would not be sensitive to the detailed nature of the electron distribution but rather to the gross electron structure, FSGO calculations of these angles are appropriate and would be additional tests of the utility of absolutely minimal basis set descriptions of class (ii) resonant systems (vide supra).



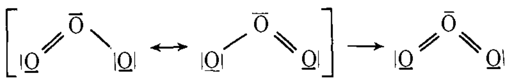
I

To reduce computational costs, FSGO exponents and locations have been frozen at values estimated from previous calculations on smaller molecules. (This has been shown to be a reliable procedure in other cases.[31]) The bond angles and lengths used by Ganellin et al.[26] in their extended Hückel calculations have been employed. Energies were calculated for both the trans and the gauche conformers at 60° intervals of τ_1. The lowest energy (−302.2444 hartree) was obtained for the $\tau_1 = 120°$, $\tau_2 = 300°$ structure. Figure 4 displays the relative energies of the two conformers as a function of τ_1. The qualitative shapes of both curves are strikingly similar to those obtained by Ganellin et al.[27] We infer, therefore, that the shapes of the $E_{\text{gauche}}(\tau_1)$ or $E_{\text{trans}}(\tau_1)$ curves are largely dependent on the *precise* bond angles and bond lengths used as input. Thus, the PCILO and STO-3G results obtained by Pullman and Port[28] should and do possess somewhat different shapes. As one would expect, the curve for $E_{\text{trans}}(\tau_1)$ is rather flat because the trans conformer cannot readily form a hydrogen bond. Richards, Hammond, and Aschman[23] have performed STO-3G calculations using the same geometries employed here to determine $E_{\text{trans}}(120°) - E_{\text{trans}}(0°)$; they obtained a value of 5.3 kcal/mol, which may be compared to the extended Hückel value of 3.2 kcal/mol and our FSGO value of 4.5 kcal/mol.

The FSGO results do differ significantly from the extended Hückel computations in regard to the relative stabilities of the two conformers. Ganellin et al.[27] predicted the trans conformer to be slightly the more stable, while more sophisticated quantum mechanical schemes predict the gauche conformer to be the more stable, by 6.2 kcal/mol (CNDO/2),[26] 11 kcal/mol (PCILO),[28] or 21 kcal/mol (STO-3G).[28] The precise value for this energy difference should depend on the geometry employed; nevertheless, it is clear that in an unsolvated environment[28] the gauche conformer should be the more stable, and it is gratifying that the FSGO energy for the lowest gauche conformer is some 9.0 kcal/mol more negative than that of the lowest trans conformer. We conclude that the FSGO description of this class of resonant systems is sufficiently accurate to allow conformational studies of side chains to be made.

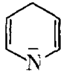
Ozone, Pyridine, and Benzene

Ozone, pyridine, and benzene are examples of resonant molecules with two or more major resonance structures. A previously reported[8] FSGO calculation on ozone suggests one line of attack for this type of system. The O_3 molecule is generally written as a combination of two resonance structures. If the FSGO wave function were based on either resonance structure, a chemically unacceptable formulation with nonequivalent oxygen-oxygen bonds would be obtained. There is, however, an alternative single resonance structure which does possess the correct symmetry:



This last structure initially appears unreasonable; in fact, however, upon orbital optimization the centers of the double bond orbitals move toward the terminal oxygen atoms and both nuclear geometry and molecular orbital structure are predicted reasonably well. The "floating" nature of the FSGO orbitals introduces sufficient flexibility into the calculation to undo the apparent violation of the octet law and allows a nominally poor resonance structure to describe the molecule.

We have attempted to use the same procedure to describe pyridine, starting with two different possible C_{2v} resonance structures (**1a** and **1b**). In each case a local minimum in the FSGO hypersurface was obtained, the double bonds moved in the anticipated directions to spread π character to other parts of the molecule, and a charge decomposition revealed the classic pattern in which α and γ carbons are more positive than β carbons. Nevertheless, these wave functions were judged unsatisfactory, in that the dipole moments were poor (5.20 D for **1a** and 0.58 D for **1b**) and that the near equivalence of the



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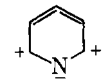

1b

Table IV. Orbital Energies for Pyridine and Benzene

	Pyridine				Benzene			
Method	FSGO 21		LCAO-SCF[a]		FSGO[b] 21		LCAO-SCF[c]	
Basis set	(18s and 3p)		175 contracted to 41		(18s and 3p)		180 contracted to 42	
Energy	−208.519		−246.3265		−194.9567		−230.3745	
	$1a_1$	−12.7913	$1a_1$	−15.6391	$1a_{1g}$	−9.2077	$1a_{1g}$	−11.35
	$2a_1$	−9.2102	$1b_2$	−11.4067	$1e_{1u}$	−9.2044	$1e_{1u}$	−11.35
	$1b_2$	−9.2045	$2a_1$	−11.4067	$1e_{2g}$	−9.0877	$1e_{2g}$	−11.35
	$3a_1$	−9.1955	$3a_1$	−11.3880	$1b_{1u}$	−9.0582	$1b_{1u}$	−11.35
	$2b_2$	−9.0684	$2b_2$	−11.3801	$2a_{1g}$	−1.0737	$2a_{1g}$	−1.173
	$4a_1$	−9.0468	$4a_1$	−11.3800	$2e_{1u}$	−0.9468	$2e_{1u}$	−1.043
	$5a_1$	−1.1883	$5a_1$	−1.2952	$2e_{1g}$	−0.7404	$2e_{2g}$	−0.848
	$6a_1$	−1.0117	$6a_1$	−1.1283	$3a_{1g}$	−0.5972	$3a_{1g}$	−0.741
	$3b_2$	−0.9514	$3b_2$	−1.0750	$2b_{1u}$	−0.5527	$2b_{1u}$	−0.674
	$7a_1$	−0.7775	$7a_1$	−0.8912	$3e_{1u}$	−0.4697	$1b_{2u}$	−0.660
	$4b_2$	−0.7505	$4b_2$	−0.8844	$1b_{2u}$	−0.4604	$3e_{1u}$	−0.626
	$8a_1$	−0.6299	$8a_1$	−0.7602	$3e_{2g}$	−0.3797	$1a_{2u}$	−0.538
	$9a_1$	−0.5157	$9a_1$	−0.6945	$1a_{2u}$	−0.2733	$3e_{2g}$	−0.526
	$5b_2$	−0.4907	$5b_2$	−0.6914	$1e_{1g}$	−0.1243	$1e_{1g}$	−0.379
	$6b_2$	−0.4704	$6b_2$	−0.6483				
	$10a_1$	−0.4614	$10a_1$	−0.6193				
	$7b_2$	−0.3810	$1b_1$	−0.5816				
	$1b_1$	−0.2895	$7b_2$	−0.5563				
	$11a_1$	−0.1950	$11a_1$	−0.4425				
	$2b_1$	−0.1404	$2b_1$	−0.4260				
	$1a_2$	−0.1190	$1a_2$	−0.4062				

[a] Reference 35. [b] FSGO orbital energies are averaged over the nearly degenerate C_{3v} orbitals to obtain approximate values for D_{6h} orbitals. [c] R. J. Buenker, J. L. Whitten, and J. D. Petke, *J. Chem. Phys.*, **49**, 2261 (1968).

C_α-C_β and C_β-C_γ bonds was not displayed. We believe that the FSGO banana bond representation of double bonds is the source of the problem. The banana bond requires σ and π orbitals to be centered at the same point. This reduces the extent to which π orbitals can float to relieve charge imbalance and prevents π electron flow through a sequence of bonds. Thus, while the approach taken for ozone should be useful for treating resonance in systems such as SO_2, $CO_3{}^{2-}$, or $NO_2{}^-$, it is less useful for aromatic rings.

As an alternative, we have performed a calculation on pyridine using separate s and p Gaussians[32] and allowing optimization of each orbital. Thus, 18 floating s-type Gaussians and 3 floating p-type Gaussians were employed. C_{2v} symmetry was forced, but, as in all our calculations, orbitals were not required to lie on bond axes. The results, as portrayed in Figure 5, are much more satisfying than those obtained earlier. The three π orbitals have moved into the interior of the ring, and are no longer localized in bonds. The π orbitals near the β carbons are very diffuse (the orbital exponent, α, is 0.246); hence they spread π electron density over a multi-bond region. Further, the C_α-C_β and C_β-C_γ bonds are predicted to be virtually identical, with orbital exponents of 0.428 and 0.429, respectively. The calculated dipole moment of 1.32 D agrees moderately well[33] with the experimental (and resonance dependent[20]) value of 2.26 D; by inspection of Figure 4, we note that the β carbons would receive a larger share of the π electrons than the α or γ carbons, in agreement with the observation that electrophilic attack occurs at the β carbon. Pictorially, the results are similar to the localized π orbitals obtained by England and Ruedenberg[34] for aromatic systems from LCAO wave functions. All of these results demonstrate that some of the qualitative features of resonance have been brought out within the absolutely minimal basis set.

Orbital energies are compiled in Table IV. The σ and π molecular orbital orderings are each in perfect agreement with the LCAO values of Petke, Whitten, and Ryan;[35] however, the $1b_1$ (π) orbital is now predicted to be less negative than the $7b_2$ (σ) orbital. This reversal is not surprising, as a single p Gaussian should have greater difficulty describing a multibond orbital than an s Gaussian does with a single bond.

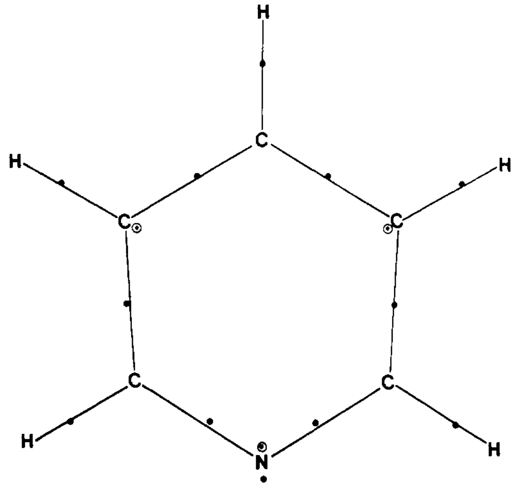

Figure 5. Minimal basis set description of pyridine. An s-type floating Gaussian orbital is indicated by a •; a p-type floating Gaussian orbital is referenced by a ⊙.

An interesting aspect of all our calculations on pyridine is that the N-C bond is "bent", in that the orbital lies inside the ring, off the N-C axis.

Benzene would likely be the most difficult aromatic molecule to describe with an absolutely minimal basis, since three local p orbitals cannot reproduce the full D_{6h} symmetry of the molecule. Accordingly, we have performed a calculation on a "C_{3v} benzene", in which p Gaussians were aligned on the bisectors of alternate C-C-C angles. Both nuclear geometries and orbital exponents and locations were optimized. As shown in Figure 6, a distorted six-membered ring is obtained. The alternating C-C-C angles are 127 and 113°. The six C-H

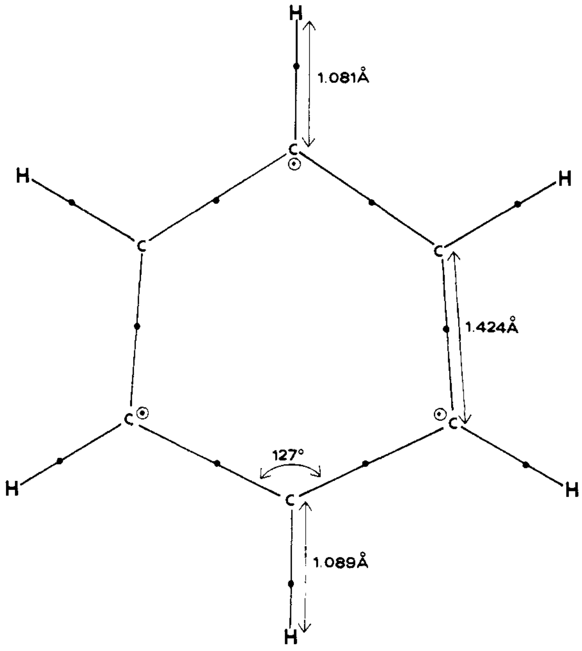

Figure 6. Minimal basis set description of benzene. s and p-type Gaussians are respectively denoted by the symbols • and ⊙. The optimized geometry is as shown.

bonds possess similar bond lengths (1.089 and 1.081 Å). The C–C bond length is calculated to be 1.424 Å, half-way between standard C–C and C═C distances and only 0.027 Å larger than the observed 1.397 Å. As in pyridine, the π orbitals are diffuse, with an exponent of 0.243, while the σ orbitals are more compact. Again as in pyridine (Table IV) the separate σ and π molecular orbital orderings are basically corect, but the $1a_{2u}$ π orbital is too positive. We suggest that similar results would be obtained for substituted benzenes, and that while useful studies of the conformations and geometries of side chains might be conducted, the geometry of the ring itself should be frozen at experimental values.

Conclusion

We conclude that many facets of the resonance phenomenon can, indeed, be described by a wave function composed of an absolutely minimal basis set. For aliphatic systems such as conjugated dienes or for aromatic rings with single dominant resonance structures, calculations can proceed in the same manner as earlier studies on nonresonant systems. We have demonstrated that in these cases values for certain properties are accurately calculated, and predict that most of the other successes of the FSGO method[6-10] will also be repeated. If better orbital energies are desired, we speculate that they could be obtained by using floating s and p Gaussians. Aromatic systems with two or more major resonance structures can also be treated. If there is only one central atom, as in ozone, the calculation can proceed via a single resonance structure. Better results are obtained for aromatic rings if both s and p Gaussians are used. In this last case, the results are conceptually satisfying, but quantitatively disappointing. A valence bond–FSGO method, in which each valence bond structure is represented by a single determinant of FSGO's, would be a logical procedure for obtaining higher accuracy. This would require slightly more than $N/2$ basis functions, but would yield a D_{6h} benzene and would be a natural quantum mechanical analogue of the Lewis diagram representation of resonance. A second possibility would be to retain the absolutely minimal σ structure but to increase the number of π basis functions.

The computational utility of absolutely minimal basis set methods is predicated, of course, on the existence of ways for determining locations and exponents for the basis functions. For small molecules, this can be done by explicit optimization. For large molecules, work in progress[31] suggests that a simulated optimization procedure, applicable to both nonresonant and resonant species, can be employed and will allow rapid calculations to be made on large systems.

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