

## Self—Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules

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## Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules

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Two extended basis sets (termed 5-31G and 6-31G) consisting of atomic orbitals expressed as fixed linear combinations of Gaussian functions are presented for the first row atoms carbon to fluorine. These basis functions are similar to the 4-31G set [*J. Chem. Phys.* **54**, 724 (1971)] in that each valence shell is split into inner and outer parts described by three and one Gaussian function, respectively. Inner shells are represented by a single basis function taken as a sum of five (5-31G) or six (6-31G) Gaussians. Studies with a number of polyatomic molecules indicate a substantial lowering of calculated total energies over the 4-31G set. Calculated relative energies and equilibrium geometries do not appear to be altered significantly.

### I. INTRODUCTION

The use of a basis of contracted Gaussian functions in molecular orbital theory has proved a valuable technique.<sup>1</sup> Pairs of electrons are assigned to molecular orbitals  $\psi_i$  which are written in the LCAO (linear combination of atomic orbital) approximation as

$$\psi_i = \sum_{\mu} c_{\mu i} \phi_{\mu} \quad (1)$$

Here  $c_{\mu i}$  are variational coefficients and the basis functions  $\phi_{\mu}$  are fixed linear combinations of Gaussian-type orbitals. In the simplest type of calculation, the  $\phi$  set is minimal, that is, consists of 1s for hydrogen, 1s, 2s, 2p for first row atoms, and so forth. However, it has been recognized for some time that a more flexible description is possible if a larger number of  $\phi$  functions is used. Such sets are referred to as extended and several have been proposed.<sup>2-9</sup>

Recently, we have presented an extended basis of contracted Gaussian functions which is simple enough

for extensive application to organic molecules.<sup>9</sup> In this set, described as 4-31G, each inner shell  $\phi_{\mu}$  is a sum of four Gaussian functions and each valence shell (hydrogen 1s, first-row atom 2s, 2p) is described by inner and outer  $\phi_{\mu}$  which are, respectively, sums of three and one Gaussian functions. The basis has the further special feature that 2s and 2p functions share common Gaussian exponents, permitting a substantial increase in computational efficiency.

Although the 4-31G basis has the merit of wide applicability, the atomic energies it gives are some way above the well-known Hartree-Fock limits because a relatively small number of Gaussian functions are used in the expansions. It is therefore desirable to compare any conclusions about relative energies at the 4-31G level with at least some computations which approach the Hartree-Fock limit more closely. In this paper, we shall present two more accurate basis sets developed in a similar manner, but with an improved inner-shell description. The numbers of Gaussian functions in the valence shell will be unaltered.

TABLE I. 5-31G first-row atom basis functions.

Atom	$\alpha_1$	$d_{1s}$	$\alpha_2'$	$d_{2s}'$	$d_{2p}'$	$\alpha_2''$	$E$
Carbon ( $^3P$ )	1.264250(+3)	5.473496(-3)	7.942731	-1.207731(-1)	6.867750(-2)	1.585120(-1)	-37.670625
	1.901443(+2)	4.079115(-2)	1.907238	-1.697932(-1)	3.141029(-1)		
	4.312859(+1)	1.812203(-1)	5.535774(-1)	1.149812	7.459685(-1)		
	1.194438(+1)	4.634825(-1)					
	3.651485	4.524712(-1)					
Nitrogen ( $^4S$ )	1.745285(+3)	5.421222(-3)	1.194496(+1)	-1.161469(-1)	6.732113(-2)	2.235978(-1)	-54.373578
	2.625413(+2)	4.043458(-2)	2.800090	-1.757314(-1)	3.221238(-1)		
	5.958251(+1)	1.804449(-1)	7.981581(-1)	1.150529	7.421562(-1)		
	1.654435(+1)	4.634396(-1)					
	5.084876	4.526307(-1)					
Oxygen ( $^3P$ )	2.296705(+3)	5.402591(-3)	1.591092(+1)	-1.118075(-1)	7.079811(-2)	2.838736(-1)	-74.765355
	3.454369(+2)	4.033912(-2)	3.695813	-1.519256(-1)	3.386959(-1)		
	7.840108(+1)	1.805909(-1)	1.043638	1.133714	7.277199(-1)		
	2.181042(+1)	4.643774(-1)					
	6.721723	4.511586(-1)					
Fluorine ( $^2P$ )	2.927123(+3)	5.380259(-3)	2.090380(+1)	-1.094196(-1)	7.156794(-2)	3.610198(-1)	-99.341221
	4.402361(+2)	4.020133(-2)	4.831642	-1.494114(-1)	3.450879(-1)		
	9.993135(+1)	1.804365(-1)	1.353752	1.130962	7.228825(-1)		
	2.783870(+1)	4.647457(-1)					
	8.602578	4.506029(-1)					

## II. ATOMIC FUNCTIONS

The theoretical methods for determining the atomic functions have been described previously<sup>9,10</sup> and full details will not be given. One  $\phi$  function is used for inner shells and two sets for the valence shells. For a first-row atom there are nine  $\phi$  functions per atom of the form

$$\begin{aligned}
 \phi_{1s}(\mathbf{r}) &= \sum_{k=1}^{N_1} d_{1s,k} g_s(\alpha_{1k}, \mathbf{r}), \\
 \phi_{2s}'(\mathbf{r}) &= \sum_{k=1}^{N_2'} d_{2s,k}' g_s(\alpha_{2k}', \mathbf{r}), \\
 \phi_{2px}'(\mathbf{r}) &= \sum_{k=1}^{N_2'} d_{2p,k}' g_{px}(\alpha_{2k}', \mathbf{r}), \\
 \phi_{2s}''(\mathbf{r}) &= \sum_{k=1}^{N_2''} d_{2s,k}'' g_s(\alpha_{2k}'', \mathbf{r}), \\
 \phi_{2px}''(\mathbf{r}) &= \sum_{k=1}^{N_2''} d_{2p,k}'' g_{px}(\alpha_{2k}'', \mathbf{r}), \quad (2)
 \end{aligned}$$

and similar expressions for  $\phi_{2py}'$ ,  $\phi_{2py}''$ ,  $\phi_{2pz}'$ , and  $\phi_{2pz}''$ .  $g_s$  and  $g_{px}$  are normalized Gaussian functions

$$\begin{aligned}
 g_s(\alpha, \mathbf{r}) &= (2\alpha/\pi)^{3/4} \exp(-\alpha r^2), \\
 g_{px}(\alpha, \mathbf{r}) &= (128\alpha^5/\pi^3)^{1/4} \times \exp(-\alpha r^2). \quad (3)
 \end{aligned}$$

The functions  $\phi'$  and  $\phi''$  represent inner and outer parts of the valence shell. It should be noted that

corresponding 2s and 2p functions share common  $\alpha$  values.

For hydrogen, inner and outer s functions of the form

$$\begin{aligned}
 \phi_{1s}'(\mathbf{r}) &= \sum_{k=1}^{N_1'} d_{1s,k}' g_s(\alpha_{1k}', \mathbf{r}), \\
 \phi_{1s}''(\mathbf{r}) &= \sum_{k=1}^{N_1''} d_{1s,k}'' g_s(\alpha_{1k}'', \mathbf{r}) \quad (4)
 \end{aligned}$$

are used.

The extended basis sets developed here are specified as follows:

5-31G: For heavy atoms  $N_1=5$ ,  $N_2'=3$ ,  $N_2''=1$ . For hydrogen  $N_1'=3$ ,  $N_1''=1$ .

6-31G: For heavy atoms  $N_1=6$ ,  $N_2'=3$ ,  $N_2''=1$ . For hydrogen  $N_1'=3$ ,  $N_1''=1$ .

Given a set of values for the  $\alpha$  and  $d$  parameters in (2) and (4), the atomic energy can be calculated by using the  $\phi$  functions as a basis for a LCAO calculation on the atom. (A spin-unrestricted method is used requiring solution of the Pople-Nesbet equations).<sup>11</sup> This gives the energy as a function of the various  $\alpha$  and  $d$  values (which are constrained only by a normalization condition). These are then varied until the atomic energy is minimized by methods described elsewhere.<sup>9,10</sup> The final values along with the corresponding atomic energies are listed in Tables I and II. The hydrogen functions are identical with those in 4-31G, as given previously.<sup>9</sup>

TABLE II. 6-31G first-row atom basis functions.

Atom	$\alpha_1$	$d_{1s}$	$\alpha_2'$	$d_{2s}'$	$d_{2p}'$	$\alpha_2''$	$E$
Carbon ( $^3P$ )	3.047525(+3)	1.834737(-3)	7.868272	-1.193324(-1)	6.899907(-2)	1.559860(-1)	-37.679335
	4.573695(+2)	1.403732(-2)	1.881289	-1.608542(-1)	3.164240(-1)		
	1.039487(+2)	6.884262(-2)	5.442493(-1)	1.143456	7.443083(-1)		
	2.921016(+1)	2.321844(-1)					
	9.286663	4.679413(-1)					
	3.163927	3.623120(-1)					
Nitrogen ( $^4S$ )	4.173511(+3)	1.834772(-3)	1.186242(+1)	-1.149612(-1)	6.757974(-2)	2.207742(-1)	-54.385385
	6.274579(+2)	1.399463(-2)	2.771431	-1.691175(-1)	3.239073(-1)		
	1.429021(+2)	6.858655(-2)	7.878976(-1)	1.145852	7.408951(-1)		
	4.023433(+1)	2.322409(-1)					
	1.282021(+1)	4.690699(-1)					
	4.390437	3.604552(-1)					
Oxygen ( $^3P$ )	5.484672(+3)	1.831074(-3)	1.585513(+1)	-1.107775(-1)	7.087427(-2)	2.811389(-1)	-74.780859
	8.252349(+2)	1.395017(-2)	3.673027	-1.480263(-1)	3.397528(-1)		
	1.880470(+2)	6.844508(-2)	1.034345	1.130767	7.271586(-1)		
	5.296450(+1)	2.327143(-1)					
	1.689757(+1)	4.701929(-1)					
	5.799635	3.585209(-1)					
Fluorine ( $^2P$ )	7.001713(+3)	1.819617(-3)	2.084795(+1)	-1.085070(-1)	7.162872(-2)	3.581514(-1)	-99.360860
	1.051366(+3)	1.391608(-2)	4.808308	-1.464517(-1)	3.459121(-1)		
	2.392857(+2)	6.840532(-2)	1.344070	1.128689	7.224700(-1)		
	6.739745(+1)	2.331858(-1)					
	2.151996(+1)	4.712674(-1)					
	7.403101	3.566185(-1)					

## III. MOLECULAR STUDIES

For molecular calculations the valence shells of the functions tabulated in Tables I and II have been scaled by the standard factors given in Ref. 9. Although these scale factors represent average molecular values for the 4-31G basis, preliminary optimization studies with the larger 5-31G and 6-31G sets show them to be quite suitable here. Inner shells, as before, remain unscaled.

Molecular geometries were chosen in accord with the standard model defined elsewhere.<sup>12</sup>

Total and atomization energies for a number of small polyatomics are listed in Tables III and IV. Although convergence of the total energies is poor in going from 4-31G to 6-31G, the corresponding energies of atomization are seen to be rapidly convergent. (Maximum deviation in atomization energy from 4-31G to 5-31G

TABLE III. Total energies (hartrees).

Molecule	4-31G	5-31G	6-31G	SB <sup>a</sup>
H <sub>2</sub>	-1.12676	-1.12676	-1.12676	-1.1266
HF	-99.88728	-99.96367	-99.98342	-100.0149
H <sub>2</sub> O	-75.90841	-75.96937	-75.98508	-76.0037
NH <sub>3</sub>	-56.10452	-56.15119	-56.16320	-56.1714
CH <sub>4</sub>	-40.13955	-40.17198	-40.18038	-40.1822
C <sub>2</sub> H <sub>6</sub>	-79.11484	-79.17971	-79.19651	-79.1981
C <sub>2</sub> H <sub>4</sub>	-77.92050	-77.98620	-78.00317	-78.0052
C <sub>2</sub> H <sub>2</sub>	-76.71105	-76.77584	-76.79261	-76.7919
CH <sub>3</sub> NH <sub>2</sub>	-95.06803	-95.14684	-95.16717	
CH <sub>3</sub> NH	-93.87561	-93.95487	-93.97527	
HCN	-92.73081	-92.80783	-92.82763	-92.8289
CH <sub>3</sub> OH	-114.87020	-114.96292	-114.98682	
H <sub>2</sub> CO	-113.69195	-113.78413	-113.80789	-113.8209
CH <sub>3</sub> F	-138.85648	-138.96419	-138.99200	

<sup>a</sup> Reference 6.

TABLE IV. Atomization energies (hartrees).

Molecule	4-31G	5-31G	6-31G	SB <sup>a</sup>	Exptl <sup>b</sup>
H <sub>2</sub>	0.1282	0.1282	0.1282	0.1280	0.1746
HF	0.1225	0.1232	0.1233	0.1293	0.2242
H <sub>2</sub> O	0.2044	0.2055	0.2057	0.2120	0.3701
NH <sub>3</sub>	0.2788	0.2798	0.2800	0.2839	0.4739
CH <sub>4</sub>	0.5055	0.5042	0.5039	0.5039	0.6686
C <sub>2</sub> H <sub>6</sub>	0.8453	0.8428	0.8422	0.8400	1.1339
C <sub>2</sub> H <sub>4</sub>	0.6495	0.6478	0.6474	0.6457	0.8970
C <sub>2</sub> H <sub>2</sub>	0.4387	0.4360	0.4354	0.4309	0.6455
CH <sub>3</sub> NH <sub>2</sub>	0.6068	0.6062	0.6061		0.9271
CH <sub>3</sub> NH	0.4129	0.4128	0.4127		
HCN	0.2667	0.2643	0.2636	0.2587	0.4964
CH <sub>3</sub> OH	0.5307	0.5298	0.5295		0.8159
H <sub>2</sub> CO	0.3510	0.3496	0.3491	0.3480	0.5983
CH <sub>3</sub> F	0.4562	0.4545	0.4540		0.6713

<sup>a</sup> Energies required for these calculations were taken from Ref. 6. The energy taken for the hydrogen atom was  $-0.4993$ , corresponding to a Slater exponent of 1.0.

<sup>b</sup> The vibrational correction has been applied to the experimental values to obtain atomization energies at 0°K for fixed nuclei. See Ref. 15 for references to experimental values. Experimental heats of formation for atoms from D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, W. M. Bailey, and R. H. Schumm, Natl. Bur. Std. (U. S.) Tech. Note 270-3 (1968).

is 0.0027 hartree, that from 5-31G to 6-31G is 0.0009 hartree). It may also be noted that atomization energies calculated with the larger double-zeta basis of Basch, Robin, and Keubler<sup>5</sup> (employing a splitting of the inner shell as well as the valence shell) are systematically close to the values determined here. It would appear the improvements made in the atomic inner-shell description are of small consequence to the formation of bonds. Finally, in accord with previous single determinant LCAO MO studies, calculated atomization energies are considerably smaller than experimental values.

TABLE V. Bond separation energies (kilocalories/mole).

Molecule	4-31G	5-31G	6-31G	Exptl <sup>a</sup>
Propane	1.2	1.2	1.1	2.2
Propene	3.9	3.9	3.9	5.3
Propyne	9.0	8.9	8.9	7.5
Allene	-2.5	-3.1	-3.3	-3.0
Dimethylamine	2.5	2.4	2.3	4.5
Acetonitrile	13.2	13.1	13.0	9.1
Dimethylether	2.3	2.2	2.2	5.9
Acetaldehyde	10.4	11.1	11.1	9.7
Ketene	13.6	11.8	11.4	17.3
Carbon dioxide	52.5	50.4	49.9	56.5
Diffuoromethane	11.5	11.2	11.1	14.1
Formamide	35.9	35.5	35.4	29.2

<sup>a</sup> See Ref. 15 for references to experimental values.

We have previously demonstrated that single determinant molecular orbital theory is capable of adequately describing molecular energetics<sup>13-15</sup> if the energy of large molecules be written in terms of two consecutive formal reactions. In the first (the bond separation reaction), the large molecule is broken down into species with two heavy (nonhydrogen) atoms, formal bond types being conserved. The resulting molecules are, in the second step, completely hydrogenated to molecules with one heavy atom (methane, ammonia, water, and hydrogen fluoride) by addition of an appropriate number of hydrogen molecules. In turn, we now consider the ability of our proposed basis sets to describe the energetics of these two types of reaction.

As outlined above the energy of bond separation is defined as the heat of a reaction in which all formal bonds between heavy (nonhydrogen) atoms are separated into the simplest (parent) molecules with the same type of bond. For example, the bond separation

TABLE VI. Hydrogenation energies (kilocalories/mole).

Molecule	4-31G	5-31G	6-31G	SB <sup>a</sup>	Exptl <sup>b</sup>
C <sub>2</sub> H <sub>6</sub>	-23.5	-23.5	-23.5	-24.9	-18.1
C <sub>2</sub> H <sub>4</sub>	-65.9	-65.4	-65.3	-66.5	-57.2
C <sub>2</sub> H <sub>2</sub>	-117.8	-117.9	-117.9	-120.9	-105.4
CH <sub>3</sub> NH <sub>2</sub>	-30.9	-31.1	-31.2		-25.7
CH <sub>3</sub> NH	-72.1	-72.0	-72.0		
HCN	-83.4	-84.8	-85.1	-90.9	-76.8
CH <sub>3</sub> OH	-32.0	-32.4	-32.6		-30.3
H <sub>2</sub> CO	-64.3	-65.1	-65.3	-70.2	-57.3
CH <sub>3</sub> F	-27.4	-28.0	-28.3		-29.5

<sup>a</sup> Energies required for these calculations were taken from Ref. 6.

<sup>b</sup> Values at 0°K for fixed nuclei. See Ref. 15 for references to experimental values.

reaction for formamide is



a molecule of methane being added to the left to achieve stoichiometric balance. Our previous studies have shown that the 4-31G basis is capable of predicting the heats of such reactions with reasonable success (mean absolute error for a large number of molecules is 3.0 kcal/mole<sup>15</sup>). Calculated heats of bond separation for a number of three heavy-atom molecules are presented in Table V. It may be noted that the maximum deviation in calculated heats between the 4-31G and 6-31G bases is less than the average deviation of either from experiment.

The energy of complete hydrogenation may now be written as the energy of bond separation plus the energies of hydrogenation of the resulting parent molecules. In the above example of formamide this is simply the bond separation energy (1) plus the energies

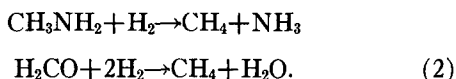
TABLE VII. Equilibrium geometries.<sup>a</sup>

Molecule	Symmetry constraint	Coordinate	4-31G	5-31G	6-31G	Exptl
H <sub>2</sub> O	C <sub>2v</sub>	r <sub>OH</sub>	0.951	0.950	0.950	0.957
		θ <sub>HOH</sub>	111.2	111.5	111.5	104.5
NH <sub>3</sub>	C <sub>3v</sub>	r <sub>NH</sub>	0.991	0.991	0.991	1.012
		θ <sub>HNH</sub>	115.9	116.1	116.2	106.7
CH <sub>4</sub>	T <sub>d</sub>	r <sub>CH</sub>	1.081	1.082	1.082	1.085
C <sub>2</sub> H <sub>4</sub>	D <sub>2h</sub>	r <sub>CH</sub>	1.073	1.074	1.074	1.076
		r <sub>CC</sub>	1.316	1.321	1.322	1.330
		θ <sub>HCH</sub>	116.0	116.1	116.1	116.6
C <sub>2</sub> H <sub>2</sub>	D <sub>∞h</sub>	r <sub>CH</sub>	1.051	1.053	1.053	1.061
		r <sub>CC</sub>	1.190	1.193	1.194	1.203
H <sub>2</sub> CO	C <sub>2v</sub>	r <sub>CH</sub>	1.081	1.082	1.082	1.101
		r <sub>CO</sub>	1.206	1.209	1.210	1.203
		θ <sub>HCH</sub>	116.4	116.6	116.6	116.5
HCN	C <sub>∞v</sub>	r <sub>CH</sub>	1.051	1.053	1.053	1.063
		r <sub>CN</sub>	1.140	1.143	1.144	1.154

<sup>a</sup> Bondlengths in angstroms and bond angles in degrees. References to experimental geometries may be found in M. D. Newton, W. A. Lathan,

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of the two reactions



Calculated 4-31G, 5-31G, and 6-31G energies of hydrogenation for all carbon containing parents are listed in Table VI, along with quantities calculated using the basis set of Basch, Robin, and Kuebler<sup>5</sup> and experimental values. Deviations in calculated heats amongst the various basis sets are again smaller than those between theory and experiment.

Finally, Table VII presents calculated equilibrium geometries. Here the three basis sets give virtually identical results in most instances in good agreement with experiment.

#### IV. CONCLUSION

From the results reported in this paper we may draw the following general conclusions:

(1) Improvement of inner-shell description leads to substantial lowering of calculated atomic and molecular total energies, but does not appear to alter calculated relative energies or equilibrium geometries significantly. Conclusions reached with the 4-31G basis, therefore, are unlikely to be modified by extension to 5-31G and 6-31G.

(2) The 6-31G basis set would seem to be, in terms of calculated total and relative energies, very similar to that proposed by Basch, Robin, and Kuebler.<sup>5</sup> It is,

however, computationally more economic, utilizing fewer primitive Gaussian functions (22 instead of 25), fewer atomic orbitals  $\phi_\mu$  per heavy atom (9 instead of 10), and employing a  $2s=2p$  constraint on the Gaussian exponents.

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