

# The Ellipsoidal Gaussian Basis in Molecular Orbital Theory

## II. Comparison with the Double-Zeta Basis

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The ellipsoidal Gaussian basis function used in a minimal valence atomic orbital representation is compared with the double-zeta spherical Gaussian basis orbital representation for some seventeen molecules made up of first row atoms and hydrogen. Except for acetylene the double-zeta basis gives consistently better total electronic energies and generally better property values than the optimized ellipsoidal single zeta basis. Difference molecular density contour maps comparing the two basis sets, as well as other one-electron property values, indicate that the ellipsoidal basis exaggerates the transfer of charge from the atomic regions to the interatomic and lone pair regions of molecules. Apparently, the forced complete elliptization of the valence atomic orbital in the single-zeta representation does not allow the basis set sufficient flexibility to simultaneously represent both the basically spherical atomic part of these orbitals and the non-spherical molecular bond formation. Other properties and aspects of the ellipsoidal Gaussian basis are also discussed.

**Key words:** Ellipsoidal Gaussian basis function

### 1. Introduction

In part I of this study [1] the potential advantage of ellipsoidal-type orbitals as simultaneously compact and accurate nuclear centered basis functions for use in *ab initio* Hartree–Fock theory were discussed, new energy and overlap integral formulas were derived, and some preliminary calculations on the HF and CO molecules were presented. In particular, the generalized ellipsoidal Gaussian [2]:

$$|E\rangle = x^l y^m z^n \exp(-\alpha x^2 - \beta y^2 - \gamma z^2) \quad (1)$$

was expressed as the product of a spherical exponential part, times a triple expansion in even powers of the Cartesian coordinates,

$$|E\rangle = x^l y^m z^n \exp(-\delta r^2) \sum_i \sum_j \sum_k A_{ijk} x^{2i} y^{2j} z^{2k} \quad (2)$$

where  $\delta$  is arbitrary and the  $A_{ijk}$  are fixed functions of  $(\delta - \alpha)$ ,  $(\delta - \beta)$  and  $(\delta - \gamma)$ . It should be noted that in practice the triple sum in (2) can always be reduced to no more than a double sum by taking  $\delta$  as equal to either  $\alpha$ ,  $\beta$  or  $\gamma$  in (1) as was done in the work carried out here. The analytic form, (2), is convenient for integral evaluation since the complexity of the energy integrals is then directly proportional to the degree of ellipticity of the orbital.

This *Ansatz* also shows how the ellipsoidal Gaussian function builds up its radially polarized character in the non-spherical molecular field as an off-center expansion of a spherical, nuclear centered basis orbital, but with fixed expansion coefficients. Thus the ellipsoidal Gaussian can in no way represent or take the place of angular polarization basis functions (such as 3d type for first row atoms) in the basis set expansion formulation of Hartree-Fock theory, but can possibly be an effective substitute for multiple-zeta [3] basis functions for valence orbitals that are partially or wholly filled in the normal atom.

In order to examine the latter point in more detail we have carried out *ab initio* self consistent field (SCF) calculations on a variety of molecules made up of first-row atoms and the hydrogen atom. The ellipticity of the valence orbitals has been obtained by energy optimization of the Cartesian components of each exponent. For each molecule the results of a single SCF calculation using a standard double-zeta [4] (DZ) spherical Gaussian basis are used as the reference data with which to compare the optimized orbitals, energies and one-electron properties obtained in the ellipsoidal orbital basis.

In general, the total electronic energy of a system has a rather low information content [5] when trying to understand the physical origin of the difference between molecular wave functions obtained in various basis sets. The expectation values of moments of the charge distribution are expected to be a more sensitive measure of these differences [6] and we have therefore here examined  $\langle \vec{r} \rangle$ ,  $\langle r^2 \rangle$ ,  $\langle 1/r \rangle$  and  $\langle \vec{r}/r^3 \rangle$  values. This set of operators is also related to familiar experimental quantities: the dipole moment, second (or quadrupole) moment, diamagnetic nuclear shielding and nuclear field gradient, respectively. Difference density contour [7-9] maps are an excellent visual means for emphasizing differences between SCF wave functions obtained with different caliber basis sets, and we have made wide use of these maps here.

## 2. Methods and Results

As in the previous paper [1] the philosophy of keeping the basis set at minimal dimensions was adopted and Dunning's [3<sup>9</sup>1<sup>9</sup>] [4] combination of Huzinaga's (9<sup>8</sup>5<sup>9</sup>) atomic orbital basis was used as the starting basis for all first-row atoms. For

the hydrogen atom the completely combined set of Basch *et al.* [10] with a scale factor of  $(1.2)^2$  was used as the initial spherical Gaussian  $1s$  atomic orbital basis. The double-zeta reference set is obtained from these more contracted atom sets by freeing the smallest exponent members of the  $2s$  and  $2p$  orbitals for first-row atoms and the  $1s$  atomic orbital for hydrogen as separate basis functions. Thus the DZ basis is  $(9^s5^p/4^s)$  contracted to  $[4^s2^p/2^s]$ .

The optimized ellipsoidal Gaussian exponents  $[\alpha, \beta$  and  $\gamma$  in Eq. (1)] were obtained as described previously, [1] in a two step process. Initially, the  $[3^s1^p/1^s]$  spherical Gaussian basis exponents were optimized by scaling all the primitive exponents of a given combined orbital by a uniform factor until an energy minimum was found. This optimization procedure was applied successively to the  $2s$  and  $2p$  atomic orbitals of the first row atoms, and to the hydrogen  $1s$  orbital, where the optimization results of the previous orbitals were incorporated into the basis set for the optimization of the next orbital. Note that different  $m_l$  components of a given  $l$ -type orbital (i.e.  $2p_x$ ,  $2p_y$  and  $2p_z$ ) were optimized separately. Starting with the optimum spherical set the elliptical optimization was carried out on the individual Cartesian exponents of each orbital (with  $\alpha = \beta$  for linear systems) where, again, the already optimized results were always incorporated into successive runs. In both optimization processes one complete round involving all the exponents was found to be sufficient with further optimizations changing the achieved result by only an insignificant amount. The dependence of the final results (i.e. exponents) on the order of optimization of Cartesian component or basis orbital was also tested on several systems and found to be negligible. In addition, some simultaneous exponent optimizations were carried out which also were found not to give end results differing substantially from those found by the less time-consuming linear optimization procedure. Initial direct elliptical optimization of the original spherical Gaussian basis exponents gave results which suggested the two-step spherical-elliptical scaling procedure finally adopted.

Thus, for each of the seventeen molecules studied here, four basis sets can be compared: original spherical, optimal spherical, optimal elliptical and double-zeta. The total energies for each of these basis sets for all the molecules studied here are tabulated in Table 1. The final spherical and ellipsoidal scale factors (relative to the original spherical  $[3^s1^p/1^s]$  basis]) are set out in Tables 2 and 3.

The fixed geometries of the molecules were mostly taken from the tabulation of Snyder and Basch [11] except for FCN (F-C=2.385 a.u., C-N=2.190 a.u.), NO<sup>+</sup> (N-O=2.00737 a.u.), CN<sup>-</sup> (C-N=2.189035 a.u.) and C<sub>2</sub> (C-C=2.3474 a.u.). For the linear molecules the atoms lie on the  $z$  axis and for the others the geometric configuration is described in the footnotes to Table 3. The electronic configuration in each case corresponds to that which gives rise to the normal closed-shell ground state except for the case of C<sub>2</sub> where the configuration is  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$ .

Expectation values of the above enumerated one-electron operators were obtained for all the molecules in each of the four different basis sets for comparison purposes. These properties were chosen as sampling the charge distribution in different regions of space. Thus, whereas  $\langle 1/r \rangle$  and  $\langle \bar{r}/r^3 \rangle$  are sensitive probes of the charge

**Table 1.** Total energies in various basis sets<sup>a</sup>

Molecule	Original single-zeta <sup>b</sup>	Optimized single-zeta <sup>b</sup>	Elliptic optimized single-zeta <sup>b</sup>	Double-zeta <sup>c</sup>
HF	-99.98842	-100.01337	-100.0167	-100.02197
C <sub>2</sub>	-75.28535	-75.32213	-75.33479	-75.35646
H <sub>2</sub> C <sub>2</sub>	-76.70089	-76.76938	-76.81041	-76.79917
HCN	-92.71720	-92.77526	-92.80833	-92.83631
N <sub>2</sub>	-108.73540	-108.78375	-108.79966	-108.87825
NO <sup>+</sup>	-128.54406	-128.69199	-128.72005	-128.82423
CN <sup>-</sup>	-92.15537	-92.17838	-92.19105	-92.25912
CO	-112.55540	-112.60685	-112.62251	-112.68499
BF	-124.02677	-124.06030	-124.06909	-124.08146
F <sub>2</sub>	-198.70116	-198.70258	-198.70618	-198.70753
CO <sub>2</sub>	-187.28620	-187.45856	-187.49506	-187.55333
NNO	-183.35679	-183.47245	-183.52730	-183.59050
FCN	-191.46229	-191.58237	-191.61158	-191.64918
H <sub>2</sub> O	-75.95952	-75.99275	-75.99780	-76.00930
C <sub>2</sub> H <sub>4</sub>	-77.91357	-77.97930	-77.99345	-78.01150
N <sub>2</sub> H <sub>2</sub>	-109.83560	-109.87376	-109.88148	-109.95022
H <sub>2</sub> CO	-113.69973	-113.75830	-113.77503	-113.82934

<sup>a</sup> Energies in a.u.

<sup>b</sup> [3<sup>1</sup>P/1<sup>s</sup>] combined set from the (9<sup>s</sup>5<sup>p</sup>/4<sup>s</sup>) primitive set.

<sup>c</sup> [4<sup>s</sup>2<sup>p</sup>/2<sup>s</sup>] combined set from the (9<sup>s</sup>5<sup>p</sup>/4<sup>s</sup>) primitive set.

distribution near the nuclei,  $\langle \vec{r} \rangle$  and  $\langle r^2 \rangle$  are measures of the charge spread especially in the peripheral regions [5]. The results are tabulated in Tables 4 to 7.

Finally, in an attempt to understand the physical difference between the various basis sets directly in terms of the molecular charge distribution, electron density difference contour maps between different quality basis molecular wave functions were drawn out to a value of 0.002 e [12]. This value has been typically found to enclose over 95 % of the molecular charge density for normal groundstate systems such as those studied here. Actual maps are presented here (Figs. 1 to 9) only for H<sub>2</sub>CO, CO and NNO for purposes of economy. The trends observed and conclusions drawn from this representative set of molecules are generally applicable to the whole group of molecules studied here. Note that because the difference density maps here compare different molecular wave functions the usual ambiguity in these contour maps, when the difference density between a molecular and superimposed constituent atomic densities is plotted, of defining the atomic densities is not present.

### 3. Discussion

The total energy results tabulated in Table 1 show immediately that, except for the case of acetylene, the (unoptimized) standard double-zeta basis consistently gives a lower total energy than the elliptically optimized [3<sup>1</sup>P/1<sup>s</sup>] basis. Here it should be recalled that the part of this latter basis set which mainly describes the 1s atomic

**Table 2.** Energy optimized exponent scale factors for spherical and ellipsoidal atomic orbitals in linear molecules

Molecule	Atomic orbital	Optimized scale factors <sup>a</sup>		
		Spherical Gaussian	Ellipsoidal Gaussian	
			$\alpha, \beta$	$\gamma$
HF	H 1s	1.612	1.739	1.521
	F 2s	0.986	1.003	0.971
	F 2p <sub>x</sub> , 2p <sub>y</sub>	0.950	0.953	0.922
	F 2p <sub>z</sub>	0.989	0.991	0.971
C <sub>2</sub>	C 2s	1.172	1.156	0.978
	C 2p <sub>x</sub> , 2p <sub>y</sub>	1.109	1.128	1.018
	C 2p <sub>z</sub>	1.118	1.183	1.090
C <sub>2</sub> H <sub>2</sub>	H 1s	1.677	1.571	1.543
	C 2s	1.194	1.218	0.682
	C 2p <sub>x</sub> , 2p <sub>y</sub>	1.066	1.074	0.946
	C 2p <sub>z</sub>	1.218	1.261	1.061
HCN	H 1s	1.760	1.533	1.592
	C 2s	1.227	1.330	0.702
	C 2p <sub>x</sub> , 2p <sub>y</sub>	1.124	1.113	0.961
	C 2p <sub>z</sub>	1.364	1.452	1.133
	N 2s	1.035	0.992	0.958
	N 2p <sub>x</sub> , 2p <sub>y</sub>	1.039	1.053	0.992
	N 2p <sub>z</sub>	1.115	1.124	1.083
N <sub>2</sub>	N 2s	1.072	1.032	0.981
	N 2p <sub>x</sub> , 2p <sub>y</sub>	1.085	1.087	1.004
	N 2p <sub>z</sub>	1.238	1.284	1.169
NO <sup>+</sup>	O 2s	1.148	1.094	1.048
	O 2p <sub>x</sub> , 2p <sub>y</sub>	1.175	1.144	1.075
	O 2p <sub>z</sub>	1.211	1.255	1.138
	N 2s	1.191	1.112	1.119
	N 2p <sub>x</sub> , 2p <sub>y</sub>	1.247	1.261	1.093
	N 2p <sub>z</sub>	1.398	1.456	1.328
CN <sup>-</sup>	N 2s	0.966	0.986	0.830
	N 2p <sub>x</sub> , 2p <sub>y</sub>	0.948	0.943	0.901
	N 2p <sub>z</sub>	1.043	1.067	0.965
	C 2s	0.889	0.849	0.780
	C 2p <sub>x</sub> , 2p <sub>y</sub>	1.033	1.029	0.971
	C 2p <sub>z</sub>	1.341	1.397	1.314
CO	O 2s	1.049	1.043	0.937
	O 2p <sub>x</sub> , 2p <sub>y</sub>	0.996	1.005	0.949
	O 2p <sub>z</sub>	1.063	1.085	0.998
	C 2s	1.044	0.962	0.966
	C 2p <sub>x</sub> , 2p <sub>y</sub>	1.324	1.313	1.152
	C 2p <sub>z</sub>	1.524	1.569	1.467
BF	B 2s	0.977	0.905	1.032
	B 2p <sub>x</sub> , 2p <sub>y</sub>	1.530	1.697	1.280

<sup>a</sup> See footnote (a) in Table 1.

Table 2—cont.

Molecule	Atomic orbital	Optimized scale factors <sup>a</sup>		
		Spherical Gaussian	$\alpha, \beta$	$\gamma$
F <sub>2</sub>	B 2p <sub>z</sub>	1.721	1.752	1.639
	F 2s	1.004	1.022	0.946
	F 2p <sub>x</sub> , 2p <sub>y</sub>	0.962	0.977	0.943
	F 2p <sub>z</sub>	0.975	1.013	0.968
F <sub>2</sub>	F 2s	1.020	1.019	1.020
	F 2p <sub>x</sub> , 2p <sub>y</sub>	1.007	1.013	0.988
	F 2p <sub>z</sub>	0.994	1.008	0.958
CO <sub>2</sub>	C 2s	1.718	1.723	0.815
	C 2p <sub>x</sub> , 2p <sub>y</sub>	1.358	1.388	1.090
	C 2p <sub>z</sub>	1.964	2.036	1.538
	O 2s	1.022	0.992	0.970
	O 2p <sub>x</sub> , 2p <sub>y</sub>	0.974	0.977	0.930
	O 2p <sub>z</sub>	1.037	1.017	1.012
NNO	N1 2s	1.050	1.016	1.002
	N1 2p <sub>x</sub> , 2p <sub>y</sub>	1.075	1.044	0.987
	N1 2p <sub>z</sub>	1.190	1.166	1.137
	N2 2s	1.423	1.469	0.873
	N2 2p <sub>x</sub> , 2p <sub>y</sub>	1.152	1.157	0.992
	N2 2p <sub>z</sub>	1.475	1.510	1.192
	O 2s	1.004	0.999	1.011
	O 2p <sub>x</sub> , 2p <sub>y</sub>	0.964	0.965	0.918
FCN	O 2p <sub>z</sub>	1.052	1.050	1.003
	F 2s	1.023	1.023	0.983
	F 2p <sub>x</sub> , 2p <sub>y</sub>	0.994	0.995	0.965
	F 2p <sub>z</sub>	0.995	1.005	0.965
	C 2s	1.604	1.737	1.031
	C 2p <sub>x</sub> , 2p <sub>y</sub>	1.246	1.243	1.106
	C 2p <sub>z</sub>	1.853	1.819	1.404
	N 2s	1.041	1.021	0.956
	N 2p <sub>x</sub> , 2p <sub>y</sub>	1.023	1.020	0.956
	N 2p <sub>z</sub>	1.081	1.098	1.066

orbital in first row atoms is the same as in the DZ [ $4^s2^p/2^s$ ] basis, and only that part of the basis set describing the valence 2s and 2p orbitals differs between the two sets. Thus, total energy differences for molecules in the two different basis sets can be directly ascribed to differences in their description of the valence charge density. In most of the cases shown in Table 1 it is found that the greater part of the energy lowering is already in the spherical optimization and that typically a proportionately smaller gain in energy is obtained by allowing the orbital to go elliptic.

These changes are dependent to a large extent on the constituent atoms of the molecule. Thus, in general, the energy differences between the various types of basis sets are largest where the most polarizable (least electronegative) atoms are found.

**Table 3.** Energy optimized exponent scale factors for spherical and ellipsoidal Gaussian atomic orbitals in non-linear molecules

Molecule	Atomic orbital	Optimized scale factors <sup>a</sup>			
		Spherical Gaussian	Ellipsoidal Gaussian		
			$\alpha$	$\beta$	$\gamma$
H <sub>2</sub> O <sup>b</sup>	H 1s	1.448	1.591	1.391	1.542
	O 2s	0.986	1.020	0.948	1.028
	O 2p <sub>x</sub>	0.894	0.909	0.856	0.883
	O 2p <sub>y</sub>	1.027	1.039	1.012	1.049
	O 2p <sub>z</sub>	0.930	0.952	0.908	0.227
C <sub>2</sub> H <sub>4</sub> <sup>c</sup>	H 1s	1.339	1.220	1.258	1.258
	C 2s	1.164	1.085	1.291	1.028
	C 2p <sub>x</sub>	1.104	1.108	1.150	1.066
	C 2p <sub>y</sub>	0.960	0.927	0.991	0.898
	C 2p <sub>z</sub>	1.234	1.269	1.265	1.171
N <sub>2</sub> H <sub>2</sub> <sup>d</sup>	H 1s	1.461	1.418	1.405	1.458
	N 2s	1.029	0.976	1.055	1.071
	N 2p <sub>x</sub>	1.161	1.140	1.241	1.215
	N 2p <sub>y</sub>	0.992	0.996	0.993	1.007
	N 2p <sub>z</sub>	0.941	0.904	0.958	0.970
H <sub>2</sub> CO <sup>e</sup>	H 1s	1.363	1.162	1.208	1.284
	C 2s	1.204	1.174	1.345	1.119
	C 2p <sub>x</sub>	1.191	1.202	1.232	1.180
	C 2p <sub>y</sub>	1.057	1.051	1.090	0.940
	C 2p <sub>z</sub>	1.510	1.606	1.576	1.409
	O 2s	1.006	1.007	1.013	0.960
	O 2p <sub>x</sub>	0.963	0.970	0.956	0.929
	O 2p <sub>y</sub>	0.963	0.984	0.964	0.923
	O 2p <sub>z</sub>	1.037	1.064	1.041	0.997

<sup>a</sup> See footnote (a) in Table 1.

<sup>b</sup> H<sub>2</sub>O lies in the *yz* plane.

<sup>c</sup> C<sub>2</sub>H<sub>4</sub> lies in the *xz* plane.

<sup>d</sup> N<sub>2</sub>H<sub>2</sub> lies in the *xy* plane.

<sup>e</sup> H<sub>2</sub>CO lies in the *xz* plane.

The acetylene molecule with its very polarizable charge distribution seems to be an extreme example of the effectiveness of allowing the orbital to go elliptic; here, as noted the total energy in the optimal ellipsoidal basis is lower than the DZ results.

The optimal spherical Gaussian basis scale factors listed in Table 2 (linear) and 3 (non-linear molecules) show the, by now, well known scaling characteristics for such atoms in molecules. For comparison purposes it is usual to relate such scaled orbitals to the corresponding scale factors in a minimal exponential set of basis functions. When this is done here, due care must be taken to compare the square root of the Gaussian scale factors to scale factors belonging to the exponential basis set [13]. In these terms the optimal spherical Gaussian orbitals show a) the usual

**Table 4.** Expectation values  $\langle 1/r \rangle$  at atomic centers in various basis sets<sup>a</sup>

Molecule	Center	Original single zeta <sup>b</sup>	Optimized single-zeta <sup>b</sup>	Elliptic optimized single-zeta <sup>b</sup>	Double-zeta <sup>c</sup>
HF	H	0.8010	0.8657	0.8758	0.8775
	F	27.2528	27.1633	27.1702	26.5941
C <sub>2</sub>	C	14.4396	14.6608	14.6426	14.6325
H <sub>2</sub> C <sub>2</sub>	H	0.8604	1.0578	1.0375	1.0159
	C	14.5022	14.7506	14.7162	14.7143
HCN	H	0.7984	1.0074	1.0006	0.9566
	C	14.4361	14.7172	14.6833	14.6889
	N	18.1678	18.3622	18.3085	18.2852
N <sub>2</sub>	N	18.0447	18.3072	18.2471	18.2376
NO <sup>+</sup>	N	17.2521	17.7600	17.6662	17.6835
	O	21.3086	21.7782	21.6820	21.6888
CN <sup>-</sup>	C	15.0607	15.0758	15.0226	15.0210
	N	18.7216	18.7200	18.6822	18.6612
CO	C	14.4143	14.6604	14.5978	14.6003
	O	22.1252	22.2830	22.2317	22.2324
BF	B	11.2555	11.3410	11.3290	11.3039
	F	26.5750	26.5222	26.5348	26.5170
F <sub>2</sub>	F	26.4213	26.4641	26.4613	26.4610
CO <sub>2</sub>	C	14.1328	14.2216	14.4565	14.4765
	O	22.1543	22.2842	22.2102	22.2339
NNO	N1	18.0503	18.2684	18.2216	18.2052
	N2	17.7881	18.1024	18.0829	18.0785
	O	22.1974	22.2841	22.2547	22.2493
FCN	F	26.4228	26.4921	26.4621	26.4561
	C	14.2528	14.5642	14.5631	14.5486
	N	18.1366	18.3288	18.3051	18.2897
H <sub>2</sub> O	H	0.8974	0.9570	0.9767	0.9720
	O	22.3857	22.3212	22.3474	22.3386
C <sub>2</sub> H <sub>4</sub>	H	0.9732	1.1157	1.1000	1.0947
	C	14.5633	14.7426	14.7255	14.7264
N <sub>2</sub> H <sub>2</sub>	H	0.9005	1.0092	1.0171	1.0077
	N	18.2240	18.3170	18.3365	18.2983
H <sub>2</sub> CO	H	0.9387	1.0896	1.0685	1.0506
	C	14.4222	14.6407	14.6171	14.6132
	O	22.2687	22.3474	22.3164	22.3177

<sup>a</sup> In atomic units.<sup>b</sup> See footnote (b) in Table 1.<sup>c</sup> See footnote (c) in Table 1.



**Table 5.** Expectation values  $\langle \bar{r}/r^3 \rangle$  at atomic centers in various basis sets<sup>a</sup>

Molecule	Center	Direction	Original single-zeta <sup>b</sup>	Optimized single-zeta <sup>b</sup>	Elliptic optimized single-zeta <sup>b</sup>	Double- zeta <sup>c</sup>
HF	H	<i>z</i>	0.1699	0.1189	0.1025	0.1167
	F	<i>z</i>	-0.2951	-0.2776	-0.2771	-0.2440
C <sub>2</sub>	C	<i>z</i>	-0.1192	-0.0927	-0.0884	-0.0677
H <sub>2</sub> C <sub>2</sub>	H	<i>z</i>	0.1512	0.0411	0.0340	0.0685
	C	<i>z</i>	0.0531	0.0419	0.0287	0.0217
HCN	H	<i>z</i>	-0.1552	-0.0331	-0.0181	-0.0628
	C	<i>z</i>	-0.0797	-0.0655	-0.0745	-0.0515
	N	<i>z</i>	0.3227	0.2680	0.2451	0.2025
N <sub>2</sub>	N	<i>z</i>	0.3713	0.2970	0.2984	0.2493
NO <sup>+</sup>	N	<i>z</i>	0.4352	0.3210	0.3098	0.3085
	O	<i>z</i>	-0.5525	-0.4365	-0.4427	-0.3782
CN <sup>-</sup>	C	<i>z</i>	0.2179	0.1631	0.1525	0.1425
	N	<i>z</i>	-0.2848	-0.2673	-0.2783	-0.1932
CO	C	<i>z</i>	0.2625	0.1700	0.1549	0.1845
	O	<i>z</i>	-0.4298	-0.3788	-0.3838	-0.2931
BF	B	<i>z</i>	-0.1520	-0.0877	-0.0722	-0.1270
	F	<i>z</i>	0.3321	0.3146	0.3092	0.2664
F <sub>2</sub>	F	<i>z</i>	-0.1856	-0.1869	-0.1859	-0.1744
CO <sub>2</sub>	O	<i>z</i>	0.4356	0.2853	0.3512	0.3029
NNO	N1	<i>z</i>	-0.3629	-0.3002	-0.2630	-0.2557
	N2	<i>z</i>	0.0572	0.0353	0.0376	0.0131
	O	<i>z</i>	0.3940	0.3704	0.3432	0.3100
FCN	F	<i>z</i>	-0.3793	-0.3417	-0.3350	-0.2911
	C	<i>z</i>	-0.0134	-0.0126	0.0023	0.0328
	N	<i>z</i>	0.3440	0.2814	0.2502	0.2211
H <sub>2</sub> O	H	<i>y</i>	-0.1457	0.1088	0.1041	0.1011
	H	<i>z</i>	0.0661	0.0383	0.0179	0.0374
	O	<i>z</i>	-0.3052	-0.2967	-0.2857	-0.2477
C <sub>2</sub> H <sub>4</sub>	H	<i>x</i>	0.1053	0.0539	0.0561	0.0571
	H	<i>z</i>	-0.0668	-0.0304	-0.0433	-0.0354
	C	<i>z</i>	-0.0335	-0.0259	-0.0206	-0.0102
N <sub>2</sub> H <sub>2</sub>	H	<i>x</i>	-0.0741	-0.0479	-0.0543	-0.0430
	N	<i>x</i>	-0.2087	-0.1865	-0.1789	-0.1621
	H	<i>z</i>	0.1314	0.0824	0.0841	0.0811
	N	<i>z</i>	-0.1796	-0.1675	-0.1648	-0.1393
H <sub>2</sub> CO	H	<i>x</i>	0.1072	0.0543	0.0630	0.0569
	H	<i>z</i>	-0.0629	-0.0155	-0.0345	-0.0312
	C	<i>z</i>	-0.0781	-0.0556	-0.0575	-0.0572
	O	<i>z</i>	0.3615	0.3288	0.3277	0.2635

<sup>a</sup> In atomic units.<sup>b</sup> See footnote (b) in Table 1.<sup>c</sup> See footnote (c) in Table 1.

**Table 6.** First moment charge distribution in various basis sets<sup>a</sup>

Molecule	Original single-zeta <sup>b</sup>	Optimized single-zeta <sup>b</sup>	Elliptic optimized single-zeta <sup>b</sup>	Double-zeta <sup>c</sup>
HF	0.7807	0.9428	0.9646	0.9356
HCN	1.0880	1.3567	1.2020	1.2290
CO	0.0846	0.3308	0.3617	0.1630
BF	0.3147	0.0317	0.0832	0.2107
NNO	0.2319	0.5319	0.4262	0.3894
FCN	0.5818	0.5906	0.6470	0.7161
H <sub>2</sub> O	0.8884	1.0687	1.0810	1.0548
H <sub>2</sub> CO	0.9141	1.3424	1.2649	1.2230

<sup>a</sup> In atomic units.<sup>b</sup> See footnote (b) in Table 1.<sup>c</sup> See footnote (c) in Table 1.**Table 7.** Second moment of charge distribution in various basis sets<sup>a</sup>

Molecule	Direction	Original single-zeta <sup>b</sup>	Optimized single-zeta <sup>b</sup>	Elliptic optimized single-zeta <sup>b</sup>	Double-zeta <sup>c</sup>
HF	<i>x, y</i>	4.1073	4.1196	4.0775	4.1304
	<i>z</i>	2.6834	2.4509	2.5080	2.4769
C <sub>2</sub>	<i>x, y</i>	10.6275	9.4788	9.3174	9.3020
	<i>z</i>	7.3850	6.7365	7.4280	7.2144
H <sub>2</sub> C <sub>2</sub>	<i>x, y</i>	11.7791	10.3955	10.2445	10.3651
	<i>z</i>	6.6983	4.4250	6.1759	5.0604
HCN	<i>x, y</i>	9.8974	8.8062	8.7465	8.8645
	<i>z</i>	8.3528	6.7230	7.8752	7.2963
N <sub>2</sub>	<i>x, y</i>	8.2379	7.5531	7.5677	7.5760
	<i>z</i>	10.1669	9.0580	9.6581	9.3851
NO <sup>+d</sup>	<i>x, y</i>	7.0847	5.9811	6.0745	5.8623
	<i>z</i>	7.1752	5.7763	6.3427	5.7071
NO <sup>+e</sup>	<i>x, y</i>	7.0847	5.9811	6.0745	5.8623
	<i>z</i>	6.0946	4.8832	5.1429	4.7793
CN <sup>-f</sup>	<i>x, y</i>	9.7766	9.8922	9.9097	10.1031
	<i>z</i>	14.4046	14.2289	15.2302	15.2853
CN <sup>-g</sup>	<i>x, y</i>	9.7766	9.8922	9.9097	10.1031
	<i>z</i>	15.3565	14.2525	15.1142	15.5275

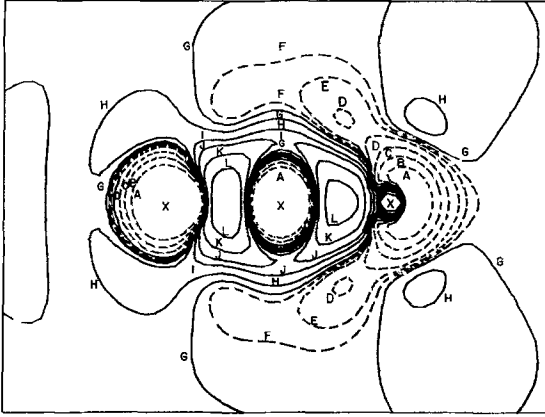
<sup>a</sup> Results are in atomic units. The origin is always at the center of mass except for NO<sup>+</sup> and CN<sup>-</sup>.<sup>b</sup> See footnote (b) in Table 1.<sup>c</sup> See footnote (c) in Table 1.<sup>d</sup> The origin at the nitrogen atom.<sup>e</sup> The origin at the oxygen atom.<sup>f</sup> The origin at the carbon atom.<sup>g</sup> The origin at the nitrogen atom.

Table 7—cont.

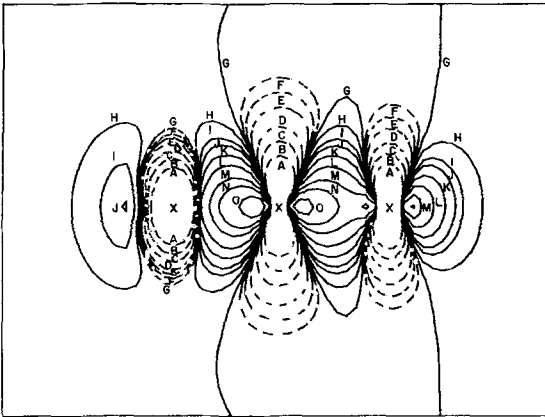
Molecule	Direction	Original single-zeta <sup>b</sup>	Optimized single-zeta <sup>b</sup>	Elliptic optimized single-zeta <sup>b</sup>	Double-zeta <sup>c</sup>
CO	<i>x, y</i>	8.1181	7.4467	7.5315	7.4711
	<i>z</i>	10.7119	9.5196	10.0317	9.8552
BF	<i>x, y</i>	7.7035	7.4807	7.5850	7.6394
	<i>z</i>	12.2219	10.6664	10.5267	11.4760
F <sub>2</sub>	<i>x, y</i>	7.1238	7.0638	7.0207	7.0439
	<i>z</i>	6.7846	6.7422	6.8585	6.8621
CO <sub>2</sub>	<i>x, y</i>	12.2638	12.2695	11.1148	11.0182
	<i>z</i>	16.4431	17.0773	17.3821	16.5116
NNO	<i>x, y</i>	12.3562	11.4792	11.4383	11.4720
	<i>z</i>	15.6133	15.7329	16.3435	15.8258
FCN	<i>x, y</i>	12.5303	11.3620	11.2553	11.2912
	<i>z</i>	15.7229	15.8682	16.4562	15.7865
H <sub>2</sub> O	<i>x</i>	5.4091	5.4867	5.3309	5.4896
	<i>y</i>	3.5999	3.1282	3.2429	3.1317
	<i>z</i>	4.5139	4.3970	4.3068	4.4501
C <sub>2</sub> H <sub>4</sub>	<i>x</i>	10.5631	9.1027	9.4907	9.1033
	<i>y</i>	13.0982	12.0702	11.6807	12.0755
	<i>z</i>	10.6951	8.6801	9.5994	9.0766
N <sub>2</sub> H <sub>2</sub>	<i>x</i>	10.1116	9.0710	9.4000	9.5997
	<i>y</i>	8.3341	7.7254	7.6984	7.9252
	<i>z</i>	9.4320	9.1965	8.9277	9.1005
H <sub>2</sub> CO	<i>x</i>	9.2964	8.3209	8.5699	8.4828
	<i>y</i>	9.7666	8.8625	8.7618	8.7836
	<i>z</i>	9.7661	8.3849	9.0574	9.0464

contraction of charge density about the hydrogen atom in molecules, b) the general trend of increased scaling in going from fluorine to boron, c) the differential contraction of the  $2p_{\sigma(z)}$  relative to the corresponding  $2p_{\pi(x,y)}$  orbitals and d) the relatively small scaling of the  $2s$  orbital in the first row atoms in molecules.

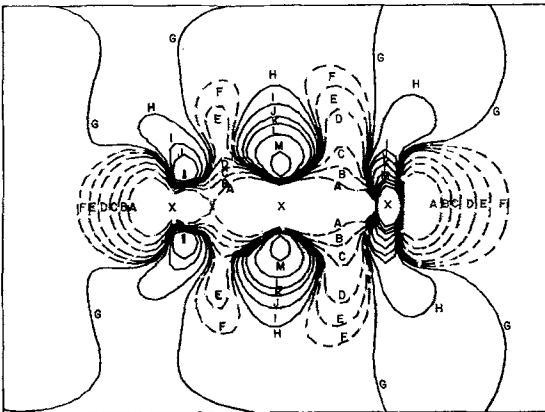
Trends in the ellipticity of the various valence orbitals have not been investigated previously and based on the results in Tables 2 and 3 the following general observations can be made. a) The hydrogen atom is generally not very elliptic when attached to carbon, but the ellipticity increases as the hydrogen atom is attached to a more electronegative atom. b) Among the first-row atoms the ellipticity of the valence atomic orbitals generally decreases in going from carbon to fluorine. These two observations, of course, reflect the usual relationship between increasing electronegativity and decreased atom deformability. c) There is no substantial difference in the degree of ellipticity of the  $2p_{\sigma(z)}$  and  $2\pi_{\pi(x,y)}$  orbitals and, generally, the same sense of elliptic polarization is found for both orbital types. d) The carbon  $2s$  orbital in linear systems in a non-terminal atom has a significantly high degree of



**Fig. 1.** Density difference contour map for  $N_2O$ : Double zeta minus spherical optimized basis sets. Values of the contours for all the figures are:  $A = -0.040$ ,  $B = -0.020$ ,  $C = -0.010$ ,  $D = -0.004$ ,  $E = -0.002$ ,  $F = -0.001$ ,  $G = 0.000$ ,  $H = 0.002$ ,  $I = 0.006$ ,  $J = 0.010$ ,  $K = 0.020$ ,  $L = 0.040$ ,  $M = 0.080$ ,  $N = 0.120$ ,  $O = 0.200$



**Fig. 2.** Density difference contour map for  $N_2O$ : Elliptical minus spherical optimized basis sets



**Fig. 3.** Density difference contour map for  $N_2O$ : Double zeta minus ellipsoidal basis sets

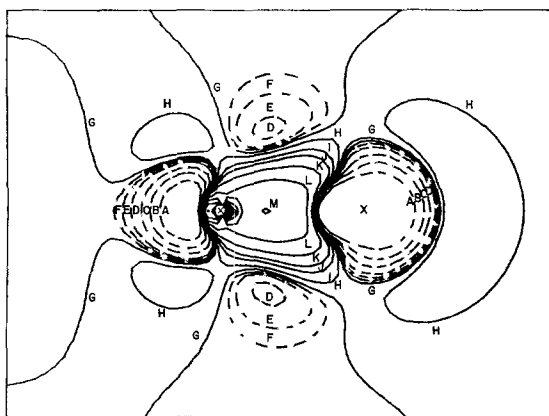


Fig. 4. Density difference contour map for CO: Double zeta minus spherical optimized basis sets

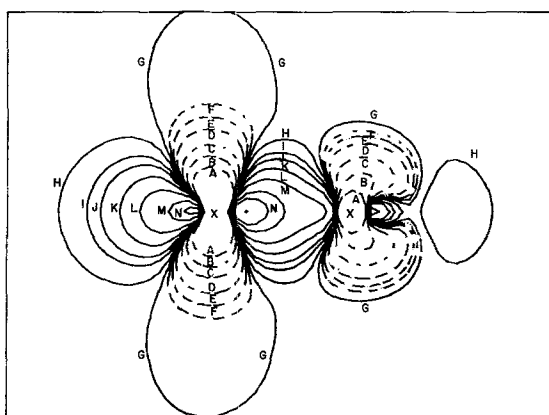


Fig. 5. Density difference contour map for CO: Ellipsoidal minus spherical optimized basis sets

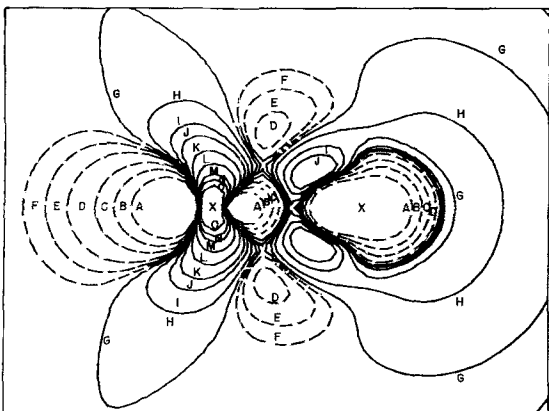


Fig. 6. Density difference contour map for CO: Double zeta minus ellipsoidal basis sets

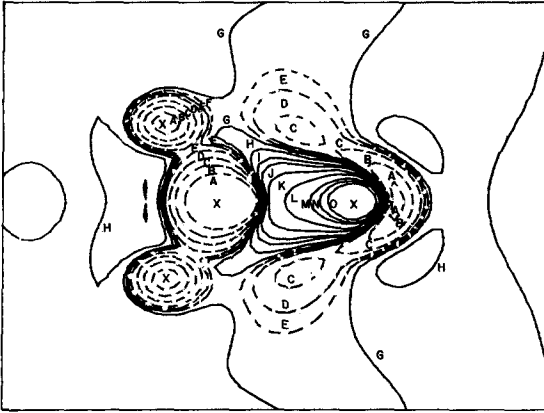


Fig. 7. Density difference contour map for  $\text{H}_2\text{CO}$ : Double zeta minus spherical optimized basis sets

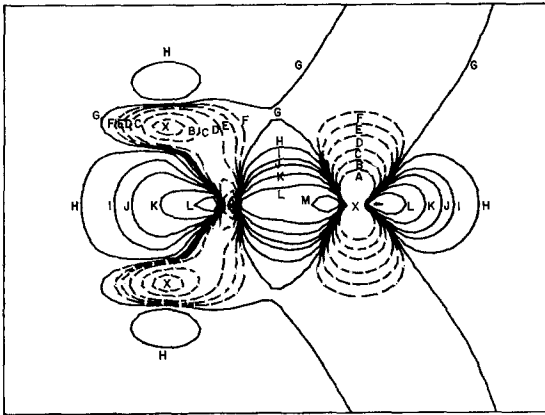


Fig. 8. Density difference contour map for  $\text{H}_2\text{CO}$ : Ellipsoidal minus spherical optimized basis sets

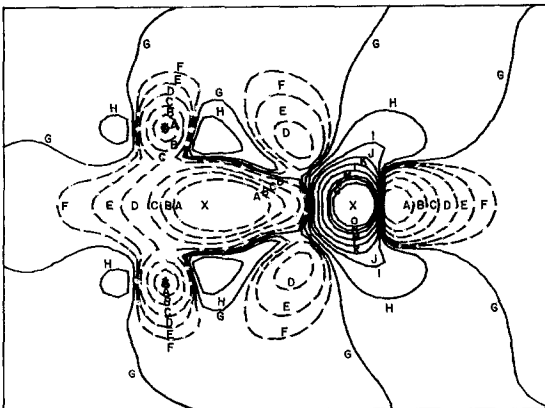


Fig. 9. Density difference contour map for  $\text{H}_2\text{CO}$ : Double zeta minus ellipsoidal basis sets

ellipticity. If we recall that the ellipticity of an orbital reflects a differential radial Cartesian polarization of the atomic charge density, these last two observations could possibly be interpreted as showing an attempt on the part of the basis set to balance energy requirements between the purely atomic aspect and the molecular environment. These features of the atomic basis sets in their molecular environment will be discussed later.

In discussing the properties set out in Tables 4–7 the point of view will be taken that the DZ results which (except for  $C_2H_2$ ) are variationally lower in energy than the corresponding optimized ellipsoidal basis energies, also give one-electron properties which are “better” than the ellipsoidal basis. Although this is not necessarily true in practice it is consistent with the known properties of the ellipsoidal basis which adds only radial polarization to the minimal zeta spherical basis. Thus the DZ property values form a convenient set of uniform reference data with which to compare the ellipsoidal basis properties where the corresponding experimental values are not always available.

In this light the following generally obeyed relationships can be discerned in these tables.

- a) From the second moment properties, for the in-plane coordinates, it can be concluded that the ellipsoidal basis wave function tends to be more spatially diffuse than the DZ basis wave function. The opposite appears to be generally true for the out-of-plane or  $\pi$  coordinate.
- b) From the average values of the potential operator, the charge density around the hydrogen atom is generally more contracted using the ellipsoidal basis than in the DZ basis. This relationship somewhat carries over to the first-row atoms but certainly in a less consistent form. One of the difficulties in establishing trends for  $\langle 1/r \rangle$  is the relatively small difference in their values between the various basis sets. The size of these differences is of the same order as for the total energies which is not surprising considering the important role played by the  $1/r$  operator in the total energy expression.
- c) Expectation values of the nuclear centered  $\vec{r}/r^3$  operator, being directly proportional to the quantum mechanical force on the nucleus, [8] have *a priori* known zero values for the real Hartree–Fock wave function at the calculated equilibrium geometry, or for limited basis set expansions such as those used here if the basis set and geometric parameters have been properly scaled by an energy optimization criterion. Since the geometries of the molecules studied here have not been optimized we can only look at the tendency of the values of  $\langle \vec{r}/r^3 \rangle$  to zero as the quality of the wave function improves. In the light of this argument the numbers in Table 6 show a generally decreasing (absolute) value with increasing quality of basis set, paralleling the decrease in total energy. This observation reinforces the idea that the DZ basis also gives better property values than the ellipsoidal basis. The few exceptions to this generalization for  $\langle \vec{r}/r^3 \rangle$  can probably be attributed to the slightly different equilibrium geometries that would be found for each type basis relative to the assumed geometry used here [14].

Although an examination of the average values of the operators discussed above does give a certain amount of general information about the various type basis sets, the most pointed indication of the advantages and disadvantages of the ellipsoidal basis comes from the molecular difference density maps. Here the difference in total electron densities obtained for the various basis sets for each molecule in a given plane is plotted [9]. Thus for example, Figs. 1, 4 and 7 show the change in charge distribution in going from the optimal spherical (OS) to the DZ basis [i.e.  $\psi_{DZ}^2(\vec{r}_i) - \psi_{OS}^2(\vec{r}_i)$ ] for the  $N_2O$ , CO and  $H_2CO$  molecules in their respective molecular planes. These molecules show effects and trends representative of the general results obtained for all the molecular species studied here.

The difference density contour maps (Figs. 1, 4 and 7) show that in going from the OS to DZ basis, electron charge density typically decreases in the lone pair and atomic regions of the molecules and increases in the interatomic bonding regions. Thus, effectively, the result of using the more flexible basis set is to cause charge to be transferred from the outer and atomic regions to the interatomic areas of the molecule [15]. The minimal zeta basis (even with optimization) is apparently insufficiently flexible to redistribute the atomic charge densities properly.

We can now gauge the effect of using the optimized ellipsoidal (OE) basis in terms of its effects on the atomic charge density. From Figs. 2, 5 and 8, again for the same 3 molecules cited above, it can be seen that in going from the OS to OE basis, charge density is also transferred from the atomic regions to the internuclear or bonding regions, although some of the electron density also goes (from the atomic regions) to the outer or lone-pair regions of the molecule. From the above noted OS  $\rightarrow$  DZ trends this latter type shift is in the wrong direction. It also turns out that the transfer from the atomic to the bonding regions, although in the right direction, is apparently exaggerated. This can be seen from Figs. 3, 6 and 9 which show the OE  $\rightarrow$  DZ density difference. Thus, in these figures, electron density is seen to be depleted from the electron lone pair regions apparently correcting for the increase in these areas of molecular space in going OS  $\rightarrow$  OE. In addition, in going OE  $\rightarrow$  DZ charge density is also seen to be depleted from the bonding regions and to increase in the atomic regions, apparently compensating for the exaggerated reverse transfer (atomic  $\rightarrow$  bond) in going OS  $\rightarrow$  OE.

In summary then, the difference density contour maps seem to indicate that the OE basis exaggerates the transfer of charge from the immediate atomic environment into the interatomic and lone-pair regions of molecules. Thus, for example, in accord with what was noted before in the linear and planar molecules, the second moment of the charge distribution is generally larger for the OE than in the DZ basis for the (internuclear)  $z$  coordinate but generally smaller for the out-of-plane coordinate where the atomic effects dominate. Thus the minimal atomic orbital ellipsoidal basis seems to be insufficiently flexible to strike the proper energy balance between the purely (spherical) atomic aspects and the anisotropic molecular environment requirements of the molecule.

Other properties and aspects of the ellipsoidal Gaussian functions also have to be considered in weighing their ultimate usefulness as expansion basis functions in



Hartree–Fock theory. Thus the transformation properties of the elliptical exponential are such that the Cartesian exponents [ $\alpha$ ,  $\beta$  and  $\gamma$  in (1)] are coordinate dependent. Therefore, this type basis set has the undesirable feature that both the total molecular energy and wave function will be coordinate dependent. This property need not be fatal if a way could be found of obtaining the optimum Cartesian components of the exponent as part of the SCF process. This would require a set of formulas relating the Cartesian components of the exponent to some function of the matrix elements of the charge density matrix computed for the same basis. This type of procedure has been discussed recently [16] for ordinary exponential type basis functions where the Mulliken population analysis is used to convert the charge density matrix to a set of orbital populations. These latter are subsequently used in a set of formulas, resembling Slater's rules [17], relating the orbital exponent to the atomic orbital populations. The orbital exponent is then iterated in the SCF process along with the charge density matrix. Such a method can also be used for ellipsoidal Gaussian orbitals if due care is taken to account for the anisotropic character of the orbital exponent.

Such a method would also remove the need to individually optimize the Cartesian components of the Gaussian exponential as was done here. This optimization is very time consuming since, with the computer programs used here, a single integrals calculation for a given molecule with all elliptic exponents typically takes two orders of magnitude longer than a single DZ basis calculation using ordinary spherical Gaussian basis functions.

#### 4. Conclusions

The ellipsoidal Gaussian basis function used in a minimal valence atomic orbital representation is generally inferior to a double-zeta spherical Gaussian basis orbital representation in energy and properties. The difficulty seems to be in the forced complete elliptization of the valence atomic orbital in the minimal atomic orbital representation which does not allow the basis set sufficient flexibility to simultaneously represent both the basically spherical atomic part of these orbitals and the non-spherical molecular bond formation. The result is an excessive transfer of charge density from the atomic to the internuclear regions forced by the analytical form of the elliptic function. This analysis suggests that a more selective use of ellipsoidal Gaussian functions in valence orbitals will lead to better results. In any event, widespread use of ellipsoidal Gaussian functions will require both a simple method for determining the anisotropic Cartesian exponential components and much faster computer programs for calculating the energy integrals entering into the solution of the matrix Hartree–Fock equations. Similar conclusions have been reached by Frost [18] with regard to the use of floating (non-nuclear centered) ellipsoidal Gaussian type orbitals.

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*Received May 26, 1978*