

Ab Initio Calculations on Large Molecules Using Molecular Fragments. Generalization and Characteristics of Floating Spherical Gaussian Basis Sets^{1a}

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Abstract: An analysis is presented that shows how floating spherical Gaussian orbital (FSGO) basis sets can be related to atomic Gaussian orbital basis sets. In addition, through the development of the concept of local rotational invariance, it is shown how FSGO basis sets can, in a systematic and straightforward manner, be generalized and extended to increase the flexibility of the basis. To illustrate the concepts, it is shown how full sets of p- and d-type atomic orbital components can be included in an FSGO basis using substantially fewer basis functions than needed in traditional lobe-function basis sets.

I. Introduction

Ever since the introduction of floating spherical Gaussian orbitals (FSGO) as basis functions for ab initio calculations,^{2,3} many generalizations and applications have occurred. For example, formulation and characterization of techniques for ab initio self-consistent field molecular orbital⁴ (SCF-MO) calculations on large molecular systems using these basis orbitals have taken place,⁵⁻¹⁸ and application to a variety of problems of biological and chemical interest has occurred.¹⁹⁻³⁴ In addition, other formulations and applications in different areas have also taken place.³⁵⁻⁶³ As is clear from an examination of these studies, FSGO basis orbitals have been used at both ends of the computational spectrum, i.e., in small basis set calculations on large molecules and in high accuracy, large basis set calculations on small molecules. As useful and convenient as such studies have been, the fundamental conceptual and computational advantages that are inherent in FSGO's as basis functions have not been exploited fully. This has been due primarily to the lack of a suitable framework for generalization that would allow higher accuracy to be obtained through a systematic and nonarbitrary increase in basis set size and flexibility without sacrificing the advantageous conceptual and computational characteristics of FSGO's.

For example, when small FSGO basis sets are employed to describe large molecules, computational considerations usually require the FSGO's to reflect a preconceived notion of the hybridization of the various atoms. As a result, changes that may alter the assumed hybridizations (e.g., inversion at a nucleus) may, in general, not be adequately described. In addition, although s, p, d, f, . . . atomic-orbital (AO) components are introduced *implicitly* when FSGO basis sets are used,¹⁶ the number and flexibility of the various components present may not be sufficient to obtain a desired accuracy.

In the case of the use of FSGO's in large basis set, high accuracy calculations (e.g., in the lobe-function approach³⁷⁻³⁸), augmentation of the basis to obtain improved accuracy is usually accomplished by adding AO analogues of higher angular momentum and/or by adding additional AO analogues of the same angular momentum (e.g., as in a double- ζ basis⁶²). In this manner, the natural atomic orbital progression, s, p, d, f, . . . , provides one way in which an FSGO basis can be expanded to reach, for example, the Hartree-Fock limit. However, in employing this particular method of basis orbital generalization, some of the conceptual and computational flexibilities of FSGO's are lost.

In the sections to follow, an analysis is presented that provides a framework for generalizing FSGO basis sets that re-

tains the conceptual and computational advantages of FSGO's, without imposing the restrictions or limitations just mentioned. In particular, it will be shown that, at least in principle, increased accuracy can be obtained from FSGO basis sets, using a straightforward and nonarbitrary generalization that does not require direct mimicking of AO basis sets. The analysis also illustrates the relationship between FSGO and atomic Gaussian basis sets, and indicates how all atomic spherical harmonic components corresponding to a given orbital angular momentum can be included in an FSGO basis with a minimum number of FSGO. Finally, the order to which local rotational invariance of the results is obtained is discussed. Following the analysis, several examples are given to illustrate the manner in which the analysis may be applied, and how a systematic approach to obtaining higher accuracy FSGO basis sets can be achieved.

II. Expansion of FSGO about an Arbitrary Point

Normalized FSGO's are defined as follows:

$$G(\mathbf{r}) = (2/\pi\rho^2)^{3/4} \exp\{-(\mathbf{r} - \mathbf{R})^2/\rho^2\} \quad (1)$$

where ρ is referred to as the "orbital radius"⁶³ and $\mathbf{R} = (X, Y, Z)$ describes the position of the FSGO relative to an arbitrary fixed origin. The above relationships are illustrated in Figure 1. Hence, the size and location of an FSGO is represented by four nonlinear adjustable parameters (ρ, X, Y, Z), which can be determined through energy minimization procedures, by ad hoc procedures based on "chemical reasoning", or by some combination of the two. The FSGO's so determined can then be used as basis functions in standard ab initio SCF-MO calculations.

However, since FSGO's are spherically symmetric about their local origin and are not necessarily confined to lie on atomic centers, comparison of results of SCF-MO calculations using FSGO basis functions with calculations carried out using atom-centered Gaussian-type orbital (GTO) basis functions⁶⁴ is more difficult. In order to analyze the relationship between FSGO's and atom-centered GTO's, and thus to facilitate comparisons between such calculations, it is necessary to examine the expansion of an FSGO about a nearby point, e.g., an atomic center. As will be shown in the next section, such an expansion also provides the necessary framework for analyzing the local rotational invariance of various FSGO arrangements about an atomic center.

In order to carry out the analysis, eq 1 is rewritten in the following Cartesian form:

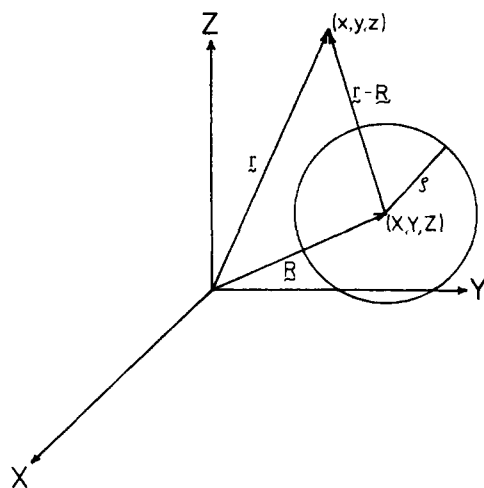


Figure 1. Description of an "off-center" FSGO located at a point relative to an arbitrary fixed origin as defined in eq 1. The orbital radius, ρ , is represented by circle.

$$G(\mathbf{r}) = (2/\pi\rho^2)^{3/4} \exp\{-[(x - X)^2 + (y - Y)^2 + (z - Z)^2]/\rho^2\} \quad (2)$$

$$= \exp\{-(R/\rho)^2\} G^0(\mathbf{r}) \exp\{(\epsilon_X x + \epsilon_Y y + \epsilon_Z z)/\rho\} \quad (3)$$

where $G^0(\mathbf{r})$ is identical with $G(\mathbf{r})$ except that its origin is at the point of expansion and the ϵ 's are unitless parameters defined by:

$$\epsilon_X = 2X/\rho, \quad \epsilon_Y = 2Y/\rho, \quad \epsilon_Z = 2Z/\rho \quad (4)$$

As is clear from eq 3, the first two terms are spherically symmetric about the chosen origin, and hence any angular dependence must come from the third term. By expanding the third term in a Taylor series, the angular dependence is seen to be:

$$\begin{aligned} \exp\{(\epsilon_X x + \epsilon_Y y + \epsilon_Z z)/\rho\} = & 1 + [\epsilon_X x + \epsilon_Y y + \epsilon_Z z]/\rho \\ & + 1/2[\epsilon_X^2 x^2 + \epsilon_Y^2 y^2 + \epsilon_Z^2 z^2 + 2\epsilon_X \epsilon_Y xy \\ & + 2\epsilon_X \epsilon_Z xz + 2\epsilon_Y \epsilon_Z yz]/\rho^2 + 1/6[\epsilon_X^3 x^3 + \epsilon_Y^3 y^3 \\ & + \epsilon_Z^3 z^3 + 3\epsilon_X \epsilon_Y^2 xy^2 + 3\epsilon_X \epsilon_Z^2 xz^2 + 3\epsilon_X^2 \epsilon_Y x^2 y \\ & + 3\epsilon_X^2 \epsilon_Z x^2 z + 3\epsilon_Y^2 \epsilon_Z y^2 z + 3\epsilon_Y \epsilon_Z^2 yz^2 \\ & + 6\epsilon_X \epsilon_Y \epsilon_Z xyz]/\rho^3 + \vartheta(\epsilon^4). \quad (5) \end{aligned}$$

It is of interest for later discussions to note that the order of the multinomial terms (i.e., 1, x , y , z , x^2 , y^2 , \dots , yz , \dots) is the same as the order of the corresponding ϵ 's. The quantity $\vartheta(\epsilon^4)$ is equivalent to the usual remainder term⁶⁵ and contains all terms of order ϵ^4 and higher. Such an expansion is uniformly convergent⁶⁵ for all r , but is of particular interest when $|er/\rho| < 1$, where $|er/\rho| = [\epsilon_X^2 x^2 + \epsilon_Y^2 y^2 + \epsilon_Z^2 z^2]^{1/2}/\rho$. This condition is satisfied in the neighborhood of the origin of $G(\mathbf{r})$ when the point of expansion lies within the orbital radius, ρ [cf. Figure 1].

Substitution of eq 5 into eq 3 then yields

$$\begin{aligned} G(\mathbf{r}) = & \exp\{-(\epsilon_X^2 + \epsilon_Y^2 + \epsilon_Z^2)/4\} \{G^1(\mathbf{r}) + [\epsilon_X G^x(\mathbf{r}) \\ & + \epsilon_Y G^y(\mathbf{r}) + \epsilon_Z G^z(\mathbf{r})]/2 + [(\sqrt{3}/2)\epsilon_X^2 G^{x^2}(\mathbf{r}) \\ & + (\sqrt{3}/2)\epsilon_Y^2 G^{y^2}(\mathbf{r}) + (\sqrt{3}/2)\epsilon_Z^2 G^{z^2}(\mathbf{r}) + \epsilon_X \epsilon_Y G^{xy}(\mathbf{r}) \\ & + \epsilon_X \epsilon_Z G^{xz}(\mathbf{r}) + \epsilon_Y \epsilon_Z G^{yz}(\mathbf{r})]/4 + [(\sqrt{15}/6)\epsilon_X^3 G^{x^3}(\mathbf{r}) \\ & + (\sqrt{15}/6)\epsilon_Y^3 G^{y^3}(\mathbf{r}) + (\sqrt{15}/6)\epsilon_Z^3 G^{z^3}(\mathbf{r}) \\ & + (\sqrt{3}/2)\epsilon_X \epsilon_Y^2 G^{x^2 y}(\mathbf{r}) + (\sqrt{3}/2)\epsilon_X \epsilon_Z^2 G^{x^2 z}(\mathbf{r}) \\ & + (\sqrt{3}/2)\epsilon_X^2 \epsilon_Y G^{x^2 y}(\mathbf{r}) + (\sqrt{3}/2)\epsilon_X^2 \epsilon_Z G^{x^2 z}(\mathbf{r}) \\ & + (\sqrt{3}/2)\epsilon_Y \epsilon_Z^2 G^{y^2 z}(\mathbf{r}) + (\sqrt{3}/2)\epsilon_Y^2 \epsilon_Z G^{y^2 z}(\mathbf{r}) \\ & + \epsilon_X \epsilon_Y \epsilon_Z G^{xyz}(\mathbf{r})\}/8 + \vartheta(\epsilon^4)\} \quad (6) \end{aligned}$$

which is an expansion of $G(\mathbf{r})$ in normalized Cartesian GTO's⁶⁴

located at the point of expansion, and of the general form

$$G^{x^a y^b z^c}(\mathbf{r}) = N x^a y^b z^c G^0(\mathbf{r}) \quad a, b, c = 0, 1, 2, \dots \quad (7)$$

where

$$N = N_a N_b N_c \quad (8a)$$

and

$$N_i = \begin{cases} (2/\rho)^i [1 \times 3 \times 5 \dots (2i - 1)]^{-1/2} & i \geq 1 \\ 1 & i = 0 \end{cases} \quad (8b)$$

where $i = a, b$, or c . The series in eq 6 is also uniformly convergent, since it arises simply from multiplication of the original uniformly convergent exponential series (eq 5) by the function $G^0(\mathbf{r})$. This uniform convergence, coupled with the linear independence of the G basis functions, implies that the set $\{G^{x^a y^b z^c}\}$ is complete.⁶⁶ A similar but less general expansion and discussion has been given earlier.¹⁶

III. Local Rotational Invariance of Off-Center Gaussian Basis Sets. Theoretical Considerations.

In developing a suitable framework for the generalization and improvement of FSGO basis sets, it is necessary not only to be able to relate the FSGO's to atomic GTO's, but also to assess the extent to which energy and/or other properties depend upon the local orientation chosen for a given set of FSGO's with respect to a particular atomic center. To do this, the concept of *local rotational invariance* will be developed.

In order to quantify this concept, consider the usual sets of s-, p-, d-, and f-type AO functions^{67,68}

$$(s) \quad (9a)$$

$$(p_x, p_y, p_z) \quad (9b)$$

$$\{\xi\}_n \equiv (d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}, d_{3z^2-2r^2}) \quad (9c)$$

$$\begin{aligned} & (f_x(5x^2-3r^2), f_y(5y^2-3r^2), f_z(5z^2-3r^2), f_x(z^2-x^2), \\ & f_y(z^2-x^2), f_z(x^2-y^2), f_{xyz}) \quad (9d) \end{aligned}$$

which form bases of dimension $n = 1, 3, 5, 7$, respectively, for the $D^{(0)}$, $D^{(1)}$, $D^{(2)}$, and $D^{(3)}$ irreducible representations of the full (three-dimensional) rotational group (R_3). Thus, each set spans an invariant subspace of dimension n under the operations of R_3 , i.e., the functions in each set transform only among themselves⁶⁹⁻⁷¹ (see also Table I). Stated mathematically,

$$\{\xi\}_n \xrightarrow{\mathcal{R}(R_3)} \{\xi\}_n \quad (10)$$

where $\{\xi\}_n$ represents one of the sets of AO functions in eq 9, and $\mathcal{R}(R_3)$ represents any symmetry operation of R_3 .

Based upon these observations, *the degree of local rotational invariance of a particular set of atomic-type functions will be taken to be equal to the dimension of the invariant subspace spanned by the set under the operations of R_3 .*⁷² Hence, the s-, p-, d-, and f-type AO's above are rotationally invariant to degree 1, 3, 5, and 7, respectively.

If the symmetry of the system is reduced from spherical to some lower symmetry, the transformation properties of the various s-, p-, and f-type AO's are altered. Under the operations of the lower symmetry group, all the functions of a particular type (e.g., d functions) no longer necessarily transform as a single irreducible representation. If, for example, the lower symmetry splits the original group of functions into two irreducible representations, the functions in either one of these taken separately will no longer span an invariant subspace under the operations of R_3 . Hence, the degree of local rotational invariance that was present in the original group of functions is no longer retained. The specific changes that occur in going from the full rotation group through finite (three-

Table I. Transformation Properties of Real Multinomial Functions With Respect to the Full Rotation, Icosahedral, Octahedral, and Tetrahedral Symmetry Groups^a

Symmetry group	Irreducible representation	Dimension of irreducible representation	Multinomial transformation properties ^{b,c}
Full rotation (R_3) (order = ∞)	$D^{(0)}$	1	1
	$D^{(1)}$	3	x, y, z
	$D^{(2)}$	5	$xy, xz, yz, x^2 - y^2, 3z^2 - r^2$
	$D^{(3)}$	7	$x(5x^2 - 3r^2), y(5y^2 - 3r^2), z(5z^2 - 3r^2),$ $x(z^2 - y^2), y(z^2 - x^2), z(x^2 + y^2), xyz$
Icosahedral (I) (order = 60)	Γ_{A_1}	1	1
	Γ_{T_1}	3	$(x, y, z), [x(y^2 + z^2), y(x^2 + z^2), z(x^2 + y^2)]$
	Γ_{T_2}	3	x^3, y^3, z^3
	Γ_G	4	$x(z^2 - y^2), y(z^2 - x^2), z(x^2 - y^2), xyz$
	Γ_H	5	$xy, xz, yz, x^2 - y^2, 3z^2 - r^2$
Octahedral (O) (order = 24)	Γ_{A_1}	1	1
	Γ_{A_2}	1	xyz
	Γ_E	2	$x^2 - y^2, 3z^2 - r^2$
	Γ_{T_1}	3	$(x, y, z), (x^3, y^3, z^3), [x(y^2 + z^2), y(x^2 + z^2), z(x^2 + y^2)]$
Tetrahedral (T) (order = 12)	Γ_{T_2}	3	$(xy, xz, yz), [x(z^2 - y^2), y(z^2 - x^2), z(x^2 - y^2)]$
	Γ_A	1	1, xyz
	Γ_E	2	$x^2 - y^2, 3z^2 - r^2$
	Γ_T	3	$(x, y, z), (xy, xz, yz), (x^3, y^3, z^3), [x(y^2 + z^2), y(x^2 + z^2), z(x^2 + y^2)],$ $[x(z^2 - y^2), y(z^2 - x^2), z(x^2 - y^2)]$

^a For a general discussion of the theory of groups, see ref 70. ^b See ref 67 and 68 for further discussion of the form of real AO's. ^c The multinomial functions, whose transformation properties are given in the table, are completely equivalent to their corresponding AO components (cf. eq 9a-d) under the operations of a given group.

dimensional) rotational groups of lower order, viz., full (R_3) \rightarrow icosahedral (I) \rightarrow octahedral (O) \rightarrow tetrahedral (T), are given in Table I.

The above descent in symmetry illustrates two points that are relevant to later discussions: (1) there exist only three finite, three-dimensional, rotation groups, (i.e., I , O , and T),⁷³ and (2) the icosahedral group represents the highest-order finite three-dimensional rotation group. The latter implies that, next to the sphere, an icosahedron is the most highly symmetric three-dimensional solid that may be constructed.⁷³

A further consequence of these changes is that a particular set of functions, while spanning an invariant subspace under the operations of a lower order group, may not possess local rotational invariance, which requires spanning an invariant subspace under the operations of R_3 . For example, the dimension of the invariant subspace spanned by any set of functions transforming as the Γ_T irreducible representation under the operations of the tetrahedral group (T) is three. If the set of functions contained only complete sets of p-type AO's, this degree of local rotational invariance can be realized, since all three p-type functions (which transform as Γ_T under T) also span an invariant three-dimensional subspace under R_3 , and thus show rotational invariance to degree three. If, however, sets of d- and/or f-type functions (which also transform as Γ_T under T , as shown in Table I) are included in or constitute the entire set, rotational invariance is completely lost, since three d- and/or f-type AO's are not sufficient to span any invariant subspace under R_3 . The above results can be summarized in general by noting that the degree of local rotational invariance equals the dimension of the invariant subspace spanned by the functions under the operations of R_3 , and is not determined only by the behavior of the functions under the operations of the lower order rotation group.

By applying arguments analogous to those in the above example to the other groups in Table I, it is seen that *the maximum possible local rotational invariance that can be obtained rigorously using functions in any system of symmetry lower than a sphere is five*. This follows directly from the fact that

the set of five d-type AOs (see Table I and eq 9c) transform as the five-dimensional Γ_H irreducible representation of the icosahedral group (I), and span an invariant subspace of dimension five under the operations of R_3 . No other irreducible representations of greater dimension are possible in any of the finite rotation groups.

To investigate the local rotational invariance properties of FSGO's, it is necessary to relate the properties of the individual terms in the FSGO expansion described in the previous section (see eq 2-6) to the rotational invariance properties of AO's just considered. For example, in the case of a single FSGO located on an atomic center, the function is spherically symmetric about this local origin, and hence is locally rotationally invariant to degree one about that point. To exhibit the effect of displacement of the FSGO from this origin on local rotational invariance, it will be assumed that the FSGO is displaced along an arbitrary axis (e.g., the x axis). From eq 6, we have

$$G(\mathbf{r}) = \exp\{-\epsilon_X^2/4\} \{G^1(\mathbf{r}) + (1/2)\epsilon_X G^2(\mathbf{r}) + (\sqrt{3}/8)\epsilon_X^2 G^3(\mathbf{r}) + \vartheta(\epsilon^3)\} \quad (11)$$

From this expression we see that, if the orbital radius ρ is sufficiently large and the point of expansion is close to the origin of the FSGO (i.e., ϵ_X is small), and if the region under consideration is sufficiently close to the origin of the expansion (i.e., r is small), the $G(\mathbf{r})$ will remain approximately locally rotationally invariant to degree one. We shall speak of this approximation to local rotational invariance in terms of the *order in ϵ to which local rotational invariance is maintained*, since it is obtained only under particular conditions in the region close to the point of expansion. However, an examination of eq 11 shows that, regardless of the magnitude of ϵ_X , local rotational invariance of degree greater than one can never be obtained rigorously with a single FSGO. Therefore, in the above case we speak of local rotational invariance of degree one through order ϵ^0 .

It is possible to construct particular arrangements of several FSGO's that can exhibit a higher degree of local rotational invariance, and do so to higher orders in ϵ . In particular, con-

Table II. Reducible Representations Generated by Specific Spatial Arrangements of FSGO's^a

Symmetry group ^b	Geometric object ^c	Number of FSGO	Irreducible representations contained in the reducible representation
<i>T</i>	Tetrahedron ^d	4	$\Gamma_{\text{red}} = \Gamma_A + \Gamma_T$
<i>O</i>	Octahedron	6	$\Gamma_{\text{red}} = \Gamma_{A_1} + \Gamma_E + \Gamma_{T_1}$
	Cube ^e	8	$\Gamma_{\text{red}} = \Gamma_{A_1} + \Gamma_{A_2} + \Gamma_{T_1} + \Gamma_{T_2}$
	Cubo-octahedron ^f	12	$\Gamma_{\text{red}} = \Gamma_{A_1} + \Gamma_E + \Gamma_{T_1} + 2\Gamma_{T_2}$
<i>I</i>	Icosahedron	12	$\Gamma_{\text{red}} = \Gamma_A + \Gamma_{T_1} + \Gamma_{T_2} + \Gamma_H$
	Dodecahedron ^g	20	$\Gamma_{\text{red}} = \Gamma_A + \Gamma_{T_1} + \Gamma_{T_2} + 2\Gamma_G + \Gamma_H$
	Icosidodecahedron ^h	30	$\Gamma_{\text{red}} = \Gamma_A + \Gamma_{T_1} + \Gamma_{T_2} + \Gamma_G + 3\Gamma_H$

^a The FSGO's are centered at the vertices of the geometric objects listed in the table (see Figure 2). ^b See ref 70, 71. ^c See ref 73 for a complete discussion of the properties of these geometric objects. ^d Note that, by connecting all the nearest-neighbor points located at the center of each of the four faces of a tetrahedron generates another tetrahedron, while connecting all nearest-neighbor points located at the midpoints of its edges generates an octahedron. ^e Generated from an octahedron by connecting all nearest-neighbor points located at the center of each of the eight faces. ^f Generated from an octahedron by connecting all nearest-neighbor points located at the midpoint of each of the twelve edges. ^g Generated from an icosahedron by connecting all nearest-neighbor points located at the center of each of the twenty faces. ^h Generated from an icosahedron by connecting all nearest-neighbor points located at the midpoint of each of the thirty edges.

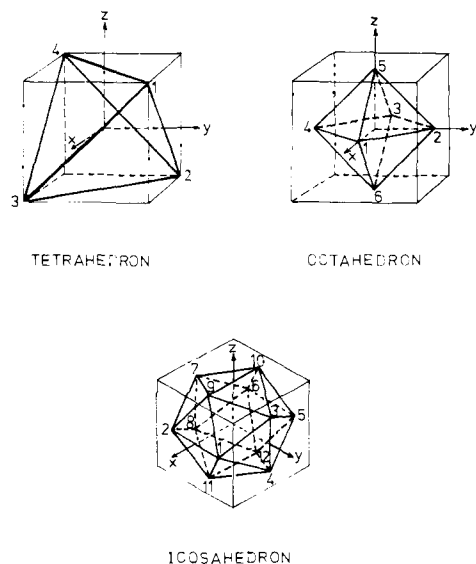


Figure 2. The position and numbering used to describe FSGO's located at the vertices of a regular tetrahedron, octahedron, icosahedron, respectively. The Cartesian coordinates of the vertices of the various figures are (ξ, ξ, ξ) , $(-\xi, \xi, -\xi)$, $(\xi, -\xi, -\xi)$, and $(-\xi, -\xi, \xi)$ for the tetrahedron, $(\pm\xi, 0, 0)$, $(0, \pm\xi, 0)$, and $(0, 0, \pm\xi)$ for the octahedron, and $(\pm\xi, 0, \pm\tau\xi)$, $(\pm\tau\xi, \pm\xi, 0)$, and $(0, \pm\tau\xi, \pm\xi)$ for the icosahedron, where ξ is arbitrary, and $\tau = (1 + \sqrt{5})/2$.

sider FSGO's placed at the vertices of the geometric objects described in Table II. Each arrangement of FSGO's provides a basis for a reducible representation (Γ_{red}) of one of the symmetry groups. Using standard group theoretical techniques,^{70,71} the irreducible representations contained within a particular reducible representation can be determined. Results for a number of different FSGO arrangements are summarized in Table II.

Examination of Table II also shows that not all irreducible representations are contained in the various reducible representations. For example, an FSGO configuration in which the individual functions are placed at the vertices of a tetrahedron will provide only a basis for Γ_A and Γ_T , while an FSGO configuration in which the individual functions are placed at the vertices of an octahedron will provide a basis for Γ_{A_1} , Γ_E , and Γ_{T_1} . Of particular interest in this regard is the fact that the placement of FSGO's at the vertices of an icosahedron provides a basis for the five-dimensional Γ_H irreducible representation of *I*, which is the irreducible representation of greatest dimension found in any finite rotation group.⁷³

By taking appropriate linear combinations of a given set of FSGO's corresponding to a particular spatial arrangement, it is possible to generate the symmetry orbitals,^{70,71} which transform under the operations of the group as the various irreducible representations contained in Γ_{red} . Hence, the set of symmetry orbitals belonging to a particular *n*-dimensional irreducible representation span an *n*-dimensional invariant subspace (i.e., transform only among themselves) under the operations of that particular group. Stated mathematically (cf. eq 10), we have

$$\{|\Gamma_i(\mu)\rangle\}_n \xrightarrow{\mathcal{R}} \{|\Gamma_i(\mu)\rangle\}_n \quad (12)$$

where $|\Gamma_i(\mu)\rangle$ represents the μ th ($\mu = 1, 2, \dots, n$) symmetry orbital belonging to Γ_i , and \mathcal{R} represents the symmetry operations of the particular finite rotation group of interest. The explicit form of a number of symmetry orbitals related to different spatial FSGO arrangements is given in Table III. The numbering and location of FSGO's is given in Figure 2.

In order to explore the relationship between the arrangement of FSGO's and local rotational invariance further, it is necessary to examine these symmetry orbitals in greater detail. As shown in eq 2-6 and 11, a single off-center FSGO can be expanded as a series of multinomials in powers of ϵ .

In general, a set of FSGO symmetry orbitals corresponding to an *n*-dimensional irreducible representation Γ_i can be written in the following form:

$$|\Gamma_i(\mu)\rangle = N_{\Gamma_i(\mu)} \{ \epsilon^0 \alpha_{\Gamma_i(\mu)} + \epsilon^1 \beta_{\Gamma_i(\mu)}(x, y, z) + \epsilon^2 \gamma_{\Gamma_i(\mu)}(x^2, y^2, \dots, yz) + \epsilon^3 \delta_{\Gamma_i(\mu)}(x^3, y^3, \dots, xyz) + \vartheta(\epsilon^4) \}, \quad \mu = 1, 2, \dots, n \quad (13)$$

where $N_{\Gamma_i(\mu)}$ is the normalization factor which also contains spherically symmetric terms common to all powers of ϵ . The $\{\alpha_{\Gamma_i(\mu)}\}_n$, $\{\beta_{\Gamma_i(\mu)}\}_n$, $\{\gamma_{\Gamma_i(\mu)}\}_n$, and $\{\delta_{\Gamma_i(\mu)}\}_n$ terms represent symmetry-adapted multinomial functions of order 0, 1, 2, and 3, which transform as Γ_i , i.e.,

$$\{\alpha_{\Gamma_i(\mu)}\}_n \xrightarrow{\mathcal{R}} \{\alpha_{\Gamma_i(\mu)}\}_n \quad (14a)$$

$$\{\beta_{\Gamma_i(\mu)}\}_n \xrightarrow{\mathcal{R}} \{\beta_{\Gamma_i(\mu)}\}_n \quad (14b)$$

$$\{\gamma_{\Gamma_i(\mu)}\}_n \xrightarrow{\mathcal{R}} \{\gamma_{\Gamma_i(\mu)}\}_n \quad (14c)$$

$$\{\delta_{\Gamma_i(\mu)}\}_n \xrightarrow{\mathcal{R}} \{\delta_{\Gamma_i(\mu)}\}_n \quad (14d)$$

under the operations \mathcal{R} of the group (cf. eq 12). The explicit form of the symmetry-adapted multinomial functions which

Table III. Symmetry Orbitals of Various FSGO Arrangements

Symmetry group ^{a,b}	Symmetry orbitals ^{c,d}	Normalization constants ^e
(T)	$ A^1\rangle = N_A(G_1 + G_2 + G_3 + G_4)$ $ T^x\rangle = N_T(G_1 - G_2 + G_3 - G_4)$ $ T^y\rangle = N_T(G_1 + G_2 - G_3 - G_4)$ $ T^z\rangle = N_T(G_1 - G_2 - G_3 + G_4)$	$N_A = \frac{1}{2}[(1 + 3S_{12})]^{-1/2}$ $N_T = \frac{1}{2}[(1 - S_{12})]^{-1/2}$
(O)	$ A^1\rangle = N_{A_1}(G_1 + G_2 + G_3 + G_4 + G_5 + G_6)$ $ E^{x^2-y^2}\rangle = N_E(G_1 - G_2 + G_3 - G_4)$ $ E^{3z^2-r^2}\rangle = N'_E(2G_5 + 2G_6 - G_1 - G_2 - G_3 - G_4)$ $ T_1^x\rangle = N_{T_1}(G_1 - G_3)$ $ T_1^y\rangle = N_{T_1}(G_2 - G_4)$ $ T_1^z\rangle = N_{T_1}(G_5 - G_6)$	$N_{A_1} = [6(1 + 4S_{12} + S_{13})]^{-1/2}$ $N_E = [4(1 - 2S_{12} + S_{13})]^{-1/2}$ $N'_E = [8(1 - 3S_{12} + \frac{3}{2}S_{13})]^{-1/2}$ $N_{T_1} = [2(1 - S_{12})]^{-1/2}$
(I)	$ A^1\rangle = N_A \sum_{i=1}^{12} G_i$ $ T_1^x\rangle = N_{T_1}[\tau(G_1 + G_2 - G_5 - G_6) + (G_9 + G_{11} - G_{10} - G_{12})]$ $ T_1^y\rangle = N_{T_1}[\tau(G_3 + G_4 - G_7 - G_8) + (G_1 + G_5 - G_2 - G_6)]$ $ T_1^z\rangle = N_{T_1}[\tau(G_9 + G_{10} - G_{11} - G_{12}) + (G_3 + G_7 - G_4 - G_8)]$ $ H^{xy}\rangle = N_H(G_1 - G_2 - G_5 + G_6)$ $ H^{xz}\rangle = N_H(G_9 - G_{10} - G_{11} + G_{12})$ $ H^{yz}\rangle = N_H(G_3 - G_4 - G_7 + G_8)$ $ H^{x^2-y^2}\rangle = N'_H[\tau(G_1 + G_2 + G_5 + G_6) - (\tau + 1)(G_3 + G_4 + G_7 + G_8) + (G_9 + G_{10} + G_{11} + G_{12})]$ $ H^{3z^2-r^2}\rangle = N''_H[(1 + 3\tau)(G_1 + G_2 + G_5 + G_6) + (G_3 + G_4 + G_7 + G_8) - (2 + 3\tau)(G_9 + G_{10} + G_{11} + G_{12})]$	$N_A = [12(1 + 5S_{12} + 4S_{17} + S_{15} + S_{16})]^{-1/2}$ $N_{T_1} = [4(\tau + 1) + 20\tau S_{12} - 16\tau S_{17} - 4\tau S_{15} + 4(\tau + 2)S_{16}]^{-1/2}$ $N_H = [4(1 - S_{12} - S_{15} - S_{16})]^{-1/2}$ $N'_H = [8(\tau + 1)(1 - \frac{1}{2}S_{12} - \frac{1}{2}S_{17} + S_{15} + S_{16})]^{-1/2}$ $N''_H = [9(\tau + \frac{3}{2})(1 - \frac{1}{2}S_{12} - \frac{1}{2}S_{17} + S_{15} + S_{16})]^{-1/2}$

^a See ref 70 and 71. ^b The FSGO are arranged at the vertices of a tetrahedron, octahedron, and icosahedron, respectively (see Figure 2). ^c The superscript designations on the symmetry orbital labels (e.g., $|T^x\rangle$) represent the multinomial function which appears to lowest order in ϵ in the expanded form of the symmetry orbital. See Table IV for the detailed expanded forms of the symmetry orbitals. ^d Only those symmetry orbitals which transform as s-, p-, and d-type AO's under the operations of I are included in the table. The symmetry orbitals belonging to the Γ_{T_2} irreducible representation which transform as (x^3, y^3, z^3) under I are not included (cf. Tables I and II). ^e S_{rs} is the overlap integral: $S_{rs} = \int G_r G_s dV$. Only unique overlap integrals are included in the normalization constants. Related overlap terms can be determined from an examination of Figure 2, which also gives the numbering system used to label the FSGO's.

Table IV. Symmetry Orbital Expansions of Vertex-Centered FSGO Basis Orbitals

Point group	Symmetry orbitals ^a
Tetrahedral	$ A^1\rangle = N_A \exp(-R^2/\rho^2) [4G^1 + (\sqrt{3}/2)\epsilon^2(G^{x^2} + G^{y^2} + G^{z^2}) + (\epsilon^3/2)G^{xyz} + \vartheta(\epsilon^4)]$ $ T^x\rangle = N_T \exp(-R^2/\rho^2) [2\epsilon G^x + \epsilon^2 G^{yz} + (\sqrt{3}/4)\epsilon^3[(\sqrt{5}/3)G^{x^3} + (G^{xy^2} + G^{xz^2})] + \vartheta(\epsilon^4)]$ $ T^y\rangle = N_T \exp(-R^2/\rho^2) [2\epsilon G^y + \epsilon^2 G^{xz} + (\sqrt{3}/4)\epsilon^3[(\sqrt{5}/3)G^{y^3} + (G^{x^2y} + G^{yz^2})] + \vartheta(\epsilon^4)]$ $ T^z\rangle = N_T \exp(-R^2/\rho^2) [2\epsilon G^z + \epsilon^2 G^{xy} + (\sqrt{3}/4)\epsilon^3[(\sqrt{5}/3)G^{z^3} + (G^{x^2z} + G^{yz^2})] + \vartheta(\epsilon^4)]$
Octahedral	$ A^1\rangle = N_A \exp(-R^2/\rho^2) [6G^1 + (\sqrt{3}/4)\epsilon^2(G^{x^2} + G^{y^2} + G^{z^2}) + \vartheta(\epsilon^4)]$ $ E^{x^2-y^2}\rangle = N_E \exp(-R^2/\rho^2) [(\sqrt{3}/4)\epsilon^2(G^{x^2} - G^{y^2}) + \vartheta(\epsilon^4)]$ $ E^{3z^2-r^2}\rangle = N'_E \exp(-R^2/\rho^2) [(\sqrt{3}/4)\epsilon^2(2G^{z^2} - G^{x^2} - G^{y^2}) + \vartheta(\epsilon^4)]$ $ T_1^x\rangle = N_{T_1} \exp(-R^2/\rho^2) [\epsilon G^x + (\sqrt{15}/24)\epsilon^3 G^{x^3} + \vartheta(\epsilon^4)]$ $ T_1^y\rangle = N_{T_1} \exp(-R^2/\rho^2) [\epsilon G^y + (\sqrt{15}/24)\epsilon^3 G^{y^3} + \vartheta(\epsilon^4)]$ $ T_1^z\rangle = N_{T_1} \exp(-R^2/\rho^2) [\epsilon G^z + (\sqrt{15}/24)\epsilon^3 G^{z^3} + \vartheta(\epsilon^4)]$
Icosahedral	$ A^1\rangle = N_A \exp(-R^2/\rho^2) [12G^1 + (\sqrt{3}/2)(\tau + 2)\epsilon^2(G^{x^2} + G^{y^2} + G^{z^2}) + \vartheta(\epsilon^4)]$ $ T_1^x\rangle = N_{T_1} \exp(-R^2/\rho^2) [2\epsilon(\tau + 2)G^x + (\sqrt{15}/4)(\tau + 1)\epsilon^3[G^{x^3} + (1/\sqrt{5})(G^{xy^2} + G^{xz^2})] + \vartheta(\epsilon^4)]$ $ T_1^y\rangle = N_{T_1} \exp(-R^2/\rho^2) [2\epsilon(\tau + 2)G^y + (\sqrt{15}/4)(\tau + 1)\epsilon^3[G^{y^3} + (1/\sqrt{5})(G^{yx^2} + G^{yz^2})] + \vartheta(\epsilon^4)]$ $ T_1^z\rangle = N_{T_1} \exp(-R^2/\rho^2) [2\epsilon(\tau + 2)G^z + (\sqrt{15}/4)(\tau + 1)\epsilon^3[G^{z^3} + (1/\sqrt{5})(G^{zx^2} + G^{zy^2})] + \vartheta(\epsilon^4)]$ $ H^{xy}\rangle = N_H \exp(-R^2/\rho^2) [\tau\epsilon^2 G^{xy} + \vartheta(\epsilon^4)]$ $ H^{xz}\rangle = N_H \exp(-R^2/\rho^2) [\tau\epsilon^2 G^{xz} + \vartheta(\epsilon^4)]$ $ H^{yz}\rangle = N_H \exp(-R^2/\rho^2) [\tau\epsilon^2 G^{yz} + \vartheta(\epsilon^4)]$ $ H^{x^2-y^2}\rangle = N'_H \exp(-R^2/\rho^2) [\sqrt{3}(\tau + 1)\epsilon^2(G^{x^2} - G^{y^2}) + \vartheta(\epsilon^4)]$ $ H^{3z^2-r^2}\rangle = N''_H \exp(-R^2/\rho^2) [-\sqrt{3}\tau^3\epsilon^2(2G^{z^2} - G^{x^2} - G^{y^2}) + \vartheta(\epsilon^4)]$

^a Normalization constants for the various symmetry orbitals are given in Table III.

arise from expansions of the symmetry orbitals in Table III can be obtained from the data in Table IV.

To assess the degree of local rotational invariance to a given order in ϵ , it is necessary to evaluate the transformation properties of the symmetry-adapted multinomial functions under the operations of R_3 . This is exactly analogous to evaluating which of eq 14a, 14b, 14c, and/or 14d are satisfied, if \mathcal{R} is now interpreted to represent the operations of R_3 . The highest power in ϵ to which these equations are satisfied then

represents the order in ϵ to which local rotational invariance is attained.

IV. Local Rotational Invariance of Off-Center Gaussian Basis Sets. Examples

As a specific example of the above procedure, consider the case of FSGO's positioned at the four vertices of a tetrahedron (cf. Figure 1). From eq 6, each FSGO can be seen to have the form

$$G_1(\mathbf{r}) = \exp\{-(3\epsilon^2/4)\}G^0(\mathbf{r})\{1 + (\epsilon/\rho)[x + y + z] + (\epsilon/\rho)^2[x^2 + y^2 + z^2 + 2xy + 2xz + 2yz]/2 + (\epsilon/\rho)^3[x^3 + y^3 + z^3 + 3xy^2 + 3xz^2 + 3x^2y + 3x^2z + 3yz^2 + 3y^2z + 6xyz]/6 + \vartheta(\epsilon^4)\} \quad (15a)$$

$$G_2(\mathbf{r}) = \exp\{-(3\epsilon^2/4)\}G^0(\mathbf{r})\{1 + (\epsilon/\rho)[-x + y - z] + (\epsilon/\rho)^2[x^2 + y^2 + z^2 - 2xy + 2xz - 2yz]/2 + (\epsilon/\rho)^3[-x^3 + y^3 - z^3 - 3xy^2 - 3xz^2 + 3x^2y - 3x^2z + 3yz^2 - 3y^2z + 6xyz]/6 + \vartheta(\epsilon^4)\} \quad (15b)$$

$$G_3(\mathbf{r}) = \exp\{-(3\epsilon^2/4)\}G^0(\mathbf{r})\{1 + (\epsilon/\rho)[x - y - z] + (\epsilon/\rho)^2[x^2 + y^2 + z^2 - 2xy - 2xz + 2yz]/2 + (\epsilon/\rho)^3[x^3 - y^3 - z^3 + 3xy^2 + 3xz^2 - 3x^2y - 3x^2z - 3yz^2 - 3y^2z + 6xyz]/6 + \vartheta(\epsilon^4)\} \quad (15c)$$

$$G_4(\mathbf{r}) = \exp\{-(3\epsilon^2/4)\}G^0(\mathbf{r})\{1 + (\epsilon/\rho)[-x - y + z] + (\epsilon/\rho)^2[x^2 + y^2 + z^2 + 2xy - 2xz - 2yz]/2 + (\epsilon/\rho)^3[-x^3 - y^3 + z^3 - 3xy^2 - 3xz^2 - 3x^2y + 3x^2z - 3yz^2 + 3y^2z + 6xyz]/6 + \vartheta(\epsilon^4)\} \quad (15d)$$

Since the absolute magnitude of the X , Y , and Z coordinates of the vertices of the tetrahedron are equal (see Figure 2), it follows that ϵ is given by

$$\epsilon = 2|X|/\rho = 2|Y|/\rho = 2|Z|/\rho. \quad (16)$$

$R^2 = X^2 + Y^2 + Z^2$ for all vertices, and the orbital radii of all FSGO must be equal if tetrahedral symmetry is to be maintained.

If the above FSGO expansions are then taken in combinations corresponding to specific symmetry orbitals (cf. Table III), the following functions result:^{74,75}

$$|A^1\rangle = N_A \exp\{-(3\epsilon^2/4)\}\{4G^1(\mathbf{r}) + (\sqrt{3}/2)\epsilon^2[G^{x^2}(\mathbf{r}) + G^{y^2}(\mathbf{r}) + G^{z^2}(\mathbf{r})] + (1/2)\epsilon^3G^{xyz}(\mathbf{r}) + \vartheta(\epsilon^4)\} \quad (17a)$$

$$|T^x\rangle = N_T \exp\{-(3\epsilon^2/4)\}\{2\epsilon G^x(\mathbf{r}) + \epsilon^2 G^{yz}(\mathbf{r}) + (\sqrt{3}/4)\epsilon^3[(\sqrt{5}/3)G^{x^3}(\mathbf{r}) + (G^{xy^2}(\mathbf{r}) + G^{xz^2}(\mathbf{r}))] + \vartheta(\epsilon^4)\} \quad (17b)$$

$$|T^y\rangle = N_T \exp\{-(3\epsilon^2/4)\}\{2\epsilon G^y(\mathbf{r}) + \epsilon^2 G^{xz}(\mathbf{r}) + (\sqrt{3}/4)\epsilon^3[(\sqrt{5}/3)G^{y^3}(\mathbf{r}) + (G^{xy^2}(\mathbf{r}) + G^{yz^2}(\mathbf{r}))] + \vartheta(\epsilon^4)\} \quad (17c)$$

and

$$|T^z\rangle = N_T \exp\{-(3\epsilon^2/4)\}\{2\epsilon G^z(\mathbf{r}) + \epsilon^2 G^{xy}(\mathbf{r}) + (\sqrt{3}/4)\epsilon^3[(\sqrt{5}/3)G^{z^3}(\mathbf{r}) + (G^{x^2z}(\mathbf{r}) + G^{y^2z}(\mathbf{r}))] + \vartheta(\epsilon^4)\} \quad (17d)$$

where N_A and N_T are given in Table III.

The degree of local rotational invariance can now be assessed in orders of ϵ . For example, $|A^1\rangle$ transforms as Γ_A under T . Thus, the maximum degree of local rotational invariance that is possible is one. In addition, examination of the terms in eq 17a reveals that local rotational invariance of degree one is maintained through order ϵ^2 , since both the terms of order ϵ^0 and ϵ^2 represent spherically symmetric s-type functions. The f-type function is the leading term in the loss of local rotational invariance. Hence, if the value of ϵ is such that this f component is large, then the calculated energy or other property may depend significantly upon the particular orientation that is chosen for the tetrahedron of FSGO's about the origin.

For the case of the three Γ_T orbitals it is seen that, through order ϵ , these orbitals are locally rotationally invariant to degree three. The leading terms in the nonrotationally invariant components of these orbitals appear at order ϵ^2 and consist of d-type functions. This nonrotational invariance arises since only three of the five components necessary for full local ro-

tational invariance of degree five are present. Thus, we have local rotational invariance of degree three through order ϵ^1 .

In considering local rotational invariance of basis sets that employ off-center FSGO's, it is also of interest to consider basis sets constructed using the lobe-function technique.³⁷⁻³⁸ In this approach, atomic orbitals having different angular dependence are created using linear combinations of FSGO's. However, complete local rotational invariance is not possible in this approach either.

For example, a p_z -type orbital that is represented using lobe functions can be written as^{37,38,76}

$$|p_z\rangle = N(G_1 - G_2) \quad (18)$$

where N is a normalization constant, and

$$G_1 = (2/\pi\rho^2)^{3/4} \exp\{-[x^2 + y^2 + (z - Z)^2]/\rho^2\} \quad (19a)$$

$$G_2 = (2/\pi\rho^2)^{3/4} \exp\{-[x^2 + y^2 + (z + Z)^2]/\rho^2\} \quad (19b)$$

Using eqs 6 and 19, the p_z -type orbital can be written as:

$$|p_z\rangle = N \exp\{-\epsilon_z^2/4\}[\epsilon_z G^z + (\sqrt{15}/24)\epsilon_z^3 G^{z^3} + \vartheta(\epsilon^4)] \quad (20)$$

Thus, if an isotropic set of p_x -, p_y -, and p_z -type orbitals are used, local rotational invariance of degree three through order ϵ^2 is achieved, and nonrotationally invariant components are of the f-type and higher. While proper choice of ϵ can be used to minimize the nonrotational invariance,⁷⁷ full rotational invariance of degree three can be achieved only in the limit of $Z \rightarrow 0$.

While the degree of local rotational invariance can be assessed rigorously for all cases using the concepts just described, it is important to note that numerical considerations also can affect the order in ϵ of local rotational invariance that can be obtained. In particular, if ϵ is chosen to be small enough, then the contribution of the nonrotationally invariant components may be numerically negligible relative to the rotationally invariant terms. In this way, approximate local rotational invariance can be obtained to higher orders in ϵ than would be expected from the strictly rigorous analysis.

To illustrate these points qualitatively with a practical example, the initial molecular fragment FSGO basis set for CH_4 is of interest.¹⁶ For this case, five FSGO are employed, one on the carbon nucleus, and one along each of the C-H bonds. Based upon the optimized FSGO parameters,¹⁶ the value of ϵ for the various orbitals is $\epsilon_{\text{IS}} = 0$ and $\epsilon_{\text{CH}} = 1.4754$. Using eq 17a, this means that the ratio of the leading nonrotationally invariant component to the preceding (rotationally invariant) term is

$$(\epsilon_{\text{CH}}^3/2)/[(\sqrt{3}/2)\epsilon_{\text{CH}}^2] = 0.8518$$

For the case of the Γ_T orbitals, the corresponding ratio is

$$\epsilon_{\text{CH}}^2/2\epsilon_{\text{CH}} = 0.7377.$$

It should be noted that this example represents an extreme case for several reasons. In particular, the C-H functions are intended to be "bond functions" and, thus, the choice of orientation of these functions about the carbon atom is defined clearly by the CH_4 molecule itself, and the question of other possible orientations for these basis functions does not arise. Also, for most other larger basis sets, the tetrahedrally arranged FSGO would be used as polarization functions in the vicinity of the carbon atom, where values of ϵ that would be encountered would be considerably smaller.⁷⁸

More generally, the degree of local rotational invariance, to a given order in ϵ , achieved for several important FSGO configurations is summarized in Table IV. Several points of interest and importance are illustrated in this table, both of conceptual and computational interest.

For example, while the maximum degree to which local rotational invariance can be achieved is five, care must be exercised in the choice of symmetry orbitals if the maximum rotational invariance is to be achieved. In particular, use of 12 edge-centered FSGO in an octahedral arrangement (i.e., a cubo-octahedral arrangement) gives rise to a reducible representation having Γ_E and Γ_{T_2} components (see Table II). However, the dimension of these irreducible representations is two and three, respectively, which implies that the maximum degree of local rotational invariance for the Γ_E symmetry orbitals that is possible is two, and three for the Γ_{T_2} symmetry orbitals. Hence while all d-type components are present in these two irreducible representations (see Table I), they cannot rigorously span a five-dimensional subspace, which would be required for local rotational invariance of degree five. On the other hand, use of the same number of FSGO's at the vertices of an icosahedron does provide local rotational invariance of degree five due to the presence of the Γ_H irreducible representation.

The above comments also imply that a full, isotropic set of f-type orbitals that are locally rotationally invariant to degree seven cannot be constructed rigorously using off-centered FSGO basis sets. Of course, just as approximate rotational invariance to higher order in ϵ than predicted rigorously can be approximately achieved by suitable choice of ϵ , construction of a set of seven f-type orbitals that closely approximate a set that is locally rotationally invariant to degree seven can be achieved through appropriate choices of ϵ , and a reducible representation that contains Γ_G and Γ_H . Examples of such a possibility arise with the use of either face- or edge-centered FSGO in the icosahedral point group.

V. Generalization and Extension of Gaussian Basis Sets. Computational and Other Considerations

Within the framework of the previous analysis, it can be seen that a new method for devising and extending Gaussian basis sets can be readily achieved. This procedure allows exploitation of the favorable computational characteristics of FSGO's, while maintaining the ability to carry out basis set extension in a systematic manner.

For representation of s-type functions, the considerations are no different than those used "traditionally", i.e., successive addition of FSGO's on the nuclei with exponent optimization (with or without contractions) can be used to obtain the desired accuracy. For representation of p-type functions, substantial savings without loss of generality can be achieved using the preceding analysis. In particular, for every set of p-type AO's (p_x, p_y, p_z) added, an appropriate set of four FSGO's arranged tetrahedrally about the nucleus may be used. As indicated previously, such a set contains all possible p components plus an s component, thus allowing for any desired hybridization of s- and p-type AO's. This can be considered to be analogous to adding a "shell" of 2s and 2p orbitals.

Next, for every set of d-type AO's desired, a set of 12 FSGO placed at the vertices of an icosahedron can be employed. Similar to the p-type AO case, each set of 12 FSGO contains all s, p, and d components, thus being analogous to adding a "shell" of 3s, 3p, and 3d orbitals.

Such choices provide substantial computational advantages. In particular, the computational complexities of evaluating electron repulsion integrals when Cartesian p- and d-type GTO's are used is not encountered, since only s-type FSGO's are used at all levels of generalization. Second, the number of FSGO (if chosen in the manner just described) is fewer than needed if p- and d-type AO's are represented by lobe functions. In particular, six FSGO are needed to represent a full set of (p_x, p_y, p_z) orbitals in the lobe-function approach, while only four FSGO are needed to provide the same components if ar-

ranged tetrahedrally. For the case of d functions, at least 18 FSGO are needed to represent a full set of five d-type orbitals using the lobe-function approach, while only 12 FSGO are needed to describe the same components if the FSGO are placed at the corners of an icosahedron.

To illustrate the savings in number of integrals that need to be evaluated, consider the CH₄ molecule. If, for example, a (9s, 5p, 1d) lobe-function basis is used on carbon and a (6s, 1p) lobe-function basis used on each hydrogen nucleus, then a total of 105 FSGO would be employed, which gives rise to a total of 15 487 395 electron repulsion integrals over FSGO to be evaluated (ignoring integrals that may be numerically approximately zero). On the other hand, if the procedure just described is used, a total of only 81 FSGO is needed, which gives rise to a total of 5 516 181 electron repulsion integrals over FSGO to be evaluated. Thus, elimination of 9 971 214 integrals is possible (a reduction of 68%) without loss of any of the s, p, or d components. Indeed, the four tetrahedrally-arranged FSGO give rise to an s component in addition to the three p-components, and the 12 icosahedrally-arranged FSGO provide an s, three p, and several f components, as well as the five d components. Hence, this basis can be considered to be richer in s and p components than the lobe-function basis, even though fewer FSGO's are used. Finally, since the integral evaluation step is usually the rate-determining step in SCF calculations using basis sets of this size, such substantial reduction in electron repulsion integrals to be evaluated can have important cost and feasibility implications.

There are, however, several potential difficulties with the approach just described that should be noted. First, as pointed out earlier, the maximum degree of rotational invariance that can be attained rigorously is five, which implies that full isotropic sets of f and higher orbitals can be constructed only approximately. Next, a set of tetrahedrally-arranged FSGO, while providing a full complement of p components, has d-orbital (and higher) components which are nonrotationally invariant. Thus, if both tetrahedrally- and icosahedrally-arranged FSGO's are used, rigorous local rotational invariance to degree five is not attained. For proper choices of ϵ , however, the nonrotationally invariant d-orbital components arising from the tetrahedrally-arranged FSGO's can be made small.

Considerable numerical exploration of these notions is clearly desirable to quantify the concepts and alternatives described above. Such studies are currently underway, and will be reported later.

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References and Notes

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- (75) The two terms $G^{xy}(r)$ and $G^{z^2}(r)$ are grouped together by parentheses in eq 17b-d in order to indicate that it is the sum of these terms (not the individual terms) which possesses the specified transformation properties.
- (76) It is of interest to note that the particular form of the functions chosen in the lobe-function approach is identical with what would be obtained in the current approach using octahedral symmetry.
- (77) Compare the discussion in ref 37.
- (78) In expanded FSGO basis set studies on CH_4 (to be published), values of $\epsilon \sim 0.10$ have typically been found for FSGO's placed in the vicinity of the carbon atom for polarization purposes.