

The Ellipsoidal Gaussian Basis in Molecular Orbital Theory

I. Integral Formulas and Test Calculations

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New analytic integral formulas are presented for the potential energy integrals over ellipsoidal Gaussian basis functions [$\sim \exp(-\alpha x^2 - \beta y^2 - \gamma z^2)$] that enter into solving the conventional expansion self-consistent field equations. Near minimal atomic orbital bases combined from large nuclear-centered primitive Gaussian sets are used in test calculations on the HF and CO molecules. The ellipsoidal exponential parameters for the valence atomic orbitals are fully optimized using a single scale factor for each atomic orbital and nuclear coordinate. The results are compared with those obtained using an unoptimized nuclear centered double-zeta spherical Gaussian basis.

Key words: Ellipsoidal Gaussian basis

1. Introduction

Boys' suggestion [1] to use generalized spherical Gaussian basis functions of the form, $\sim x^l y^m z^n \exp(-\alpha r^2)$ in molecular quantum mechanical calculations opened a new era in computational chemistry. As used to solve the matrix Hartree-Fock equations, combined sets of Gaussian functions proved to be reasonably accurate and required an integral evaluation time that was not excessive compared to the time and effort needed to solve the conventional self-consistent field (SCF) equations. Today the time-consuming step in carrying out a molecular *ab initio* SCF calculation is typically in the latter step and those steps subsequent or alternate to it such as, for example, configuration interaction.

The use of different size extended (larger than minimal atomic) basis sets with the same number of primitive (individual) Gaussian functions results in the integral evaluation time remaining essentially unchanged with extension of the basis set while the solution of the SCF equations becomes more and more time consuming. This specific example clearly demonstrates the practical and general need of using the smallest possible basis set size to achieve maximum accuracy even at the possible expense of larger integral evaluation times. Exponential basis functions (Slater orbitals) do not seem to answer this need because of their relatively high integral evaluation times and, more importantly, the additional requirement of an extended basis set for reasonably accurate results. Ideally, one needs a basis set that will give good results at, or very near to, the minimal atomic orbital basis level.

An extension and improvement on the conventional (spherical) Gaussian set has been

suggested by Browne and Poshusta [2] in the generalized ellipsoidal Gaussian, $\sim x^l y^m z^n \exp(-\alpha x^2 - \beta y^2 - \gamma z^2)$. This function can be written in the following way:

$$\begin{aligned}
 & x^l y^m z^n \exp(-\alpha x^2 - \beta y^2 - \gamma z^2) \\
 &= x^l y^m z^n \exp(-\delta r^2) \exp[(\delta - \alpha)x^2] \exp[(\delta - \beta)y^2] \exp[(\delta - \gamma)z^2] \\
 &= x^l y^m z^n \exp(-\delta r^2) \sum_i \frac{(-1)^i (\delta - \alpha)^i x^{2i}}{i!} \sum_j \frac{(-1)^j (\delta - \beta)^j y^{2j}}{j!} \sum_k \frac{(-1)^k (\delta - \gamma)^k z^{2k}}{k!} \\
 &= x^l y^m z^n \exp(-\delta r^2) \sum_i \sum_j \sum_k A_{ijk} x^{2i} y^{2j} z^{2k} \tag{1}
 \end{aligned}$$

where A_{ijk} in the last row contains all the missing terms found in the previous row and the value of δ is arbitrary. This formulation shows that the ellipsoidal Gaussian can be considered to be equivalent to a spherical Gaussian multiplied by a fixed sum of all products of even powers of the coordinates. The expansion form in Eq. (1) is similar to the use of a complete system of functions suggested by Boys and Rajagopal [3, 4] with the restrictions here that each function has a fixed, pre-determined weighting or coefficient and that the type or symmetry of the base function (defined by the values of l , m , and n) is not changed by the expansion. Thus the expansion part of (1) has the property of preserving the base function type while increasing its flexibility as a basis function. This description is similar to that of using a double-zeta set of functions of a given orbital type in place of a single-zeta representation in ordinary exponential or spherical Gaussian basis sets. Thus it is possible that a properly optimized single-zeta (meaning really as many as three different exponential factors, α , β , and γ) ellipsoidal function could be equivalent to a double-zeta representation in a spherical Gaussian basis.

In most actual applications of ellipsoidal Gaussians to date advantage has been taken of their increased functional flexibility to construct single ellipsoidal Gaussian floating bond orbitals, which are the localized electron pair orbitals of the system [5-13]. This limited application is presumably due to the integral evaluation having been found to be very time consuming. There appears to have been only one serious effort at using ellipsoidal Gaussians as conventional nuclear centered basis function using a combined set of functions [18]. This study found that the improvement obtained for the ground state energy of H_2^+ in the ellipsoidal limit was some 40% of the difference between the spherical limit and the exact energy.

Integral formulas for the overlap and energy (kinetic, nuclear attraction, and electron repulsion) integrals involving ellipsoidal Gaussians have been published typically in a form that included numerical integration [2, 11, 14, 17]. Katriel and co-workers [15, 16] derived analytic formulas for the overlap and energy integrals based on the following one-dimensional product expansion:

$$\exp(-\alpha_1 x_A^2) \exp(-\alpha_2 x_B^2) = \sum_{j=0}^{\infty} C_j \exp(-\frac{1}{2}\alpha x_P^2) H_j(\sqrt{\alpha} x_P) \tag{2}$$

where α is arbitrary, the functions on the right-hand side are harmonic oscillator eigenfunctions, and the coordinate x_P can be chosen in the usual manner [19]. This approach suffers from the well-known disadvantages of trying to expand the product of two differently centered functions about a third center with severe constraints upon the parameters defining the functional form on the third center. In this case, these restrictions take the form of requiring a common α for all three coordinate direction (x , y , and z) expansions, and, in the case of the potential energy integrals, limitations on the location of the expan-

sion center. Thus in Eq. (2) for functions where the centers A and B are far apart or where one of the exponents (α_1 or α_2) is large, convergence is very slow.

In order to investigate the possible large basis-analogue properties of ellipsoidal functions and test their use as a conventional nuclear centered basis using combined sets of functions we have carried out near-minimal atomic orbital basis ellipsoidal SCF calculations on the CO and HF molecules. New, completely analytic integral evaluation formulas, based on the analysis in Eq. (1), for the potential energy integrals have been developed which have been found to be considerably more efficient than previous methods [15, 18].

2. Integral Formulas

The product of two ellipsoidal Gaussians on centers A and B is given by,

$$N_1 \exp(-\alpha_1 x_A^2 - \beta_1 y_A^2 - \gamma_1 z_A^2) N_2 \exp(-\alpha_2 x_B^2 - \beta_2 y_B^2 - \gamma_2 z_B^2) = \left\{ N_1 N_2 \exp \left[\frac{-\alpha_1 \alpha_2 \overline{AB}_x^2}{\alpha'} \right] \exp \left[\frac{-\beta_1 \beta_2 \overline{AB}_y^2}{\beta'} \right] \exp \left[\frac{-\gamma_1 \gamma_2 \overline{AB}_z^2}{\gamma'} \right] \right\} \exp(-\alpha' x_P^2 - \beta' y_P^2 - \gamma' z_P^2) \quad (3)$$

where N_1 and N_2 are the single ellipsoidal Gaussian normalization constants, $P_x = (\alpha_1 A_x + \alpha_2 B_x)/\alpha'$, and $\alpha' = \alpha_1 + \alpha_2$ etc., and the notation is the usual one [20-23]. The non-constant part of the right-hand side of (3) can be written as,

$$\begin{aligned} \exp(-\alpha' x_P^2 - \beta' y_P^2 - \gamma' z_P^2) &= \exp(-\alpha' r_P^2) \exp[(\alpha' - \beta') y_P^2] \exp[(\alpha' - \gamma') z_P^2] \\ &= \exp(-\alpha' r_P^2) \sum_{j=0}^{j_{\max}} (-1)^j \frac{(\alpha' - \beta')^j y_P^{2j}}{j!} \sum_{k=0}^{k_{\max}} (-1)^k \frac{(\alpha' - \gamma')^k z_P^{2k}}{k!} \end{aligned} \quad (4)$$

j_{\max} and k_{\max} are set by some pre-determined accuracy criterion for convergence of the integral value. Eqs. (3) and (4), together with the usual method of integral evaluation [20-23] for spherical Gaussians of the general form,

$$x_P^{2i} y_P^{2j} z_P^{2k} \exp(-\alpha' r_P^2) \quad (5)$$

are the basis of the integral formulas used in this study for the nuclear attraction and electron repulsion integrals.

We here present integral formulas only for s -type ($l = m = n = 0$ in Eq. (1)) Gaussians for simplicity. Extension to higher angular momentum types (i.e. p -type, for example) is straightforward with the recognition that, for example, for the x -coordinate:

$$x_A^{l_1} x_B^{l_2} = (x_P + \overline{PA}_x)^{l_1} (x_P + \overline{PB}_x)^{l_2}$$

which is then expanded by the usual binomial expansion [20-23]. This adds a fixed sum of terms each of which modifies the power of x_P in Eq. (5).

2.1. Nuclear Attraction Integrals

$$I_{NA} = N_1 N_2 \langle \exp(-\alpha_1 x_A^2 - \beta_1 y_A^2 - \gamma_1 z_A^2) | 1/r_C | \exp(-\alpha_2 x_B^2 - \beta_2 y_B^2 - \gamma_2 z_B^2) \rangle$$

The final formula is:

$$\begin{aligned}
 I_{NA} &= N_1 N_2 \exp \left[\frac{-\alpha_1 \alpha_2 \overline{AB}_x^2}{\alpha'} \right] \exp \left[\frac{-\beta_1 \beta_2 \overline{AB}_y^2}{\beta'} \right] \exp \left[\frac{-\gamma_1 \gamma_2 \overline{AB}_z^2}{\gamma'} \right] \times \\
 &\times \sum_{\mu}^{j_{\max}} D_{\mu}(\overline{PC}_y, \alpha', \gamma') \sum_{\nu}^{k_{\max}} D_{\nu}(\overline{PC}_z, \alpha', \gamma') F_{\mu+\nu} \left(\frac{\overline{PC}^2}{4\delta} \right) \\
 D_{\nu}(\overline{PC}_z, \alpha', \gamma') &= \sum_{\omega=0}^{[\nu, j_{\max}-\nu]} \frac{(-1)^{\omega}}{\omega!(\nu-\omega)!} \left(\frac{\overline{PC}_z}{\sqrt{\delta}} \right)^{\nu-\omega} B_{\nu+\omega}(\alpha', \gamma') \\
 B_{\nu}(\alpha', \gamma') &= \nu! \sum_{u=v(2)}^{j_{\max}} \frac{(-1)^{u/2} u! (\alpha' - \gamma')^{u/2}}{\left[\frac{u-\nu}{2} \right]! (2\sqrt{\alpha'})^u (u/2)!} \quad (v\text{-even}) \\
 F_{\mu+\nu} \left(\frac{\overline{PC}^2}{4\delta} \right) &= \text{Incomplete Gamma Function}; \quad \delta = \frac{1}{4\alpha'}
 \end{aligned}$$

The brackets for the upper limit in the sum over ω in the D -function signifies the smaller of the two numbers within the brackets.

2.2. Electron Repulsion Integrals

$$\begin{aligned}
 I_{ER} &= N_1 N_2 N_3 N_4 \langle \exp(-\alpha_1 x_A^2 - \beta_1 y_A^2 - \gamma_1 z_A^2) \exp(-\alpha_2 x_B^2 - \beta_2 y_B^2 - \gamma_2 z_B^2) | 1/r_{12} | \\
 &\exp(-\alpha_3 x_C^2 - \beta_3 y_C^2 - \gamma_3 z_C^2) \exp(-\alpha_4 x_D^2 - \beta_4 y_D^2 - \gamma_4 z_D^2) \rangle
 \end{aligned}$$

The final formula is:

$$\begin{aligned}
 I_{ER} &= N_1 N_2 N_3 N_4 \exp \left[\frac{-\alpha_1 \alpha_2 \overline{AB}_x^2}{\alpha'} \right] \exp \left[\frac{-\beta_1 \beta_2 \overline{AB}_y^2}{\beta'} \right] \exp \left[\frac{-\gamma_1 \gamma_2 \overline{AB}_z^2}{\gamma'} \right] \times \\
 &\exp \left[\frac{-\alpha_3 \alpha_4 \overline{CD}_x^2}{\alpha''} \right] \exp \left[\frac{-\beta_3 \beta_4 \overline{CD}_y^2}{\beta''} \right] \exp \left[\frac{-\gamma_3 \gamma_4 \overline{CD}_z^2}{\gamma''} \right] \times \\
 &\times \sum_{\mu}^{j_{\max}+r_{\max}} H_{\mu}(\overline{QP}_y, \alpha', \alpha'', \beta', \beta'') \sum_{\nu}^{k_{\max}+s_{\max}} H_{\nu}(\overline{QP}_z, \alpha', \alpha'', \gamma', \gamma'') F_{\mu+\nu} \left(\frac{\overline{QP}^2}{4\delta} \right) \\
 H_{\nu}(\overline{QP}_z, \alpha', \alpha'', \gamma', \gamma'') &= \sum_{n=0}^{[\nu, k_{\max}+s_{\max}-\nu]} \frac{(-1)^n}{n!(\nu-n)!} \left(\frac{\overline{QP}_z}{\sqrt{\delta}} \right)^{\nu-n} G_{\nu+n}(\alpha', \alpha'', \gamma', \gamma'') \\
 G_m(\alpha', \alpha'', \gamma', \gamma'') &= \left(\frac{1}{2\sqrt{\delta}} \right)^m m! \sum_{u=0(2)}^m E_u(\alpha', \gamma') E_{m-u}(\alpha'', \gamma'') \quad (m \text{ even}) \\
 E_{\nu}(\alpha', \gamma') &= \frac{1}{\nu!} \left(\frac{1}{\sqrt{\alpha'}} \right)^{\nu} \sum_{t=v(2)}^{k_{\max}} \frac{(-1)^t}{\left[\frac{t-\nu}{2} \right]!} \left(\frac{1}{2\sqrt{\alpha'}} \right)^t \frac{(\gamma' - \alpha')^{t/2} t!}{(t/2)!} \quad (v \text{ even}) \\
 \delta &= \frac{1}{4} \left[\frac{1}{\alpha'} + \frac{1}{\alpha''} \right], \quad Q_x = \frac{\alpha_3 C_x + \alpha_4 D_x}{\alpha''}, \quad \alpha'' = \alpha_3 + \alpha_4, \text{ etc.}
 \end{aligned}$$

r_{\max} and s_{\max} are the respective analogous parameters for electron two corresponding to j_{\max} and k_{\max} for electron one. \overline{QP}^2 is defined as $|Q - P|^2$.

2.3. Overlap and Kinetic Energy

The overlap and kinetic energy integrals were computed according to the methods of Browne and Poshusta [2].

The incomplete gamma function appearing in the potential energy integrals was evaluated using a FORTRAN subroutine found in POLYATOM/II [24] for the highest index needed with subsequent recursion downwards for smaller indices. For the (geometrically) linear systems studied here the sum over j in Eq. (4) does not appear since $\alpha' = \beta'$. The value of k_{\max} was chosen to insure an accuracy of at least 10^{-8} a.u. in the integral values.

3. Basis Set

Based on the arguments presented previously it was thought desirable and appropriate to try a minimal or near-minimal atomic orbital basis. Additional consideration centered about the shape of the charge density in molecules both close to the atomic nuclei and in the valence region. In the former it is clearly expected that the charge distribution will remain spherical about the atoms and very much atomic-like. Thus a very limited basis representation could very well show only a small tendency to go elliptical. An adequate basis description for the core region is also required to prevent the valence shell basis on one center from tending only to improve the core region on an adjacent center. The 3^s basis contraction of Dunning [25] ($1s, 1s', 2s$) for first-row atoms made up from the nine spherical Gaussian primitives of Huzinaga [26] is sufficiently small in terms of number of basis functions, and sufficiently flexible and accurate in the core region so as to serve the objectives of this work. The atomic orbitals for the first-row atoms were taken as the completely contracted (or combined) five p -type primitives of Huzinaga [26]. For the hydrogen atom the completely combined set of Basch [27] with a scale factor of $(1.2)^2$ was used. Thus we will refer to the contracted basis used here as $[3^s 1^p / 1^s]$ and the primitive basis as $(9^s 5^p / 4^s)$.

4. Methods and Results

Self-consistent field calculations were carried out on the ground electronic states of HF ($R = 1.7328$ a.u.) and CO ($R = 2.13$ a.u.) in the Gaussian basis and using the integral formulas described in the previous sections. Initially results were obtained in the $[3^s 1^p / 1^s]$ and $[4^s 2^p / 2^s]$ spherical Gaussian bases. The latter is the traditional double-zeta (spherical) Gaussian basis set. All subsequent work was done with the former size basis.

Optimized ellipsoidal Gaussian exponents (α, β and γ in Eq. (1) where for the coordinate system used here for linear molecules $\alpha = \beta$) for the valence atomic orbitals ($2s, 2p_x, 2p_y$, and $2p_z$ on carbon, oxygen and fluorine, and $1s$ on hydrogen) were obtained for both the HF and CO molecules each in a two-step process. Initially, the spherical Gaussian basis exponents were optimized by scaling all the primitives of a given combined atomic orbital until an energy minimum was found. For this purpose the STEPIT program of J. P. Chandler [28] was used optimizing one atomic orbital at a time. Subsequently, the z exponential factor alone (γ) of each atomic orbital was optimized in the same fashion, again using a common scale factor for all primitives of a given orbital. Finally, the entire process was

Table 1. Energy optimized exponent scale factors for spherical and ellipsoidal Gaussian atomic orbitals in HF

Atomic orbital	Optimized scale factors ^a		
	Spherical Gaussian	Ellipsoidal Gaussian	
		α, β	γ
H 1s	1.612	1.739	1.521
F 2s	0.986	1.003	0.971
F 2p _x , 2p _y	0.950	0.953	0.922
F 2p _z	0.989	0.991	0.971

^a Actual exponents are obtained by multiplying the scale factor times all Gaussian primitives of a given atomic orbital in the basis described in the text.

repeated for the x, y exponents (α, β) starting with the already obtained optimized spherical and ellipsoidal results. In all the optimization procedures the coefficients of the individual Gaussian functions in a given atomic orbital were kept at their initial values [25, 27].

The results are tabulated in Tables 1 and 2 for the optimized scale factors and in Table 3 for the corresponding energy quantities.

5. Discussion

The total energies for the HF and CO molecules in Table 3 can be used immediately to test the expectation that a minimal atomic orbital ellipsoidal Gaussian basis set will give roughly similar results to a standard double-zeta spherical Gaussian basis. For HF the ellipsoidal basis gives some 83% of the energy difference between the unoptimized spherical [$3^s 1^p / 1^s$] Gaussian basis and the corresponding double-zeta set results, while for CO this percentage drops to 51%. For both systems, however, the greater part of the energy lowering is due to the spherical optimization rather than to the ellipticity. Clearly more experience is needed with a variety of systems and choice of optimization methods to fully judge the usefulness of generalized ellipsoidal Gaussian basis functions.

Table 2. Energy optimized exponent scale factors for spherical and ellipsoidal Gaussian atomic orbitals in CO

Atomic orbital	Optimized scale factors ^a		
	Spherical Gaussian	Ellipsoidal Gaussian	
		α, β	γ
O 2s	1.049	1.043	0.937
O 2p _x , 2p _y	0.996	1.005	0.949
O 2p _z	1.063	1.085	0.998
C 2s	1.044	0.962	0.966
C 2p _x , 2p _y	1.324	1.313	1.152
C 2p _z	1.524	1.569	1.467

^a See footnote 1 in Table 1.

Table 3. Total energies of HF and CO in various basis sets^a

	HF	CO
Spherical Gaussian set		
Original double-zeta ^b	-100.02197	-112.68488
Original single-zeta ^c	-99.98842	-112.55545
Optimized single-zeta ^c	-100.01342	-112.60690
Ellipsoidal Gaussian set ^c	-100.01622	-112.62200

^a Energies in a.u.

^b $[4^s 2^p / 2^s]$ combined set from the $(9^s 5^p / 4^s)$ primitive set.

^c $[3^s 1^p / 1^s]$ combined set from the $(9^s 5^p / 4^s)$ primitive set.

Previous minimal atomic orbital basis calculations on HF [29] and CO [30] using exponential functions (Slater orbitals) with optimized exponential factors can be compared with the optimized spherical Gaussian results in Tables 1 and 2. Due care, however, must be taken to compare the square root of the scale factors in these tables with the ratios of optimized and initial exponential factors found previously. When this is done the results are seen to be generally similar in spite of the great difference in basis type between the corresponding investigations.

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