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Computation of Electron Repulsion Integrals Involving Contracted Gaussian Basis Functions

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A computational procedure is outlined for efficient evaluation of four-center coulomb repulsion integrals using contracted Gaussian basis functions. By utilizing information common to a shell of basis functions (such as *s*, *px*, *py*, and *pz*) and by transforming to alternative axes within the contraction loops, this method achieves high efficiency. The technique has been incorporated into the GAUSSIAN-70 molecular orbital program.

1. INTRODUCTION

One of the major computational tasks in ab initio molecular orbital theory is the evaluation of the two-electron interaction integrals

$$(\varphi_\mu\varphi_\nu \mid \varphi_\lambda\varphi_\sigma) = \iint \varphi_\mu(1)\,\varphi_\nu(1)(1/r_{12})\,\varphi_\lambda(2)\,\varphi_\sigma(2)\,d\tau_1\,d\tau_2\,, \tag{1}$$

where $\varphi_\mu \cdots$ are one-electron basis functions. These φ-functions are commonly chosen to be contracted Gaussian functions (linear combinations of primitive Gaussian functions),

$$\varphi_\lambda = \sum_{k=1}^{K} d_{k\lambda}\, g_k\,. \tag{2}$$

The primitive functions g_k have the form

$$g_k = X \exp(-\alpha_k r^2), \tag{3}$$

where α_k is a constant (exponent), r is the distance from the center of the function g_k, and $X = 1$ for zero-order Gaussians (s-type), $X = x$, y, or z for first-order Gaussians (p-type), $X = x^2$, y^2, z^2, xy, yz, or zx for second-order Gaussians, and so forth (x, y, z being Cartesian coordinates relative to the center of g_k).

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A direct approach to this problem is substitution of the linear expansions (2) into (1) leading to a quadruple sum involving integrals $(g_i g_j \mid g_k g_l)$ similar to (1) but with the primitive g-functions. These can be evaluated analytically by methods originally due to Boys [1, 2]. However, if there are K terms in each φ-expansion (2), K^4 such primitive integrals are required for each two-electron integral $(\varphi_\mu \varphi_\nu \mid \varphi_\lambda \varphi_\sigma)$. Consequently, the computation time per contracted integral becomes long even for modest values of K and more efficient procedures are desirable.

There are two features of Gaussian basis sets that can be exploited to achieve more rapid computation of the integrals (1). In the first place, the basis functions φ_μ themselves are normally specified in sets which share common information. For example, three basis functions representing px-, py-, and pz-atomic orbitals on the same atom are usually chosen to have the same contraction coefficients in (2) and the same set of exponents α_k so that they differ only by taking $X = x$, y, or z in (3). Improved efficiency is therefore possible if all 81 (3^4) integrals (1) involving such related φ-functions are evaluated together, so that computation involving the common information is not repeated unnecessarily. Even greater savings may be achieved in the simultaneous evaluation of two-electron integrals involving second-order (d-type) Gaussians. Here the six atomic orbital components ($X = x^2$, y^2, z^2, xy, xz, and yz) result in 1296 (6^4) integrals. Other benefits arise from the grouping of related atomic orbitals. For example, the magnitudes of two-electron integrals over individual Gaussian functions may be estimated from consideration of the expansion coefficients ($d_{k\lambda}$ in (2)) and the Gaussian exponents (α_k in (3)), information which is shared by atomic orbitals within a set. Therefore, it is possible to ascertain whether any member of an entire set of two-electron integrals (involving related atomic orbitals on up to four different centers) is large enough to warrant evaluation. If not, as is often the case for integral sets involving inner shell functions or those on far removed centers, then calculation of the entire set of integrals may be eliminated. The use of molecular symmetry in the calculation of two-electron integrals is also facilitated by the grouping of atomic orbitals into sets of related functions. Thus, instead of applying a molecule's symmetry operations to individual two-electron integrals, it is possible, and far more efficient, to transform entire sets of integrals.

A second approach to greater efficiency is modification to make those parts of the computation which have to be performed K^4 times as simple as possible, even though this might require more elaborate procedures elsewhere. For example, it may be worthwhile to use a different system of coordinate axes in the innermost (K^4) part of the computation and then transform the integrals to the prescribed axes at a later stage. Modifications of this sort may not be of any value for uncontracted basis functions but their utility is likely to increase rapidly with the degree of contraction K.

The purpose of the present paper is to outline some computational procedures which have been developed with these ends in mind. Only contracted s- and p-type basis functions will be considered although extension to d-type and higher is possible [3]. The procedures described are utilized in the ab initio molecular orbital program GAUSSIAN 70 which is generally available [4].

2. Definitions, Notation, and Coordinate Axes

We define a *shell* of contracted Gaussian basis functions as a set of φ_λ, given by (2), which have the same center, the same expansion length K, and the same exponents α_k ($k = 1, 2 \cdots K$). A single s-type contracted function ($X = 1$ in Eq. (3)) constitutes an s-shell. A set of three p-functions φ_x, φ_y, φ_z, which differ only by the choice of X (x, y, or z) in (3), constitutes a p-shell. We can also define an sp-shell as a set of one s- and three p-functions φ_s, φ_x, φ_y, φ_z where φ_s has $X = 1$ and has the same exponents α_k as φ_x, φ_y, φ_z. However, the d-coefficients in (2) will generally differ from φ_s to φ_x, φ_y, φ_z.

Since considerable computational savings can be achieved by grouping the basis functions into shells, it is often worthwhile to deal with sp-shells rather than p-shells separately. Further justification of this is that s- and p-type atomic orbitals are frequently located in similar regions of space. For example, the optimum exponents for $2s$ and $2p$ Slater-type atom orbitals are quite close. In the following discussion, we shall restrict ourselves to the evaluation of integrals involving sp-shells. The corresponding theory for s-shells, p-shells, or mixed cases is similar and need not be discussed explicitly.

Let us consider the integrals arising from four sp-shells at different points A, B, C, D. There will be 256 (4^4) such integrals which may be described collectively as $(AB \mid CD)$. We shall suppose that the degree of contraction (K in Eq. (2)) is the same for all four shells. The individual basis functions on center A may then be written

$$\varphi_{Ar} = \sum_{i=1}^{K} d_{iAr} g_{iAr} \tag{4}$$

where g_{iAr} is a primitive Gaussian function

$$g_{iAr} = X_{Ar} \exp(-\alpha_{iA} r_A^2). \tag{5}$$

Here the suffix r runs over the four component functions with $X_{Ar} = 1, x_A, y_A, z_A$ for $r = 1, 2, 3, 4$ (i.e., s, px, py, and pz primitives, respectively). x_A, y_A, and z_A are Cartesian coordinates relative to center A and r_A is the scalar distance to center A. Note that the exponent α_{iA} is independent of the suffix r. A similar notation is used for the other shells.

As mentioned in the introduction, it is helpful for computational efficiency to use several sets of cartesian axes. We shall actually use three sets. The outermost, which will be termed axes-3, is the prescribed set to which the basis functions (4) are referred. The second intermediate set (axes-2) is determined by the points A, B, C, and D (Fig. 1). The z-direction is chosen to be along AB and the y-direction to be perpendicular to AB and CD (actually along the vector product $AB \times CD$). The x-direction then completes a right-handed coordinate system. The origin for axes-2 is shown as on AB in Fig. 1. However, this location need not be specified as only relative position vectors are used.

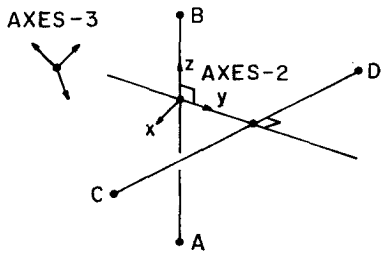

FIG. 1. Intermediate Cartesian axes (axes-2) relative to prescribed axes (axes-3).

Before describing the inner Cartesian axes, we note, following Boys [1], that

$$\exp(-\alpha_{iA}r_A^2 - \alpha_{jB}r_B^2) = L_P \exp(-\alpha_P r_P^2) \tag{6}$$

where r_P is the distance from the point P with position vector

$$\mathbf{P} = \alpha_P^{-1}[\alpha_{iA}\mathbf{A} + \alpha_{jB}\mathbf{B}], \tag{7}$$

$$\alpha_P = \alpha_{iA} + \alpha_{jB}\,. \tag{8}$$

The constant L_P is

$$L_P = \exp(-\alpha_{iA}\alpha_{jB}\alpha_P^{-1}R_{AB}^2), \tag{9}$$

R_{AB} being the AB distance.

The point P lies on the line AB and depends on the contraction suffixes i and j. As a result of (6), the product of the primitive Gaussian g_{iAr} at A and the primitive Gaussian g_{jBs} at B can be expressed as a linear combination of primitive Gaussians g_{Pj} at P,

$$g_{iAr}g_{jBs} = \sum_t E_{Prst}g_{Pt}\,. \tag{10}$$

The E_{Prst} are constants and the sum over t runs over the 10 primitive Gaussians of zero, first, and second order,

$$X_{Pj} = 1, x_P, y_P, z_P, x_P^2, y_P^2, z_P^2, x_P y_P, y_P z_P, z_P x_P, \tag{11}$$

the coordinates being measured relative to P. For given i, j, there will be 16 products (10) ($r, s = 1, 2, 3, 4$). Examples are

$$g_{iA1}g_{jB1} = L_P g_{P1}, \tag{12}$$

$$\begin{aligned} g_{iA1}g_{jB2} &= L_P x_B \exp(-\alpha_P r_P^2) \\ &= L_P(X_{BP}g_{P1} + g_{P2}), \end{aligned} \tag{13}$$

$$\begin{aligned} g_{iA2}g_{jB3} &= L_P x_A y_B \exp(-\alpha_P r_P^2) \\ &= L_P(X_{AP}Y_{BP}g_{P1} + Y_{BP}g_{P2} + X_{AP}g_{P3} + g_{P8}). \end{aligned} \tag{14}$$

Here X_{AP} is the x-component of the position vector AP, etc. These relations apply in any of the coordinated systems considered.

In exactly the same way, products of primitive Gaussians g_{kCu} at C and g_{lDv} at D can be written

$$g_{kCu}g_{lDv} = \sum_w E_{Quvw}g_{Qw} \tag{15}$$

where Q is a point on the line CD

$$\begin{aligned} \mathbf{Q} &= \alpha_Q^{-1}[\alpha_{kC}\mathbf{C} + \alpha_{lD}\mathbf{D}], \\ \alpha_Q &= \alpha_{kC} + \alpha_{lD}\,. \end{aligned} \tag{16}$$

We now define the inner Cartesian axes (axes-1) as shown in Fig. 2. The z-axis is again taken along the line AB (as in axes-2). The x-axis is chosen to pass through the point Q and the y-axis to complete the right-handed system. Note that the directions of axes-1 depend on the position of Q but not on P. Transformation from axes-1 to axes-2 is accomplished by rotation about the common z-axis.

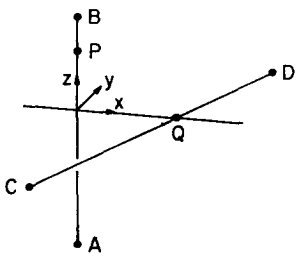

FIG. 2. Inner Cartesian axes (axes-1).

3. COMPUTATIONAL PROCEDURE

The integrals to be evaluated are $(\varphi_{Ar}\varphi_{Bs} \mid \varphi_{Cu}\varphi_{Dv})$ where the suffixes r, s, u, v take four values, giving 256 integrals in all. Using the expansions (4) and (10), these may be written

$$(\varphi_{Ar}\varphi_{Bs} \mid \varphi_{Cu}\varphi_{Dv}) = \sum_{kl} d_{kCu}d_{lDv} \sum_w E_{Quvw} \sum_{ij} d_{iAr}d_{jBs}(g_{iAr}g_{jBs} \mid g_{Qw}). \tag{17}$$

The sum over k, l is equivalent to a sum over distinct points Q and that over i, j to a sum over points P. Writing

$$D_{Quv} = d_{kCu}d_{lDv}\,, \tag{18}$$

$$D_{Prs} = d_{iAr}d_{jBs}\,, \tag{19}$$

the expression (17) takes the simpler form

$$(\varphi_{Ar}\varphi_{Bs} \mid \varphi_{Cu}\varphi_{Dv}) = \sum_Q D_{Quv} \sum_w E_{Quvw} \sum_P D_{Prs}(g_{iAr}g_{jBs} \mid g_{Qw}). \tag{20}$$

Optimization of computational efficiency requires (1) that the summations in Eq. (20) are moved as far as possible to the right and (2) that the number of operations to the right of each summation is made as small as possible. The second requirement is met by working in axes-1 to the right of the P-summation and transforming the results to axes-2 to the left of (i.e., after) the P-summation. This is possible because the orientation of axes-1 is independent of the position of P on the line AB.

Since the suffixes r, s, and w take on 4, 4, and 10 values, respectively, there will be 160 integrals $(g_{iAr}g_{jBs} \mid g_{Qw})$. However, only 88 of these are nonzero in axes-1. This is because the coordinate y (Fig. 2) must appear an even number of times. This reduction from 160 to 88 integrals is the main reason for switching to axes-1.

Further improvement can be achieved by noting that the computation of the 88 three-center integrals $(g_{iAr}g_{jBs} \mid g_{Qw})$ can be accomplished in part by operations which are independent of P. In fact, each such integral can be written as a linear combination of terms

$$(g_{iAr}g_{jBs} \mid g_{Qw}) = \sum_m \Gamma_{Qrswm}\Delta_{PQrswm}\,, \tag{21}$$

where the quantity Γ_{Qrswm} depends only on the position of Q relative to A, B and on the exponent α_Q. We shall not give full expressions for the quantities Γ and Δ as it is easily confirmed from the general theory of the primitive integrals that such expressions are possible [1, 2].

Making use of (21), full evaluation of the integrals can be accomplished by

$$(\varphi_{Ar}\varphi_{Bs} \mid \varphi_{Cu}\varphi_{Dv}) = \sum_Q D_{Quv} \sum_w E_{Quvw}(\varphi_{Ar}\varphi_{Bs} \mid g_{Qw}), \tag{22}$$

where

$$(\varphi_{Ar}\varphi_{Bs} \mid g_{Qw}) = \sum_m \Gamma_{Qrswm}\Omega_{Qrswm} \tag{23}$$

and

$$\Omega_{Qrswm} = \sum_P D_{Prs}\Delta_{PQrswm}\,. \tag{24}$$

There are still 88 nonvanishing integrals (23) in axes-1. After evaluation, they may be rotated to 160 values in axes-2 before the further summations in (22) are carried out.

The program loop structure that is used in GAUSSIAN-70 to accomplish the computation is shown in Fig. 3. The outermost loop (actually four loops) is over the shells, denoted by A, B, C, and D. This is followed by computation of features independent of contraction indices, principally the direction cosines of axes-2 in the frame of axes-3. Next a preliminary P-loop is used to collect and store information which depends on the position of P but not on the position of Q. This includes the product of the first exponential on the right-hand side of (6), the inverse constant in (7), and D_{Prs} from (19). After this, the main Q-loop and comparable information about Q (independent of P) are collected. The innermost part of the routine is the

	Gaussian-70 Location
Begin ABCD-loop	SHELL
Information about A, B, C, D	SINFO, SGEOM
Begin preliminary P-loop	PINF
Information about P	PINF
End preliminary P-loop	PINF
Begin Q-loop	SHELL
Information about Q	SHELL
Begin P-loop	SP1111
Information requiring P and Q	SP1111
Increment Ω_{Qrswm} by $D_{Prs}\Delta_{PQrswm}$ (Eq. (24))	SP1111
End P-loop	SP1111
Evaluate 88 integrals $(\varphi_{Ar}\varphi_{Bs} \mid g_{Qw})$ in axes-1 (eq. (23))	SP1111
Transform $(\varphi_{Ar}\varphi_{Bs} \mid g_{Qw})$ to axes-2 giving 160 integrals	ROT2
Increment 256 integrals $(\varphi_{Ar}\varphi_{Bs} \mid \varphi_{Cu}\varphi_{Dv})$ in axes-2 (Eq. (22))	TQ1111
End Q-loop	SHELL
Transform $(\varphi_{Ar}\varphi_{Bs} \mid \varphi_{Cu}\varphi_{Dv})$ to axes-3	R31111
End ABCD-loop	SHELL

FIG. 3. Loop structure of SHELL integral routine in GAUSSIAN-70 program [4] together with associated subroutines.

P-loop (traversed K^4 times for each set of shells). This collects information depending on P and Q and evaluates (usually by interpolation in a table) the functions

$$F_m(t) = \int_0^1 u^{2m} \exp(-tu^2)\, du \qquad (n = 0,\ldots, 4),$$
$$t = (\alpha_P + \alpha_Q)^{-1} \alpha_P \alpha_Q r_{PQ}^2 , \tag{25}$$

that appear in the full expressions for the integrals [2]. In the remainder of the P-loop, the quantities $D_{Prs}\Delta_{PQrswm}$ are evaluated and added on to the parts of Ω_{Qrswm} already formed, thereby carrying out the summation over P in (24). The number of independent Ω_{Qrswm} is actually only 70 and these can be calculated from the $F_m(t)$ in less than 100 multiplications. This is the end of the P-loop.

The evaluation of the 88 three-center integrals (23) takes place in the latter part of the Q-loop. This part of the process has to be carried out only K^2 times. These integrals are then transformed to axes-2. This involves rotation about the common z-axis and increases the number of nonzero integrals to 160 (4 values for suffices r, s, and 10 for w). In the final part of the Q-loop, the w-summation in Eq. (22) is carried out, the sum is multiplied by D_{Quv}, and is added as an increment to the partially formed integrals $(\varphi_{Ar}\varphi_{Bs} \mid \varphi_{Cu}\varphi_{Dv})$. This corresponds to the sum over Q in (22). The final transformation to the external axes-3 is then made outside of the Q-loop.

The high efficiency of this program structure can be illustrated by a count of the number of multiplications involved. For a single set of *sp* shells *ABCD*, producing 256 integrals, this number is approximately

$$N_{\text{mult}} = 2400 + 1450K^2 + 120K^4. \tag{26}$$

The very small K^4-coefficient (i.e., multiplications inside the *P*-loop) is really achieved by extra operations, such as transformation of axes, in the outer parts. It follows that the procedure is most valuable for highly contracted functions. For $K = 3$ (as with the STO-3G basis [5]), the number of multiplictaions is about 26,000, approximately 100 per complete contracted integral. Since a direct expansion in terms of integrals over primitive Gaussians would involve $3^4 = 81$ component integrals per complete contracted integral, it is evident that major saving has been achieved.

Some modifications of the procedure are necessary in special cases. If some of the points coincide, axes can be chosen with some element of arbitrariness. For example, if *A* and *B* coincide, the *y*-axis in Fig. 1 is still determined but the *z*-axis can be chosen as any direction perpendicular to the *y*-axis. If *AB* and *CD* are parallel [6], the *y*-axis in Fig. 1 can be in any direction perpendicular to *AB*. If some of the shells coincide (e.g., $A = B$ or $C = D$), the number of distinct integrals is reduced so that duplicates must be rejected.

Acknowledgments

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5. W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.* **51** (1969) 2657.
6. If AB and CD are nearly but not exactly parallel, some instability is encountered since the vector product direction is imprecisely defined. Special procedures must be adopted to avoid error in such cases.