JOURNAL OF COMPUTATIONAL PHYSICS 26, 218–231 (1978)

One- and Two-Electron Integrals over Cartesian Gaussian Functions

LARRY E. MCMURCHIE AND ERNEST R. DAVIDSON

Department of Chemistry BG-10, University of Washington, Seattle, Washington 98195

Received March 23, 1977

A formalism is developed which allows overlap, kinetic energy, potential energy, and electron repulsion integrals over cartesian Gaussian functions to be expressed in a very compact form involving easily computed auxiliary functions. Similar formulas involving the same auxiliary functions are given for the common charge moments, electric-field operators, and spin-interaction operators. Recursion relations are given for the auxiliary functions which make possible the use of Gaussian functions of arbitrarily large angular momentum. An algorithm is described for the computation of electron repulsion integrals.

1. INTRODUCTION

Cartesian Gaussian functions of the form $x_A{}^n y_A{}^l z_A{}^m \exp(-\alpha_A r_A{}^2)$ were first proposed as basis functions by Boys [1]. The obvious exploitable advantage of Gaussian functions over Slater-type orbitals (STO's) is the ease with which a product of Gaussians on two different centers can be written as a simple function on a common center [2]. In the 1960's when calculations on diatomic systems were already common, the intractability of the four-center integral over STO's appeared to present a major block to polyatomic calculations [3]. Gaussians began to enjoy increased popularity when it was found that a fixed linear combination (a so-called "contracted Gaussian") could be used to approximate an atomic orbital to good accuracy. Initially the trend was to use combinations of simple Gaussian "lobes" ($n = l = m = 0$) [4]. The resulting electron repulsion integral had been shown by Boys [1–3] to involve only a square root, an exponential, and the error function. Functions of p or d type were approximated by differences of Gaussian lobes displaced slightly from each other. For high angular momentum basis functions this approach becomes intractable both because of the large numbers of lobes involved and because of large differencing errors in combining the integrals over the basic lobes.

The obvious alternative to contracted Gaussian lobes was contracted Cartesian Gaussians. Basis sets involving these functions are now more or less standardized [5]. Formulas for integrals over p-type Gaussians were easily derived [2] and programmed. Standard program packages such as POLYATOM [6] and GAUSSIAN 70 [6] have been available for some time. Some versions of these packages have included d and f orbitals. The formulas available for these integrals [2], while completely general, do not allow systematic calculation of integrals for higher angular momentum.

0021-9991/78/0262–0218$02.00/0

In this paper we present auxiliary functions and recursion relations from which integrals for all values of $n + l + m$ can be systematically (and efficiently) computed.

2. Charge Distributions

An unnormalized Gaussian function on center A will be given by

$$\phi(n, l, m, \alpha_A, A) = x_A{}^n y_A{}^l z_A{}^m \exp(-\alpha_A r_A{}^2) \tag{2.1}$$

where (x_A, y_A, z_A) are the components of the vector $\mathbf{r}_A = \mathbf{r} - \mathbf{A}$ with norm r_A. The normalization constant for this function is

$$N_{nlm}(\alpha_A) = N_n(\alpha_A)\, N_l(\alpha_A)\, N_m(\alpha_A) \tag{2.2}$$

where

$$N_k(\alpha) = (2\alpha/\pi)^{1/4}(4\alpha)^{k/2}[(2k-1)!!]^{-1/2}. \tag{2.3}$$

Such functions are referred to as *s*, *p*, *d*,... when $L = n + l + m$ is 0, 1, 2,..., respectively. Contracted basis functions can be formed from the ϕ's in various ways. For example, it is usual to define

$$f_{nlmA} = \sum_{\alpha_A} C^L(\alpha_A)\, N_{nlm}(\alpha_A)\, \phi(n, l, m, \alpha_A, A) \tag{2.4}$$

where $C^L(\alpha_A)$ is independent of n, l, m (for fixed L). Alternatively a more general

$$g_{LMA} = \sum_{\alpha_A} C^L(\alpha_A) \sum_{nlm} B^{LM}_{nlm} \phi(n, l, m, \alpha_A, A) \tag{2.5}$$

can be considered which allows true angular momentum eigenfunctions to be formed (with the α dependent part of $N_{nlm}(\alpha)$, $\alpha^{(2L+3)/4}$, absorbed in $C^L(\alpha_A)$ and the α independent factors absorbed into B^{LM}_{nlm}).

Efficient computation of integrals requires that f_{nlmA} or g_{LMA} which involve the same α's and the same nucleus be treated as sets. For maximum efficiency these sets should be large enough that calculation of the auxiliary functions common to a block of integrals becomes insignificant. On the other hand, excessively large blocks of integrals which result from treating all 15 $L = 4$ functions as one set should be avoided.

For the sake of simplicity, the formulas in this paper will be given only for integrals over ϕ's rather than f's or g's, in order to avoid writing explicitly the sums over α. To this end it is convenient to define the charge distribution Ω_{IJ} of two functions $\phi_I(n, l, m, \alpha_A, A)$ and $\phi_J(\bar{n}, \bar{l}, \bar{m}, \alpha_B, B)$ as

$$\Omega_{IJ} = \phi_I \phi_J = x_A{}^n x_B{}^{\bar{n}} y_A{}^l y_B{}^{\bar{l}} z_A{}^m z_B{}^{\bar{m}} \exp[-(\alpha_A r_A{}^2 + \alpha_B r_B{}^2)]. \tag{2.6}$$

The key to the utility of Gaussians is the well-known identity which transforms the above exponential to a single exponential about a center **P** on the line segment $\overline{AB}$:

$$\exp[-(\alpha_A r_A^2 + \alpha_B r_B^2)] = E_{IJ} \exp(-\alpha_P r_P^2) \quad (2.7)$$

where

$$\mathbf{P} = (\alpha_A \mathbf{A} + \alpha_B \mathbf{B})/(\alpha_A + \alpha_B), \quad (2.8)$$

$$\alpha_P = \alpha_A + \alpha_B, \quad (2.9)$$

and

$$E_{IJ} = \exp\{-\alpha_A \alpha_B (\alpha_A + \alpha_B)^{-1} \mid \mathbf{A} - \mathbf{B} \mid^2\}. \quad (2.10)$$

Since molecular calculations usually require absolute rather than relative accuracy, all integrals involving Ω_{IJ} can be neglected if the constant E_{IJ} is sufficiently small.

The products $x_A^n x_B^{\bar{n}}$, $y_A^l y_B^{\bar{l}}$, and $z_A^m z_B^{\bar{m}}$ could be converted into polynomials in x_P, y_P, and z_P using relations like

$$x_A = x_P + \overline{PA}_x, \quad (2.11)$$

where

$$x_A = x - A_x, \quad (2.12)$$

$$x_P = x - P_x, \quad (2.13)$$

and

$$\overline{PA}_x = P_x - A_x. \quad (2.14)$$

It is more convenient in what follows, however, to define

$$\Lambda_j(x_P ; \alpha_P) \exp(-\alpha_P x_P^2) = (\partial/\partial P_x)^j \exp(-\alpha_P x_P^2), \quad (2.15)$$

from which it follows that Λ_j is related to the Hermite polynomial H_j by

$$\Lambda_j(x_P ; \alpha_P) = \alpha_P^{j/2} H_j(\alpha_P^{1/2} x_P). \quad (2.16)$$

The utility of the Λ's is obvious—they will allow the charge distribution to be written as a sum of derivatives with respect to the coordinates of **P** and these derivatives can be taken outside of any integral over electronic coordinates.

Now let us find the coefficients for expanding $x_A^n x_B^{\bar{n}}$ in the Λ's:

$$x_A^n x_B^{\bar{n}} = \sum_{N=0}^{n+\bar{n}} d_N^{n\bar{n}} \Lambda_N(x_P ; \alpha_P). \quad (2.17)$$

The recursion relation for the Hermite polynomials is

$$\xi H_N(\xi) = N H_{N-1}(\xi) + \tfrac{1}{2} H_{N+1}(\xi). \quad (2.18)$$

Consequently

$$x_A \Lambda_N(x_P ; \alpha_P) = N \Lambda_{N-1} + \overline{PA}_x \Lambda_N + \tfrac{1}{2} \Lambda_{N+1}/\alpha_P. \quad (2.19)$$

The recursion relations on the $d_N^{n\bar{n}}$ are then easily seen to be

$$d_N^{n+1,\bar{n}} = (2\alpha_P)^{-1} d_{N-1}^{n\bar{n}} + \overline{PA}_x d_N^{n\bar{n}} + (N+1)\, d_{N+1}^{n\bar{n}}, \tag{2.20}$$

$$d_N^{n,\bar{n}+1} = (2\alpha_P)^{-1} d_{N-1}^{n\bar{n}} + \overline{PB}_x d_N^{n\bar{n}} + (N+1)\, d_{N+1}^{n\bar{n}}, \tag{2.21}$$

where

$$d_0^{00} = 1. \tag{2.22}$$

Similarly we can write

$$y_A^{\ l} y_B^{\ \bar{l}} = \sum_{L=0}^{l+} e_L^{l\bar{l}} \Lambda_L(y_P\,;\,\alpha_P) \tag{2.23}$$

and

$$z_A^{\ m} z_B^{\ \bar{m}} = \sum_{M=0}^{m+\bar{m}} f_M^{m\bar{m}} \Lambda_M(z_P\,;\,\alpha_P) \tag{2.24}$$

so that

$$\Omega_{IJ} = E_{IJ} \sum_{NLM} d_N^{n\bar{n}} e_{LJ}^{l\bar{l}} f_M^{m\bar{m}} \Lambda_N(x_P)\, \Lambda_L(y_P)\, \Lambda_M(z_P) \exp(-\alpha_P r_P^{\,2}). \tag{2.25}$$

It is often convenient to write Ω_{IJ} as

$$\Omega_{IJ} = \sum_k D_k \Lambda_{N_k}(x_P)\, \Lambda_{L_k}(y_P)\, \Lambda_{M_k}(z_P) \exp(-\alpha_P r_P^{\,2}), \tag{2.26}$$

where

$$D_k = E_{IJ} d_{N_k}^{n\bar{n}} e_{L_k}^{l\bar{l}} f_{M_k}^{m\bar{m}}. \tag{2.27}$$

This allows generalization to include spherical harmonic basis functions when D_k is replaced by

$$D_k = E_{IJ} \sum_{n,l,m} \sum_{\bar{n},\bar{l},\bar{m}} B_{nlm}^{\lambda\mu} B_{\bar{n},\bar{l},\bar{m}}^{\bar{\lambda}\bar{\mu}} d_{N_k}^{n\bar{n}} e_{L_k}^{l\bar{l}} f_{M_k}^{m\bar{m}}. \tag{2.28}$$

In these equations k indexes all (N, L, M) combinations for which D is nonzero and the charge distribution is specified by a list of the nonzero D_k and the corresponding (N_k, L_k, M_k). In practice the $C^L(\alpha_A)\, C^{\bar{L}}(\alpha_B)$ and normalization are also incorporated into the D_k.

Some integrals which must be evaluated involve derivatives of the basis functions. Consequently, it is convenient to define the additional charge distributions

$$G_{IJ} = \phi_I \nabla \phi_J, \tag{2.29}$$

$$T_{IJ} = \nabla\phi_I \cdot \nabla\phi_J, \tag{2.30}$$

and

$$Q_{IJ} = (\nabla\phi_I) \times (\nabla\phi_J). \tag{2.31}$$

The x component of G_{IJ} is easily obtained from

$$\partial/\partial x\ \phi(\bar{n}, \bar{l}, \bar{m}, \alpha_B, B) = \bar{n}\phi(\bar{n}-1, \bar{l}, \bar{m}, \alpha_B, B) - 2\alpha_B\phi(\bar{n}+1, \bar{l}, \bar{m}, \alpha_B, B) \quad (2.32)$$

so that

$$G_{IJ}^{(x)} = \sum_k g_k^{(x)} \Lambda_{N_k}\Lambda_{L_k}\Lambda_{M_k} \exp(-\alpha_P r_P^2) \quad (2.33)$$

with

$$g_k^{(x)} = E_{IJ}(\bar{n} d_{N_k}^{n,\bar{n}-1} - 2\alpha_B d_{N_k}^{n,\bar{n}+1})\, e_{L_k}^{l\bar{l}} f_{M_k}^{m\bar{m}}. \quad (2.34)$$

The distribution T_{IJ} may be expanded in an analogous manner to give

$$T_{IJ} = \sum_k t_k \Lambda_{N_k}\Lambda_{L_k}\Lambda_{M_k} \exp(-\alpha_P r_P^2) \quad (2.35)$$

with

$$t_k = (t_k^{xx} + t_k^{yy} + t_k^{zz})\, E_{IJ}, \quad (2.36)$$

$$t_k^{xx} = [n\bar{n} d_{N_k}^{n-1,\bar{n}-1} - 2n\alpha_B d_{N_k}^{n-1,\bar{n}+1} - 2\bar{n}\alpha_A d_{N_k}^{n+1,\bar{n}-1} + 4\alpha_A\alpha_B d_{N_k}^{n+1,\bar{n}+1}]\, e_{L_k}^{l\bar{l}} f_{M_k}^{m\bar{m}}, \quad (2.37)$$

and similar expressions for t_k^{yy} and t_k^{zz}. The z component of Q_{IJ} may be similarly shown to be of the form

$$Q_{IJ}^{(z)} = \sum_k q_k^{(z)} \Lambda_{N_k}\Lambda_{L_k}\Lambda_{M_k} \exp(-\alpha_P r_P^2), \quad (2.38)$$

where

$$q_k^{(z)} = f_{M_k}^{m\bar{m}} E_{IJ} q_k^{xy}. \quad (2.39)$$

The q_k^{xy} obtained directly from $\partial\phi_I/\partial x\ \partial\phi_J/\partial y - \partial\phi_I/\partial y\ \partial\phi_J/\partial x$ involve new ϕ's of total powers of x, y, and z higher by two than the starting ones. These highest powers cancel since

$$\begin{aligned}
&\phi(n+1, l, m, \alpha_A, A)\, \phi(\bar{n}, \bar{l}+1, \bar{m}, \alpha_B, B) - \phi(n, l+1, m, \alpha_A, A)\, \phi(\bar{n}+1, \bar{l}, \bar{m}, \alpha_B, B) \\
&\quad = (x_A y_B - y_A x_B)\, \phi(n, l, m, \alpha_A, A)\, \phi(\bar{n}, \bar{l}, \bar{m}, \alpha_B, B) \qquad (2.40) \\
&\quad = [\overline{AB}_y \phi(n+1, l, m, \alpha_A, A) - \overline{AB}_x \phi(n, l+1, m, \alpha_A, A)]\, \phi(\bar{n}, \bar{l}, \bar{m}, \alpha_B, B).
\end{aligned}$$

Consequently,

$$\begin{aligned}
q_k^{xy} = {}& \bar{l}(n d_{N_k}^{n-1,\bar{n}} - 2\alpha_A d_{N_k}^{n+1,\bar{n}})\, e_{L_k}^{l,\bar{l}-1} - 2n\alpha_B d_{N_k}^{n-1,n} e_{L_k}^{l,\bar{l}+1} \\
& - l(\bar{n} d_{N_k}^{n,\bar{n}-1} - 2\alpha_B d_{N_k}^{n,\bar{n}+1})\, e_{L_k}^{l-1,\bar{l}} - 2\bar{n}\alpha_A d_{N_k}^{n,\bar{n}-1} e_{L_k}^{l+1,\bar{l}} \\
& + 4\alpha_A\alpha_B[\overline{AB}_y d_{N_k}^{n+1,\bar{n}} e_{L_k}^{l,\bar{l}} - \overline{AB}_x d_{N_k}^{n,\bar{n}} e_{L_k}^{l+1,\bar{l}}]. \qquad (2.41)
\end{aligned}$$

It is important to note that different sets of (N_k, L_k, M_k) appear in (2.27), (2.28), (2.33), (2.35), and (2.38). Also, larger values of $N + L + M$ appear in the derivatives than in the charge distribution.

3. Basic Integrals

From the previous section it is clear that the one-electron integrals to be evaluated all reduce to the form

$$[NLM \mid \theta] = \int \theta(\mathbf{r}_1)\, \Lambda_N(x_{1P}\,;\alpha_P)\, \Lambda_L(y_{1P}\,;\alpha_P)\, \Lambda_M(z_{1P}\,;\alpha_P) \times \exp(-\alpha_P r_{1P}^2)\, d\tau_1\,. \tag{3.1}$$

Likewise the basic two-electron integrals all take the form

$$[NLM \mid \theta \mid N'L'M'] = \int \theta(\mathbf{r}_1, \mathbf{r}_2)\, \Lambda_N(x_{1P}\,;\alpha_P)\, \Lambda_L(y_{1P}\,;\alpha_P)\, \Lambda_M(z_{1P}\,;\alpha_P) \times \exp(-\alpha_P r_{1P}^2)\, \Lambda_{N'}(x_{2Q}\,;\alpha_Q)\, \Lambda_{L'}(y_{2Q}\,;\alpha_Q)\, \Lambda_{M'}(z_{2Q}\,;\alpha_Q) \times \exp(-\alpha_Q r_{2Q}^2)\, d\tau_1\, d\tau_2\,. \tag{3.2}$$

The one-electron integrals can be further classified as (a) those that can be done in closed form and (b) those that require the same numerically approximated auxiliary functions as the two-electron integrals.

A. *One-Electron Integrals, Closed Form*

The basic integral of this type is the one-dimensional integral

$$\int dx\, \Lambda_N(x_P\,;\alpha) \exp(-\alpha x_P{}^2) = \delta_{N,0}(\pi/\alpha)^{1/2} \tag{3.3}$$

(the $\delta_{N,0}$ arises from the orthogonality of the Hermite polynomials). Thus the overlap integral is simply

$$[NLM \mid 1] = \delta_{N,0}\delta_{L,0}\delta_{M,0}(\pi/\alpha_P)^{3/2}. \tag{3.4}$$

The relation

$$x_C \Lambda_N(x_P\,;\alpha_P) = N\Lambda_{N-1} + \tfrac{1}{2}\Lambda_{N+1}/\alpha_P + \overline{PC}_x \Lambda_N \tag{3.5}$$

then gives

$$[NLM \mid x_C] = (\delta_{N,1} + \overline{PC}_x \delta_{N,0})\, \delta_{L,0}\delta_{M,0}(\pi/\alpha_P)^{3/2} \tag{3.6}$$

with similar results for y_c and z_c. The second moments are just

$$[NLM \mid x_C{}^2] = [2\delta_{N,2} + 2\overline{PC}_x \delta_{N,1} + (\overline{PC}_x{}^2 + \tfrac{1}{2}\alpha_P^{-1})\, \delta_{N,0}]\, \delta_{L,0}\delta_{M,0}(\pi/\alpha_P)^{3/2} \tag{3.7}$$

and

$$[NLM \mid x_C y_C] = (\delta_{N,1} + \overline{PC}_x \delta_{N,0})(\delta_{L,1} + \overline{PC}_y \delta_{L,0})\, \delta_{M,0} (\pi/\alpha_P)^{3/2} \tag{3.8}$$

with similar results for y_C^2, z_C^2, $x_C z_C$, or $y_C z_C$.

The kinetic energy and gradient matrix elements are given directly by the formula for $[NLM \mid 1]$. Notice that only the t_k (and g_k) coefficients for $(N_k, L_k, M_k) = (0, 0, 0)$ are required to evaluate the kinetic energy and gradient matrix elements.

B. *Other One-Electron Integrals*

The basic integral in this category is the nuclear attraction integral $[NLM \mid r_C^{-1}]$. From the definition of the Λ's, this may be written as

$$[NLM \mid r_C^{-1}] = (\partial/\partial P_x)^N (\partial/\partial P_y)^L (\partial/\partial P_z)^M [000 \mid r_C^{-1}]. \tag{3.9}$$

The integral $[000 \mid r_C^{-1}]$ was shown by Boys to be given by

$$[000 \mid r_C^{-1}] = (2\pi/\alpha_P)\, F_0(T), \tag{3.10}$$

where

$$T = \alpha_P \overline{CP}^2, \tag{3.11}$$

and

$$F_0(T) = \int_0^1 \exp(-Tu^2)\, du. \tag{3.12}$$

If we define the auxiliary function R_{NLM} by

$$R_{NLM} = (\partial/\partial P_x)^N (\partial/\partial P_y)^L (\partial/\partial P_z)^M F_0(T) \tag{3.13}$$

then

$$[NLM \mid r_C^{-1}] = (2\pi/\alpha_P)\, R_{NLM}. \tag{3.14}$$

The computation of R_{NLM} will be described in a later section.

Matrix elements of the components of the electric field, such as $x_C r_C^{-3}$, can be evaluated in two ways which illustrate the tricks needed for more complicated integrals. First

$$x_C r_C^{-3} = \partial r_C^{-1}/\partial C_x, \tag{3.15}$$

where it should be noted that differentiation is with respect to the nuclear position. Therefore

$$[NLM \mid c_C r_C^{-3}] = (\partial/\partial C_x)[NLM \mid r_C^{-1}]. \tag{3.16}$$

But since T depends on $C_x - P_x$,

$$(\partial/\partial C_x)\, g(T) = -(\partial/\partial P_x)\, g(T) \tag{3.17}$$

for any function $g(T)$. Hence,

$$[NLM \mid x_C r_C^{-3}] = -(2\pi/\alpha_P)\, R_{N+1,L,M}\,. \tag{3.18}$$

Alternatively this integral can be evaluated by noting that

$$x_C r_C^{-3} = -\partial r_C^{-1}/\partial x. \tag{3.19}$$

Hence, by integration by parts,

$$[NLM \mid x_C r_C^{-3}] = [\partial(NLM)/\partial x \mid r_C^{-1}]. \tag{3.20}$$

But, from the definition of Λ_N,

$$\partial(N, L, M)/\partial x = -(N+1, L, M),$$

so

$$[NLM \mid x_C r_C^{-3}] = -(2\pi/\alpha_P)\, R_{N+1,L,M}\,. \tag{3.21}$$

The components of the electric field gradient are similarly obtained using

$$(\partial^2/\partial C_x^{\,2} - \partial^2/\partial C_y^{\,2})\, r_C^{-1} = 3(x_C^{\,2} - y_C^{\,2})\, r_C^{-5}\,, \tag{3.22}$$

$$\tfrac{1}{3}(2\partial^2/\partial C_z^{\,2} - \partial^2/\partial C_x^{\,2} - \partial^2/\partial C_y^{\,2})\, r_C^{-1} = (3z_C^{\,2} - r_C^{\,2})\, r_C^{-5}, \tag{3.23}$$

and

$$(\partial^2/\partial C_x \partial C_y)\, r_C^{-1} = 3x_C y_C r_C^{-5}. \tag{3.24}$$

Notice these formulas are written so as to avoid problems with the delta function which arises in $\nabla^2 r_C^{-1}$. Hence the electric field gradient integrals are given by

$$[NLM \mid 3(x_C^{\,2} - y_C^{\,2})\, r_C^{-5}] = (2\pi/\alpha_P)(R_{N+2,L,M} - R_{N,L+2,M}), \tag{3.25}$$

$$[NLM \mid (3z_C^{\,2} - r_C^{\,2})\, r_C^{-5}] = (2\pi/\alpha_P)(2R_{N,L,M+2} - R_{N+2,L,M} - R_{N,L+2,M})/3, \tag{3.26}$$

$$[NLM \mid 3x_C y_C r_C^{-5}] = (2\pi/\alpha_P)\, R_{N+1,L+1,M}\,. \tag{3.27}$$

Matrix elements over the one-electron spin–orbit operator may be evaluated by two different methods. If the space part of the basic spin–orbit operator is considered to be $r_C^{-3}\mathbf{r}_C \times \boldsymbol{\nabla}$ then the z component, for example, is $r_C^{-3}(x_C\, \partial/\partial y - y_C\, \partial/\partial x)$. Matrix elements of this operator can be evaluated by combining the results given above for the electric field with the g_k expansion coefficients given previously for the gradient. Alternatively integration by parts gives

$$\left\langle \phi_I \,\middle|\, r_C^{-3}\left(x_C \frac{\partial}{\partial y} - y_C \frac{\partial}{\partial x}\right) \middle|\, \phi_J \right\rangle = \left[\frac{\partial \phi_I}{\partial x}\frac{\partial \phi_J}{\partial y} - \frac{\partial \phi_I}{\partial y}\frac{\partial \phi_J}{\partial x} \,\middle|\, r_C^{-1}\right]. \tag{3.28}$$

The spin–orbit integral then reduces to using the q_k coefficients in summing $[NLM \mid r_C^{-1}$ matrix elements.

C. *Two-Electron Integrals*

The simplest integral in this category is the electron repulsion

$$[NLM \mid r_{12}^{-1} \mid N'L'M'] = (\partial/\partial P_x)^N (\partial/\partial P_y)^L (\partial/\partial P_z)^M (\partial/\partial Q_x)^{N'} (\partial/\partial Q_y)^{L'} (\partial/\partial Q_z)^{M'} [000 \mid r_{12}^{-1} \mid 000]. \tag{3.29}$$

Boys evaluated the basic integral as

$$[000 \mid r_{12}^{-1} \mid 000] = \lambda F_0(T) \tag{3.30}$$

where

$$\lambda = 2\pi^{5/2}\alpha_P^{-1}\alpha_Q^{-1}(\alpha_P + \alpha_Q)^{-1/2} \tag{3.31}$$

and

$$T = \alpha_P\alpha_Q(\alpha_P + \alpha_Q)^{-1}\,\overline{PQ}^2. \tag{3.32}$$

Because T involves only the combination $\mathbf{P} - \mathbf{Q}$,

$$(\partial/\partial Q_x)^N g(T) = (-\partial/\partial P_x)^N g(T) \tag{3.33}$$

for any function $g(T)$. Hence

$$[NLM \mid r_{12}^{-1} \mid N'L'M'] = \lambda(-1)^{N'+L'+M'} R_{N+N',L+L',M+M'}. \tag{3.34}$$

Just as for the electric field and field gradient, integrals over $x_{12}r_{12}^{-3}$, $x_{12}\,y_{12}r_{12}^{-5}$, etc., are easily evaluated. For example,

$$[NLM \mid x_{12}r_{12}^{-3} \mid N'L'M'] = -\lambda(-1)^{N'+L'+M'} R_{N+N'+1,L+L',M+M'}, \tag{3.35}$$

$$[NLM \mid 3x_{12}\,y_{12}r_{12}^{-5} \mid N'L'M'] = \lambda(-1)^{N'+L'+M'} R_{N+N'+1,L+L'+1,M+M'}, \tag{3.36}$$

$$[NLM \mid 3(x_{12}^2 - y_{12}^2)\, r_{12}^{-5} \mid N'L'M'] = \lambda(-1)^{N'+L'+M'} (R_{N+N'+2,L+L',M+M'} - R_{N+N',L+L'+2,M+M'}), \tag{3.37}$$

$$[NLM \mid (3z_{12}^2 - r_{12}^2)\, r_{12}^{-5} \mid N'L'M'] = \lambda(-1)^{N'+L'+M'} (2R_{N+N',L+L',M+M'+2} - R_{N+N'+2,L+L',M+M'} - R_{N+N',L+L'+2,M+M'})/3. \tag{3.38}$$

Integrals over these r_{12}^{-5} operators appear in calculation of spin–spin interaction matrix elements.

The space part of the two-electron spin–orbit operator has the form $r_{12}^{-3}\mathbf{r}_{12} \times \nabla_1$. The z component of this operator is then

$$r_{12}^{-3}\left(x_{12}\frac{\partial}{\partial y_1} - y_{12}\frac{\partial}{\partial x_1}\right).$$

Integration by parts yields a result similar to that obtained for the one-electron integral,

$$\left\langle \phi_I(1)\,\phi_K(2) \middle| r_{12}^{-3}\left(x_{12}\frac{\partial}{\partial y_1} - y_{12}\frac{\partial}{\partial x_1}\right) \middle| \phi_J(1)\,\phi_L(2) \right\rangle$$

$$= \left[\frac{\partial\phi_I}{\partial x_1}\frac{\partial\phi_J}{\partial y_1} - \frac{\partial\phi_I}{\partial y_1}\frac{\partial\phi_J}{\partial x_1} \middle| r_{12}^{-1} \middle| \phi_K\phi_L\right]. \tag{3.39}$$

Consequently, this integral is given simply as a sum over $[NLM \mid r_{12}^{-1} \mid N'L'M']$ using coefficients q_k for the IJ orbitals and D_k for the KL orbitals. Alternatively, of course, the integral could be written as a sum over integrals like $[NLM \mid x_{12}r_{12}^{-3} \mid N'L'M']$ with g_k coefficients for the IJ orbitals.

4. Auxiliary Functions

A. R_{NLM}

The function R_{NLM} is defined as

$$R_{NLM} = (\partial/\partial a)^N\,(\partial/\partial b)^L\,(\partial/\partial c)^M \int_0^1 e^{-Tu^2}\,du \tag{4.1}$$

where

$$T = \alpha(a^2 + b^2 + c^2). \tag{4.2}$$

By direct chain-rule differentiation an explicit formula for R can be found:

$$R_{NLM} = \sum_{n=0}^{[N/2]}\sum_{l=0}^{[L/2]}\sum_{m=0}^{[M/2]} a^{N-2n}b^{L-2l}c^{M-2m}$$
$$\times \frac{N!}{(2n)!!\,(N-2n)!}\,\frac{L!}{(2l)!!\,(L-2l)!}\,\frac{M!}{(2m)!!\,(M-2m)!}\,F_{N+L+M-n-l-m}.$$

For generating a table of all R_{NLM} up to some maximum $N + L + M$, as is needed in doing blocks of integrals, recursion relations are more useful. These can be found from introduction of the more general integral:

$$R_{NLMj} = (-\alpha^{1/2})^{N+L+M}\,(-2\alpha)^j \int_0^1 u^{N+L+M+2j}H_N(\alpha^{1/2}au)\,H_L(\alpha^{1/2}bu)\,H_M(\alpha^{1/2}cu)\,e^{-Tu^2}\,du.$$

Let us first note that

$$R_{000j} = (-2\alpha)^j\,F_j(T), \tag{4.4}$$

where

$$F_j(T) = \int_0^1 u^{2j} \exp(-Tu^2)\, du. \tag{4.5}$$

From the recursion relations for the Hermite polynomials, it follows that

$$R_{0,0,M+1,j} = cR_{0,0,M,j+1} + MR_{0,0,M-1,j+1}\,, \tag{4.6}$$

$$R_{0,L+1,M,j} = bR_{0,L,M,j+1} + LR_{0,L-1,M,j+1}\,, \tag{4.7}$$

$$R_{N+1,L,M,j} = aR_{N,L,M,j+1} + NR_{N-1,L,M,j+1}\,. \tag{4.8}$$

Thus the desired R_{NLM} (given as R_{NLM0}) can be generated from a table of $F_j(T)$ for all j between 0 and the maximum $N + L + M$.

B. F_j

Shavitt [2] has given several formulas useful for evaluating $F_j(T)$. Rapid and accurate evaluation of this function for a wide range of j and T requires some care, however. Our best program at present evaluates $F_j(T)$ by different formulas depending on T.

For $0 < T < 12$ and $0 \leqslant j \leqslant J$, $F_J(T)$ is first evaluated using the seven term Taylor expansion

$$F_J(T) = \sum_{k=0}^{6} F_{J+k}(T^*)(T^* - T)^k/k! \tag{4.9}$$

where $F_{J+k}(T^*)$ has been pretabulated for T^* at intervals of 0.1. With $|T^* - T| \leqslant 0.05$ this formula has a relative accuracy of 10^{-13} for all $J \leqslant 16$. The downward recursion relation

$$F_j(T) = [2TF_{j+1}(T) + \exp(-T)]/(2j + 1) \tag{4.10}$$

can then be used to obtain all $F_j(T)$.

For the range $12 < T < 30$ we note that

$$F_0(T) = \tfrac{1}{2}\pi^{1/2}/T^{1/2} - \int_1^\infty \exp(-Tu^2)\, du. \tag{4.11}$$

If the integral $\int_1^\infty \exp(-Tu^2)\, du$ is now expressed as $\exp(-T)\, g/T$, then $F_0(T)$ can be found with a relative accuracy of 10^{-14} from the modified asymptotic series for g: $12 < T < 15$

$$g = 0.4999489092 - 0.2473631686\, T^{-1} + 0.321180909\, T^{-2} - 0.3811559346\, T^{-3}; \tag{4.12}$$

$15 < T < 18$

$$g = 0.4998436875 - 0.24249438\, T^{-1} + 0.24642845\, T^{-2}; \tag{4.13}$$

$18 < T < 24$

$$g = 0.499093162 - 0.2152832\, T^{-1}; \tag{4.14}$$

$24 < T < 30$

$$g = 0.490. \tag{4.15}$$

Upward recursion, which is unstable for small T or large j, can be used to obtain $F_j(T)$ with a relative accuracy of 10^{-12} for $j \leqslant 16$ and $T \geqslant 12$.

For $T > 30$, $F_0(T) = \frac{1}{2}\pi^{1/2}/T^{1/2}$ combined with upward recursion is accurate to 14 significant figures. Finally, for $T > 2J + 36$ the exact upward recursion

$$F_{j+1}(T) = (2T)^{-1}[(2j+1)\, F_j(T) - \exp(-T)] \tag{4.16}$$

can be replaced by

$$F_{j+1}(T) = (2T)^{-1}(2j+1)\, F_j(T) \tag{4.17}$$

without loss of accuracy.

The series for g was derived from the definition

$$g = Te^{-T} \int_1^\infty du \exp(-Tu^2)$$

by the change of variable $\nu = 2T(u - 1)$ which gives

$$2g = \int_0^\infty d\nu \exp[-\nu(1 + \alpha\nu)]$$

with $\alpha = (4T)^{-1}$. Since decreasing accuracy in g is required as T increases, a Taylor's series expansion of g,

$$g = \sum (n!)^{-1}\, \partial^n g/\partial\alpha^n \,|_{\alpha^*} (\alpha - \alpha^*)^n,$$

was found with α^* corresponding to the smallest T in the interval. Truncation and rearrangement of this series gave 4.12 – 4.15. As is well known in the special case $\alpha^* = 0$, this is really an asymptotic series for g; but, for $| \alpha - \alpha^* |$ sufficiently small, the truncated series gives g to the accuracy required for finding $F_0(T)$ quite precisely.

5. Computational Considerations

The tractability of the two-electron integral formulas hinges upon doing all integrals involving four sets of basis functions concurrently, as all require the same R table. If the sets are large enough (say all four are p's) then the calculation of R requires only a small fraction of the total time. It then becomes important to perform the loops over basis functions and sums over contraction terms efficiently.

Table I shows one such scheme. A significant advantage is gained by forming the intermediate array I which allows the actual integral to be formed outside the sums over α_C and α_D. It is noteworthy that with only obvious minor modifications this scheme may be employed to calculate spin–spin and spin–orbit two-electron integrals.

TABLE I

Scheme for the Computation of All Two-Electron Repulsion Integrals over $[f_{iIA}]$, $[f_{jJB}]$, $[f_{gGC}]$, and $[f_{hHD}]$[a]

- Sum over α_A, α_B
    - Zero I
    - Sum over α_C, α_D
        - Compute $\lambda F_j(T)$
        - Compute λR_{nlm}
        - Loop over g, h
            - Sum over $(N', L', M')_{k'}$
                - Loop over $(N, L, M)_k$
                    - $I(k, g, h) = I(k, g, h) + (-1)^{N'+L'+M'} D_{k'}^{gh} R_{N+N', L+L', M+M'}$,
    - Loop over g, h
        - Loop over i, j
            - Sum over k
            - $X(i, j, g, h) = X(i, j, g, h) + D_k^{ij} I(k, g, h)$

[a] F_{iIA} denotes the ith member of set I on center A.

A program has been written employing the scheme in Table I for the repulsion integrals. Explicit formulas for the elements of I were added for certain s and p integrals. The computation time for a STO-3G set on hydrogen peroxide is 38.5 sec on a CDC 6400. Dupuis *et al.* [7] performing the same calculation on a CDC 6400, obtained times of 8.4 sec for GAUSSIAN 70; 39.9 sec for HONDO, a program of their own; and, 132.7 sec for PHANTOM 75, the most recent version of POLYATOM. Upon adding two sets of d functions to the STO-3G set we obtained a computation time of about 124.3 sec, somewhat less than HONDO's 152.2 sec and considerably less than PHANTOM's 775.6 sec.

It is obvious from these running times that GAUSSIAN 70 is clearly superior for integrals over s and p functions. There are three reasons for this superiority: (1) GAUSSIAN 70's integrals are accurate to only eight figures owing to a less accurate but faster calculation of $F_m(T)$; (2) a coordinate transformation is employed to maximize the local symmetry of the integral over primitive Gaussians, a distinct advantage for highly contracted basis sets [8]; and (3) s and p basis functions are combined into one set. GAUSSIAN 70 and HONDO, like our program, compute all integrals over four sets of basis functions (or "shells" in the terminology of Dupuis, Rys, and King) concurrently. Judging from the running times this structure has a clear advantage over the one-integral-at-a-time method of PHANTOM 75. Our method and the quadrature scheme employed by HONDO seem to be roughly equivalent, at least for s's and p's.

References

1. S. F. Boys, *Proc. Roy. Soc. Ser. A* **200** (1950), 542.
2. See, for example, I. Shavitt, *in* "Methods in Computational Physics" (B. Alder, S. Fernback, and M. Rotenberg, Eds.), Vol. 2, pp. 1–45, Academic Press, New York, 1963.
3. For a good review, see S. Huzinaga, *Supp. Prog. Theor. Phys.* **40**, 52 (1967).
4. J. L. Whitten, *J. Chem. Phys.* **39**, (1963), 349.
5. S. Huzinaga, *J. Chem. Phys.* **42** (1965), 1293; T. H. Dunning, Jr. and P. J. Hay, *in* "Modern Theoretical Chemistry" (H. F. Schaefer III, Ed.) Vol. 3; T. H. Dunning, *J. Chem. Phys.* **53** (1970, 2823; R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.* **52** (1970), 5001; W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.* **51** (1969), 2657.
6. Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.
7. M. Dupuis, J. Rys, and H. F. King, *J. Chem. Phys.* **65** (1976), 111.
8. J. A. Pople and W. J. Hehre, *J. Comput. Phys.*, in press.