

One and Two Electron Integrals over  
Cartesian Gaussian Functions

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Abstract

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.

## I. 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.<sup>1</sup> 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.<sup>2</sup> 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.<sup>3</sup> 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" ( $n+l+m=0$ ).<sup>4</sup> The resulting electron repulsion integral had been shown by Boys<sup>1,2,3</sup> 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.<sup>5</sup> Formulas for integrals over p-type Gaussians were easily derived<sup>2</sup> and programmed. Standard program packages such as POLYATOM<sup>6</sup> and GAUSSIAN 70<sup>6</sup> have been available for some time. Some versions of these packages have included d and

f orbitals. The formulas available for these integrals,<sup>2</sup> while completely general, do not allow systematic calculation of integrals for higher angular momentum. 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

## II. CHARGE DISTRIBUTIONS

An unnormalized Gaussian function on center A will be given by

$$\phi(n, \ell, m, \alpha_A, A) = x_A^n y_A^\ell z_A^m \exp(-\alpha_A r_A^2) \quad (2.1)$$

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

$$N_{n\ell m}(\alpha_A) = N_n(\alpha_A) N_\ell(\alpha_A) N_m(\alpha_A) \quad (2.2)$$

where

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

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

$$\bar{f}_{n\ell mA} = \sum_{\alpha_A} C^L(\alpha_A) N_{n\ell m}(\alpha_A) \phi(n, \ell, m, \alpha_A, A) \quad (2.4)$$

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

$$g_{LMA} = \sum_{\alpha_A} C^L(\alpha_A) \sum_{n\ell m} B_{n\ell m}^{LM} \phi(n, \ell, m, \alpha_A, A) \quad (2.5)$$

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

Efficient computation of integrals requires that  $f_{n\ell mA}$  or  $g_{LMA}$  which involve the same  $\alpha$ 's and 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 fifteen  $L=4$  functions as one set should be avoided.

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

$$\Omega_{IJ} = \phi_I \phi_J = x_A^{n_A} x_B^{\bar{n}_B} y_A^{\ell_A} y_B^{\bar{\ell}_B} z_A^{m_A} z_B^{\bar{m}_B} \exp[-(\alpha_A r_A^2 + \alpha_B r_B^2)] \quad (2.6)$$

The key to the utility of Gaussians is the well-known identity which transforms the above exponential to a single exponential about a center  $\underline{P}$  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

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

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

and

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

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

The products  $x_A^{n_A} x_B^{\bar{n}_B}$ ,  $y_A^{\ell_A} y_B^{\bar{\ell}_B}$ , and  $z_A^{m_A} z_B^{\bar{m}_B}$  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

$$\Lambda_j(x_P; \alpha_P) \exp(-\alpha_P x_P^2) = \left( \frac{\partial}{\partial P_x} \right)^j \exp(-\alpha_P x_P^2), \quad (2.15)$$

from which it follows that  $\Lambda_j$  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  $\Lambda$ 's is obvious - they will allow the charge distribution to be written as a sum of derivatives with respect to the coordinates of  $\underline{P}$  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  $\Lambda$ '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

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

Consequently

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

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

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

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

where

$$d_0^{00} = 1. \quad (2.22)$$

Similarly we can write

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

and

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

so that

$$\Omega_{IJ} = E_{IJ} \sum_{NLM} d_N^{n\bar{n}} e_L^{\ell\bar{\ell}} f_M^{m\bar{m}} \Lambda_N(x_P) \Lambda_L(y_P) \Lambda_M(z_P) \exp(-\alpha_P r_P^2) \quad (2.25)$$

It is often convenient to write  $\Omega_{IJ}$  as

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

where

$$D_k = E_{IJ} d_{N_k}^{n\bar{n}} e_{L_k}^{\ell\bar{\ell}} f_{M_k}^{m\bar{m}}. \quad (2.27)$$

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

$$D_k = E_{IJ} \sum_{n, \ell, m, \bar{n}, \bar{\ell}, \bar{m}} B_{n\ell m}^{\lambda\mu} B_{\bar{n}\bar{\ell}\bar{m}}^{\lambda\bar{\mu}} d_{N_k}^{n\bar{n}} e_{L_k}^{\ell\bar{\ell}} f_{M_k}^{m\bar{m}}, \quad (2.28)$$

In these equations  $k$  indexes all  $(N, L, M)$  combinations for which  $D$  is non-zero and the charge distribution is specified by a list of the non-zero  $D_k$  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

$$G_{IJ} = \phi_I \nabla \phi_J \quad (2.29)$$

$$T_{IJ} = \nabla \phi_I \cdot \nabla \phi_J \quad (2.30)$$

and

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

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

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

so that

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

with

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

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

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

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

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

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

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  $\phi$ 's of total powers of  $x$ ,  $y$ , and  $z$  higher by two than the starting ones. These highest powers cancel since

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

Consequently,

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

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.

### III. BASIC INTEGRALS

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

$$[NLM|\theta] = \int \theta(\underline{r}_1) \Lambda_N(x_{1P}; \alpha_P) \Lambda_L(y_{1P}; \alpha_P) \Lambda_M(z_{1P}; \alpha_P) \exp(-\alpha_P r_{1P}^2) d\tau_1 \quad (3.1)$$

Likewise the basic two-electron integrals all take the form

$$[NLM|\theta|NLM] = \int \theta(\underline{r}_1, \underline{r}_2) \Lambda_N(x_{1P}; \alpha_P) \Lambda_L(y_{1P}; \alpha_P) \Lambda_M(z_{1P}; \alpha_P) \exp(-\alpha_P r_{1P}^2) \Lambda_N(x_{2Q}; \alpha_Q) \Lambda_L(y_{2Q}; \alpha_Q) \Lambda_M(z_{2Q}; \alpha_Q) \exp(-\alpha_Q r_{2Q}^2) d\tau_1 d\tau_2 \quad (3.2)$$

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

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

(the  $\delta_{N,0}$  arises from the orthogonality of the Hermite polynomials).

Thus the overlap integral is simply

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

The relation

$$x_C \Lambda_N(x_P; \alpha_P) = N \Lambda_{N-1} + \frac{1}{2} \Lambda_{N+1} / \alpha_P + \overline{PC} x \Lambda_N \quad (3.5)$$

then gives

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

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

$$[\text{NLM}|x_c^2] = [2\delta_{N,2} + 2\overline{PC}_x \delta_{N,1} + (\overline{PC}_x^2 + \frac{1}{2}\alpha_P^{-1}) \delta_{N,0}] \delta_{L,0} \delta_{M,0} (\pi/\alpha_P)^{3/2} \quad (3.7)$$

and

$$[\text{NLM}|x_c y_c] = (\delta_{N,1} + \overline{PC}_x \delta_{N,0}) (\delta_{L,1} + \overline{PC}_y \delta_{L,0}) \delta_{M,0} (\pi/\alpha_P)^{3/2} \quad (3.8)$$

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  $[\text{NLM}|1]$ . 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  $[\text{NLM}|r_c^{-1}]$ . From the definition of the  $\Lambda$ 's, this may be written as

$$[\text{NLM}|r_c^{-1}] = (\partial/\partial P_x)^N (\partial/\partial P_y)^L (\partial/\partial P_z)^M [000|r_c^{-1}] \quad (3.9)$$

The integral  $[000|r_c^{-1}]$  was shown by Boys to be given by

$$[000|r_c^{-1}] = (2\pi/\alpha_P) F_0(T), \quad (3.10)$$

where

$$T = \alpha_P \overline{CP}^2, \quad (3.11)$$

and

$$F_0(T) = \int_0^1 \exp(-Tu^2) du. \quad (3.12)$$

If we define the auxiliary function  $R_{NLM}$  by

$$R_{NLM} = (\partial/\partial p_x)^N (\partial/\partial p_y)^L (\partial/\partial p_z)^M F_0(T) \quad (3.13)$$

then

$$[NLM|r_C^{-1}] = (2\pi/\alpha_p) R_{NLM}. \quad (3.14)$$

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

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

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

$$[NLM|x_C r_C^{-3}] = (\partial/\partial C_x) [NLM|r_C^{-1}] \quad (3.16)$$

But since  $T$  depends on  $C_x^{-1} p_x$ ,

$$(\partial/\partial C_x) g(T) = -(\partial/\partial p_x) g(T) \quad (3.17)$$

for any function  $g(T)$ .

Hence,

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

Alternatively this integral can be evaluated by noting that

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

Hence, by integration by parts,

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

But, from the definition of  $\Lambda_N$ ,

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

so

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

The components of the electric field gradient are similarly obtained using

$$(\partial^2/\partial x^2 - \partial^2/\partial y^2) r_C^{-1} = 3(x_C^2 - y_C^2) r_C^{-5} \quad (3.22)$$

$$(2\partial^2/\partial z^2 - \partial^2/\partial x^2 - \partial^2/\partial y^2) r_C^{-1} = 3(3z_C^2 - r_C^2) r_C^{-5} \quad (3.23)$$

and

$$(\partial^2/\partial x \partial y) r_C^{-1} = 3x_C y_C r_C^{-5} \quad (3.24)$$

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

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

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

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

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  $r_C^{-3} r_C \nabla^2$  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

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

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

C. Two electron integrals

The simplest integral in this category is the electron repulsion

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

Boys evaluated the basic integral as

$$[000|r_{12}^{-1}|000] = A P_0(T) \quad (3.30)$$

where

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

and

$$T = \alpha_P \alpha_Q (\alpha_P + \alpha_Q)^{-1} P^2 \quad (3.32)$$

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

$$(\partial/\partial Q_x)^N g(T) = (-\partial/\partial P_x)^N g(T) \quad (3.33)$$

for any function  $g(T)$ .

Hence

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

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

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

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

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

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

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  $r_{12}^{-3} \nabla_{12}$ . 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,

$$\begin{aligned} & \langle \phi_I(1)\phi_K(2) | r_{12}^{-3} \left( x_{12} \frac{\partial}{\partial y_1} - y_{12} \frac{\partial}{\partial x_1} \right) | \phi_J(1)\phi_L(2) \rangle \\ & = \left[ \frac{\partial \phi_I}{\partial x_1} \frac{\partial \phi_J}{\partial y_1} - \frac{\partial \phi_I}{\partial y_1} \frac{\partial \phi_J}{\partial x_1} \right] r_{12}^{-1} \langle \phi_K \phi_L \rangle \end{aligned} \quad (3.39)$$

Consequently, this integral is given simply as a sum over  $[NLM|r_{12}^{-1}|N'L'M']$  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  $[NLM|x_{12}r_{12}^{-3}|N'L'M']$  with  $g_k$  coefficients for the IJ orbitals.



IV. AUXILIARY FUNCTIONS

A.  $R_{NLM}$

The function  $R_{NLM}$  is defined as

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

where

$$T = \alpha(a^2 + b^2 + c^2) \quad (4.2)$$

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

$$R_{NLM} = \sum_{n=0}^{[N/2]} \sum_{l=0}^{[L/2]} \sum_{m=0}^{[M/2]} a^{N-2n} b^{L-2l} c^{M-2m} \frac{N!}{(2n)!!(N-2n)!} \frac{L!}{(2l)!!(L-2l)!} \frac{M!}{(2m)!!(M-2m)!} F_{N+L+M-n-l-m} \quad (4.3)$$

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:

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

Let us first note that

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

where

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

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

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

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

$$R_{N+1,L,M,j} = a R_{N,L,M,j+1} + N R_{N-1,L,M,j+1} \quad (4.8)$$

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<sup>2</sup> 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  $0 \leq j \leq J$ ,  $F_j(T)$  is first evaluated using the seven term Taylor expansion

$$F_j(T) = \sum_{k=0}^6 F_{j+k}(T^*) (T^*-T)^k / k! , \quad (4.9)$$

where  $F_{j+k}(T^*)$  has been pretabulated for  $T^*$  at intervals of 0.1.

The downwards recursive relation

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

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

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

$$F_0(T) = \frac{1}{2\sqrt{\pi}} \int_1^{\infty} \exp(-Tu^2) du . \quad (4.11)$$

If the integral  $\int_1^{\infty} \exp(-Tu^2) du$  is now expressed as  $\exp(-T)g/T$ , then  $g$  can be computed from

$12 < T < 15$

$$g = 0.4999489092 - 0.2473631686 T^{-1} + 0.321180909 T^{-2} - 0.3811559346 T^{-3} \quad (4.12)$$

15 < T < 18

$$g = 0.4998436875 - 0.24249438 T^{-1} + 0.24642845 T^{-2} \quad (4.13)$$

18 < T < 24

$$g = 0.499093162 - 0.2152832 T^{-1} \quad (4.14)$$

24 < T < 30

$$g = 0.490. \quad (4.15)$$

Upwards recursion, which is unstable for small T or large j, can be used to obtain  $F_j(T)$  with a relative accuracy of  $3 \times 10^{-12}$  for  $j \leq 16$  and  $T \geq 12$ .

For  $T > 30$ ,  $F_0(T) = \frac{1}{2}\sqrt{\pi}/\sqrt{T}$  combined with upwards recursion is accurate to fourteen significant figures. Finally, for  $T > 2J+35$  the exact upwards recursion

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

can be replaced by

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

without loss of accuracy.

## V. 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.

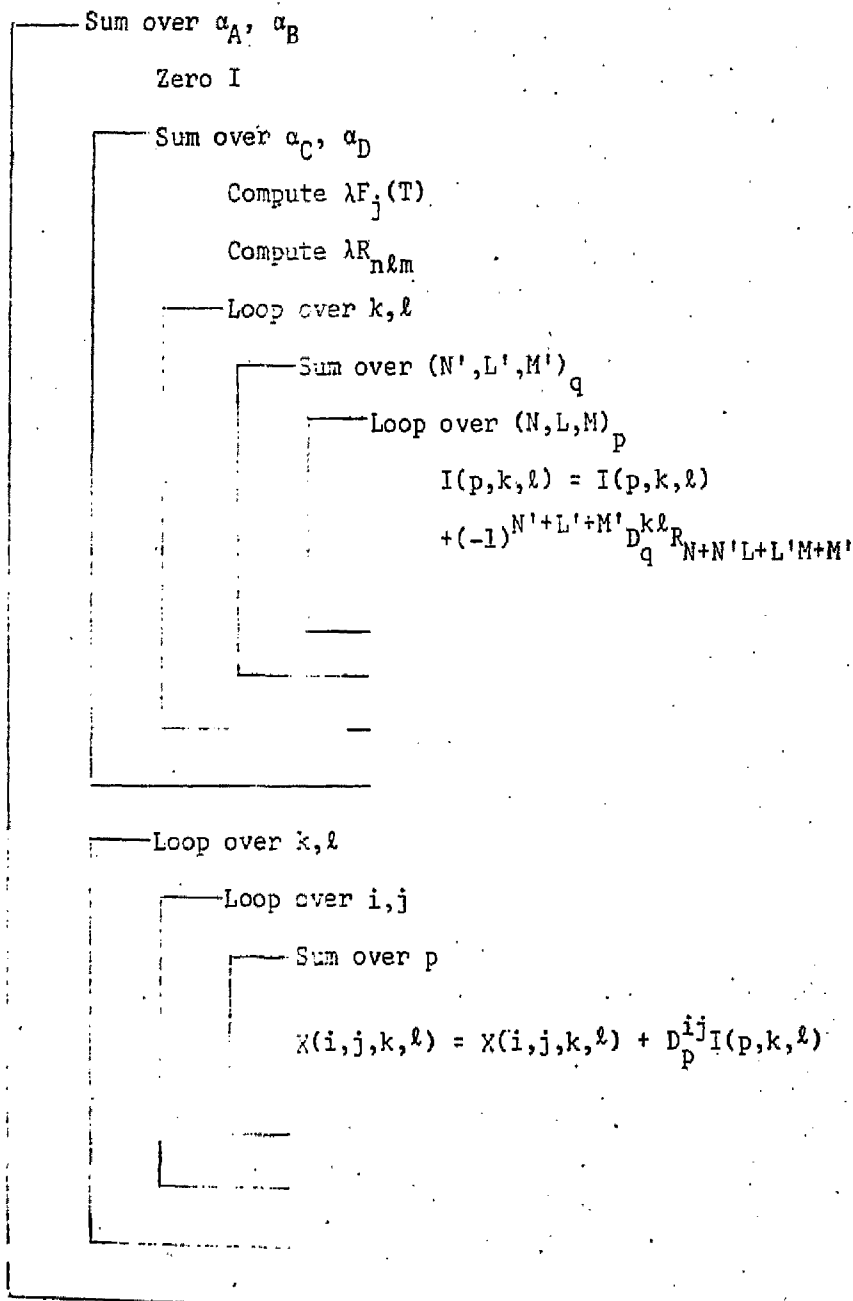
Table 1 shows one such scheme. A significant advantage is gained by forming the intermediate array I which allows the actual integral to be formed outside the sums over  $\alpha_C$  and  $\alpha_D$ . It is noteworthy that with only obvious minor modifications this scheme may be employed to calculate spin-spin and spin-orbit two electron integrals.

A program has been written employing the scheme in table 1 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, Rys, and King,<sup>7</sup> 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 8 figures owing to a less accurate but faster calculation of  $\Gamma_m(T)$ , (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,<sup>8</sup> 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.

Table 1. Scheme for the computation of all two electron repulsion integrals over  $[f_{iIA}]$ ,  $[f_{jJB}]$ ,  $[f_{kKC}]$ , and  $[f_{lLD}]$ .<sup>a</sup>



<sup>a</sup> $F_{iIA}$  denotes the  $i$ th member of set I on center A.

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