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ANALYTICAL METHODS USING SLATER-TYPE ORBITALS IN QUANTUM CHEMISTRY

Final Technical Report
Period: October 1, 1988 - November 30, 1991
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Our main concern is with the development of a Slater-type orbital (STO) multicenter molecular integral package for use with standard ab initio quantum chemistry codes such as the Columbus code and Alchemy. Significant advances have been made toward this goal.

A new strategy has been adopted: First program all molecular integrals in Mathematica (a computer algebra language that can give arbitrary precision with our alpha-function method); then, using assured accurate results as a guide, use FORTRAN to obtain speed and acceptable accuracy. We believe that this dual thrust will finally crack the "intractable" problem of STO multicenter integrals. Applications will soon be made to real molecules.

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Our main concern is with the development of a Slater-type orbital (STO) multicenter molecular integral package for use with standard ab initio quantum chemistry codes such as the Columbus code and Alchemy. Significant advances have been made toward this goal, as shown by the enclosed papers.

A new strategy has been adopted: First program all molecular integrals in *Mathematica* (a computer algebra language that can give arbitrary precision with our alpha-function method); then, using assured accurate results as a guide, use FORTRAN to obtain speed and acceptable accuracy. We believe that this dual thrust will finally crack the "intractable" problem of STO multicenter integrals. Applications will soon be made to real molecules.

PAPERS PUBLISHED AND WRITTEN

1. H.W. Jones, "Lowdin Alpha Function, Overlap Integrals, and Computer Algebra", Int. J. Quantum Chem. (1992).

2. H.W. Jones, "Benchmark Values for Two-Center Coulomb Integrals over Slater-Type Orbitals".

3. H.W. Jones, "Analytic Lowdin Alpha Function Method for Two-Center Electron Repulsion Integrals Over Slater-Tupe Orbitals", J. Computational Chemistry (December, 1991).

4. H.W. Jones, "Semi-Analytical Method for Four-Center Molecular Integrals over Slater-Type Orbitals", Int. J. Quantum Chem. (1992).

5. H.W. Jones and B. Eteamdi, "Multicenter Molecular Integrals Using Harmonic Expansions of Slater-Type Orbitals and Numerical Integrations", Int. J. Quantum Chem. Symp. **24**, 405 (1990).

6. H.W. Jones, "Analytical Method for Two- and Three-Center Molecular Integrals over Slater-Type Orbitals using Expansions in Spherical Harmonics".

Löwdin Alpha-Function, Overlap Integral, and Computer Algebra

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Abstract

A commerical computer algebra programme, *Mathematica*, is used to generate the C matrix that characterizes our implementation of the Löwdin alpha-function method as applied to Slater-type orbitals. An example of a two-center overlap integral is done to show how the arbitrary precision capability of *Mathematica* can overcome severe cancellation errors encountered with programming in FORTRAN. This strategy is capable of being generalized to other multicenter molecular integrals. *Mathematica* programmes are included.

Introduction

Efforts continue to be made to make Slater-type orbitals (STOs) a viable alternative to Gaussian-type orbitals (GTOs) when dealing with problems of ab initio chemistry [1]. The more physical nature of STOs should give advantages over GTOs when working in structural chemistry and in studies of reaction dynamics, and density functional theory [2]. Other investigators [3] have recently made considerable progress in this essentially multicenter molecular integral problem.

In this paper, we will initiate a new line of action that takes advantage of the availability of commerical computer algebra programmes of evolving power and flexibility. We will repeat our work on the Löwdin alpha-function and, by an example, show how overlap integrals may be computed to arbitrary accuracy.

The Alpha-Function and C, E, and F Matrices

The Löwdin α-function method expands displaced orbitals in an infinite series of spherical harmonics about a single-center (the origin) before the required integration is attempted [4]. The functional coefficients of the spherical harmonics are designated as α-functions. We take a displaced STO to be centered at $(0,0,a)$ in its local coordinate system (R, Θ, ϕ), and write it in terms of the original coordinate system (r, θ, ϕ) [5,6]. Thus,

$$\chi = AR^{N-1}\, e^{-\zeta R}\, Y_L^M(\Theta, \phi),$$

$$\chi = \frac{A}{\zeta^{N-1}} \left[\frac{(2L+1)(L+M)!}{4\pi(L-M)!} \right]^{1/2} \sum_{\ell=M}^{\infty} \left[\frac{4\pi(\ell+M)!}{(2\ell+1)(\ell-M)!} \right]^{1/2} (-1)^M$$

$$\times\; \alpha_\ell^{NLM}(\zeta a, \zeta r)\, Y_\ell^M(\theta, \phi),$$

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where

$$\alpha_\ell^{NLM}(\zeta a, \zeta r) = \frac{(2\ell+1)(\ell+M)!}{2(\ell+M)!} \sum_{i=0}^{N+L+\ell} \sum_{j=0}^{N+\ell} C_\ell^{NLM}(i,j)$$

$$\times \; H_{ij} \; (\zeta a)^{i-L-\ell-1} \; (\zeta r)^{j-\ell-1}$$

and

$$H_{ij} = \begin{cases} e^{-\zeta a}\,[(-1)^j\,e^{\zeta r} - e^{-\zeta r}] & , \; r<a \\[12pt] e^{-\zeta r}\,[(-1)^i\,e^{\zeta a} - e^{-\zeta a}] & , \; r>a. \end{cases}$$

$A = (2\zeta)^{N+1/2}\,[(2N)!]^{-1/2}$ is the normalization factor, N, L, and M are the quantum numbers of the orbital, and ζ is the screening constant or orbital exponent. For convenience we will now set $a = \xi' a$ ~~~~~ $b = \xi a$, and $r = \xi r$

Most importantly for our developments the elements of the C matrix are integers. Originally, it was obtained by programming the following expression, using FORTRAN and a simple in-house version of computer algebra [7]:

$$\sum_{i=0} \sum_{j=0} C_\ell^{NLM}(i,j)\,a^i\,r^j = \sum_{p=0}^{[(L+M)/2]} \sum_{q=0}^{L+M-2p} \sum_{v=0}^{L+M-2p-q}$$

$$\times \; \sum_{p'=0}^{[(\ell-M)/2]} \sum_{q'=0}^{\ell-M-2p'} \sum_{v'=0}^{\ell-M-2p'-q'} \sum_{k=0}^{t} \sum_{k'=0}^{t-k}$$

$$\times \; \frac{a^x\,r^y\,(-1)^{v+q'+p+p'+L}\,(2L-2p)!\,(2\ell-2p')!}{4^{L+\ell+p-p'}\,(L-p)!\,p!\,p'!\,q!\,q'!\,v!\,v'!\,(L+M-2p-q-v)!}$$

$$\times \; \frac{(N-L+2p+2q+2q')!}{(\ell-p')!\,(\ell-M-2p'-q'-v')!\,k'!\,(N-L+2p+2q+2q'-k-k')!} \; ,$$

where

$$x = N + L + 2\ell - 2p' - 2v' - 2v - k - k',$$

$$y = 2p' + 2v + 2v' + k',$$

and

$$t = N - L + 2p + 2q + 2q'$$

In Table I we use the programming language *Mathematica* [8] to generate the polynomial in a and r for the zeroth harmonic ($\ell = 0$) for the 2p orbital (N=2, L=1, M=0). (For our example, we multiply by $(-1)^L$ so that the positive lobe will face toward the origin [9]). This being accomplished, the next line selects the coefficients of the polynomial to obtain the C matrix, whose elements are given by C [[i+1, j+1]] which corresponds to our form C_0^{210} (i,j). Our programming notation conforms to *Mathematica* protocol and is chosen for ease in typing. Thus, N=nn, L=hh, M=mm, ℓ=h, p'=pp, q'=qp, v'=vp, k'=kp. Floor [ ] means reduce to integer. The curly brackets represent the eight summations and their limits. One of the great advantages of *Mathematica* is that its high level language is remarkably analogous to standard mathematical notation.

Now that we have obtained the C matrix, we will next generate the E matrix [10], which is a matrix of coefficients of the expansion of the α-function in a Taylor series about r=0, that is, for the case r<a. In Table II we use two lines to type in the definitions of the α-function, alpha. The *Mathematica* command Series [ ] expands alpha in a Taylor series about r=0 to r^5. We again collect these coefficients and print out the E matrix, e = E_0^{210} (i,j). The F matrix may be obtained by expanding the α-function for r>a in terms of a, in a similar manner.

($\alpha^{-L-\ell-1}$ has been omitted).

(The factor $e^{-a/2 L+\ell+1}$ has been removed/omitted)

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Overlap Integral

We will find the value of an overlap integral given by Bhattacharrya and Dhabal [11]. However, for convenience, our value will be positive to conform to the convention of Mulliken, et al. [9]. The definition of the overlap integral is

$$S = \int \chi_a^* \; \chi_b \, dv \quad \text{where}$$

$\chi_a = A_a \, r^{N'-1} \, e^{-\zeta' r} \, Y_{L'}^M(\theta, \phi)$, and for the displaced orbital $\chi_b = A_b \, R^{N-1} \, e^{-\zeta R} Y_L^M(\theta, \phi)$.

Expanding χ_b, and invoking the orthogonality of spherical harmonics, and performing the radial integration we get [12]

$$S = K \left(\frac{\zeta'}{\zeta}\right)^{N'+1/2} \sum_{i=0}^{N+L+L'} \sum_{j=0}^{N+L'} n! C_{L'}^{NLM}(i,j)(\zeta a)^{N'-2L'-L+i+j}$$

$$\times \left[e^{-\zeta a}\left(\frac{(-1)^i}{[a(\zeta'-\zeta)]^{n+1}} - \frac{1}{[a(\zeta'+\zeta)]^{n+1}}\right) \right.$$

$$\left. + e^{-\zeta' a} \sum_{k=0}^{n} \frac{1}{(n-k)!}\left(\frac{(-1)^i}{[a(\zeta'+\zeta)]^{k+1}} - \frac{(-1)^i}{[a(\zeta'-\zeta)]^{k+1}}\right)\right],$$

where

$$n = N' - L' + j$$

and

$$K = 2^{N'+N}(-1)^M \left(\frac{(2L+1)(2L'+1)(L+M)!(L'-M)!}{(2N')!(2N)!(L'+M)!(L-M)!}\right)^{1/2}.$$

Table III shows the programming of the overlap formula. We have set N' = nnp, L' = hhp, K = kk. For clarity, the overlap formula is assembled from parts to get, S = overlap. To compare with the literature [11], we set ζ' = 10, and ζ = 2, and the distance between orbits as 1.4. Then we let a = ζ'(1.4) = 14, b = ζ(1.4) = 2.8 = 2(14/10). *Mathematica* can give arbitrary precision for arithmetic operations if it

is given numbers as the ratio of integers. This applies also to roots and exponentiations. The operation N[overlap, 20] means for *Mathematica* to try and get 20 significant figures using the overlap formula. This it succeeds in doing as confirmed by Bhattacharya and Dhabal [11]. With the command N[overlap, 30] we request 30 digits, and get 29.

A more revealing set of parameters for this problem is a = 102/100 and b = 101/100. Now cancellation errors become evident. Thus N[overlap, 20] yields 0.4338568005, which is only 10 digits. *Mathematica* trys not to return worthless digits. The loss, we suspect, must be due to cancellation errors. This becomes obvious if the positive parts and the negative parts of the overlap formula are programmed separately for 20 digits. Then

overlap = 921614991.7515037098 - 921614991.3176469093 = .4338568005.

We may obtain 20 digits using the command N[overlap, 30], which gives

.43385680048834139559.

Hence, by the simple expedient of changing the number of digits requested we may obtain arbitrary precision. *Mathematica* can easily deal with large numbers of digits, so that any physical system can be computed. (The exceptional case of ζ = ζ' (a = b) can be programmed separately from a simpler overlap formula [13]).

Conclusion

Recent investigators [11, 14, 15] working with overlap integrals have found that more than one formulation is needed in order to cover the range of useful parameter values and avoid intolerable cancellation errors. This is necesary when using programmes that utilize a finite computer word length. In this paper, it has been shown that by use of a variable word length, it is possible to absorb cancellation errors and still work to a specified accuracy.

We have employed an Apple Macintosh IIx computer using the 1.2 version of *Mathematica*. Benchmark values for overlap integrals have been achieved (in a

few seconds). Other multicenter molecular integrals are under investigation. The general usefulness of our methods for integral packages depends on newer and faster versions of computer algebra schemes and the employment of mainframes or workstations.

Acknowledgment

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```
nn=2;hh=1;mm=0;h=0;

cpolynomial=Sum[a^ (nn+hh+2h-2pp-2vp-2v-k-kp) *
          r^ (2pp+2v+2vp+kp) * (-1) ^ (v+qp+p+pp+hh) * (-1) ^hh*
          (2hh-2p) ! * (2h-2pp) ! /4^ (hh+h-p-pp) / ( (hh-p) ! *
          p! *pp ! *q! *qp ! *v! *vp! * (hh+mm-2p-q-v) ! ) *
          (nn-hh+2p+2q+2qp) ! / ( (h-pp) ! * (h-mm-2pp-qp-vp) ! *
          kp! * (nn-hh+2p+2q+2qp-k-kp) ! ),
          {p, 0, Floor [ (hh+mm) / 2] } , {q, 0, hh+mm-2p} ,
          {v, 0, hh+mm-2p-q} , {pp, 0, Floor [ (h-mm) / 2] } ,
          {qp, 0, h-mm-2pp} , {vp, 0, h-mm-2pp-qp} ,
          {k, 0, nn-hh+2p+2q+2qp} ,
          {kp, 0, nn-hh+2p+2q+2qp-k} ]
```

$$3 + 3\,a + 2\,a^2 + a^3 + 3\,r + 3\,a\,r + 2\,a^2\,r + r^2 + a\,r^2$$

```
cmatrix=CoefficientList [cpolynomial, {a,r} ];

c=cmatrix;


MatrixForm [c]
```

3	3	1
3	3	1
2	2	0
1	0	0

Table I. Generation of the zeroth harmonic of the C matrix for the 2p orbital
starting with the C matrix polynomial.

```
alpha=Sum [c [ [i+1, j+1 ] ] * ( (-1) ^ j*Exp [r] - Exp [-r] ) * a^i*
            r^ (j-h-1) , {i, 0, nn+hh+h} , {j, 0, nn+h} ] ;
```

```
alpha=(2h+1) * (h-mm) ! / (2* (h+mm) ! ) *alpha ;
```

```
alphae=Series [alpha, {r,0,5} ] ;
```

```
e=CoefficientList [alphae, {r,a} ] ;
```

```
MatrixForm [e]
```

0	0	0	1
0	0	0	0
0	0	-2/3	1/6
0	0	0	0
1/15	1/15	-1/15	1/120

Table II. Generation of the zeroth harmonic of the E matrix for the 2p orbital. The alpha function polynomial is expanded in a Taylor series in r, and the coefficients are collected in matrix form.

```
nnp=1; hhp=0;

a=14; b=2* (14/10) ;

kk=2^ (nnp+nn) * (-1) ^mm*Sqrt [ (2hh+1) * (2hhp+1) * (hh+mm) ! *
    (hhp-mm) ! / ((2nnp) ! * (2nn) ! * (hhp+mm) ! * (hh-mm) ! ) ]

s1=Sum [ (nnp-hhp+j) ! *c [ [i+1, j+1]] *b^ (nnp-2hhp-hh+i+j) *
    ((-1) ^j / (a-b) ^ (nnp-hhp+j+1) -1 / (a+b) ^ (nnp-hhp+j+1)) ,
    {i, 0, nn+hh+hhp} , {j, 0, nn+hhp} ] ;

s2=Sum [(nnp-hhp+j) ! *c [[i+1, j+1]] *b^ (nnp-2hhp-hh+i+j) /
    (nnp-hhp+j-k) ! * ((-1) ^ i / (a+b) ^ (k+1) - (-1) ^j / (a-b) ^ (k+1)) ,
    {i, 0, nn+hh+hhp} , {j, 0, nn+hhp} , {k, 0, nn-hhp+j} ] ;

s12=Exp [-b] * s1+Exp [-a] *s2

overlap=kk* (a/b) ^ (nnp+1/2) * s12 ;

N [overlap, 20]

0.11741378968662828485

N [overlap, 30]

0.11741378968662828485490731401
```

(arrow annotation pointing to `nn-hhp+j`): ? → nnp

Table III. The implementation of the overlap formula to find S(1s, 2p). The 1s
orbital has a screening constant of 10, and the 2p orbital has a
screening constant of 2. The orbitals have a 1.4 unit separation.
Mathematica is requested to produce a 20 digit result and a 30 digit
result.

Benchmark values for two-center Coulomb integrals over Slater-type orbitals

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Abstract

The Löwdin alpha-function method, in which displaced orbitals are expanded in an infinite series of spherical harmonics, is implemented for Slater-type orbitals using a commerical computer algebra program, *Mathematica*. The program, which is included, generates a C matrix with integer elements that characterizes our approach to multicenter molecular integrals. The general two-center, two-electron Coulomb repulsion integral is produced analytically with a finite number of terms. Each Coulomb formula may be evaluated to arbitrary precision, since *Mathematica* works with integer arithmetic. Hence, cancellation errors can be overcome.

Introduction

The difficulties of working with Slater-type orbitals (STOs) when doing variational treatments of molecules are proverbial [1]. Nevertheless, progress continues to be made [2]. The hope is that the integrals resulting from use of STOs will be efficiently done so that their good physical characteristics can be utilized.

In this paper, two-center, two-electron repulsion integrals of the Coulomb type will be evaluated to specified accuracy by use of a commerical computer algebra program called *Mathematica* [3]. Our method is that of the Löwdin alpha-function [4], in which displaced orbitals are expanded in an infinite series of spherical harmonics with functional coefficients (alpha-functions). By use of an in-house version of computer algebra we have been able to characterize each STO by a C matrix [5]. The fact that these matrix elements are integers is the key to our being able to take advantage of the high level language and power of *Mathematica*.

We have already shown [6] how *Mathematica* can generate a C matrix for each displaced STO and how a formula for overlap integals can be evaluated to arbitrary accuracy. The more difficult Coulomb problem involves the integration over two electrons and thereby casts light on how all multicenter molecular integrals may be done.

The Alpha-function and C matrix

The Löwdin α-function method expands displaced orbitals in an infinite series of spherical harmonics about a single center (the origin) before the required integration is attempted [4]. The functional coefficients of the spherical harmonics are designated as α-functions. We take a displaced STO to be centered at $(0,0,a)$ in its local coordinate system (R, Θ, ϕ), and write it in terms of the original coorinate system (r, θ, ϕ) [5,7]. Thus,

$$\chi = AR^{N-1} e^{-\zeta R} Y_L^M(\Theta, \phi),$$

$$\chi = \frac{A}{\zeta^{N-1}} \left[\frac{(2L+1)(L+M)!}{4\pi(L-M)!} \right]^{\frac{1}{2}} \sum_{\ell=M}^{\infty} \left[\frac{4\pi(\ell+M)!}{(2\ell+1)(\ell-M)!} \right]^{\frac{1}{2}} (-1)^M$$

$$\times \ \alpha_\ell^{NLM}(\zeta a, \zeta r) Y_\ell^M(\theta, \phi),$$

where

$$\alpha_\ell^{NLM}(\zeta a, \zeta r) = \frac{(2\ell+1)(\ell+M)!}{2(\ell+M)!} \sum_{i=0}^{N+L+\ell} \sum_{j=0}^{N+\ell} C_\ell^{NLM}(i,j)$$

$$\times \ H_{ij}(\zeta a)^{i-L-\ell-1}(\zeta r)^{j-\ell-1}$$

and

$$H_{ij} = \begin{cases} e^{-\zeta a} \ [(-1)^j \ e^{\zeta r} - e^{-\zeta r}] \ , \ r < a \\ e^{-\zeta r} \ [(-1)^i \ e^{\zeta a} - e^{-\zeta a}] \ , \ r > a \end{cases}$$

$A = (2\zeta)^{N+1/2} \ [(2N)!]^{-1/2}$ is the normalization factor, N, L, and M are the quantum numbers of the orbital, and ζ is the screening constant or orbital exponent.

Most importantly for our developments the elements of the C matrix are integers. Originally, they were obtained by programming the following expression, using FORTRAN and a simple in-house version of computer algebra [5,7]:

$$\sum_{i=0} \sum_{j=0} C_\ell^{NLM}(i,j) a^i r^j = \sum_{p=0}^{[(L+M)/2]} \sum_{q=0}^{L+M-2p} \sum_{v=0}^{L+M-2p-q}$$

$$\times \sum_{p'=0}^{[(\ell-M)/2]} \sum_{q'=0}^{\ell-M-2p'} \sum_{v'=0}^{\ell-M-2p'-q'} \sum_{k=0}^{t} \sum_{k'=0}^{t-k}$$

$$\times \frac{a^x r^y (-1)^{v+q'+p+p'+L} (2L-2p)! \, (2\ell-2p)!}{4^{L+\ell+p-p'|}(L-p)! \, p! \, p'! \, q! \, q'! \, v! \, v'! \, (L+M-2p-q-v)!}$$

$$\times \frac{(N-L+2p+2q+2q')!}{(\ell-p')! \, (\ell-M-2p'-q'-v')! \, (N-L+2p+2q+2q'-k-k')!}$$

where

$$x = N + L + 2\ell - 2p' - 2v' - 2v - k - k',$$

$$y = 2p' + 2v + 2v' + k'.$$

and

$$t = N - L + 2p + 2q + 2q'$$

Coulomb Integral

The definition [8] of the Coulomb two-center, two-electron repulsion integral is

$$J = \iint \chi_a^*(1) \, \chi_b(1) \, r_{12}^{-1} \, \chi_c(2) \, \chi_d^*(2) \, dv_1 \, dv_2$$

We superimpose $\chi_a(1)$ and $\chi_b(1)$ at the origin, and $\chi_c(2)$ and $\chi_d(2)$ at a distance of a along the z axis $(0, 0, a)$. The superimposed orbitals may be merged

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and expressed as a linear sum of orbitals upon expanding the spherical harmonics.

The Coulomb integral may be written as

$$J = \int \chi_c(2) \; \chi_d^*(2) \; V(\vec{r}_2) \; dv_2$$

with the potential given as

$$V(\vec{r}_2) = \int \chi_a^*(1) \; \chi_b(1) \, / \, r_{12} \; dv_1.$$

The Laplace expression of r_{12}^{-1} is

$$\frac{1}{r_{12}} = \sum_{\ell=0}^{\infty} \; \sum_{\mu=-\ell}^{\ell} \; \frac{4\pi}{2\ell+1} \; \frac{r_<^\ell}{r_>^{\ell+1}} \; Y_\ell^\mu(\theta_1, \varphi_1) \, Y_\ell^{\mu *}(\theta_2, \varphi_2),$$

where $r_<$ is the smaller of r_1, r_2 and $r_>$ is the larger.

Using orthogonality of spherical harmonics, the potential may be determined. In our developments, in order to avoid having to distinguish between real STOs and complex STOs, and to facilitate comparisons with the literature, only the case of orbitals with magnetic quantum M=0 will be considered. This is a mild restriction easily removed once the chief problem of dealing with radial integrals is worked out. Thus the potential becomes [8]

$$V(r_2, \theta_2) = k_1 \; \sum \langle L_a, L_b, \ell \rangle \; V_\ell \, (r_2) \; P_\ell(\theta_2),$$

where

$$V_\ell(r_2) = \left\{ \frac{1}{r_2^{\ell+1}} \int_0^{r_2} dr_1 \, r_1^n \, e^{-\omega r_1} + r_2^\ell \int_{r_2}^\infty dr_1 \, r_1^m e^{-\omega r_1} \right\},$$

with $\langle L_a, L_b, \ell \rangle = \int P_{L_a}(\theta) \, P_{L_b}(\theta) \, P_\ell(\theta) \sin\theta \, d\theta$, representing the Gaunt coefficients, with $\omega = \zeta_a + \zeta_b$, $n = N_a + N_b + \ell$, $m = N_a + N_b - \ell - 1$, $k_1 = A_a A_b \left[(2L_a + 1)(2L_b + 1) \right]^{1/2} / 2$. Note that $Y_\ell^0(\theta, \varphi) = \sqrt{\frac{2\ell+1}{4\pi}} P_\ell(\theta)$.

We perform the indicated integration to get

$$V_\ell(r_2) = \frac{1}{r_2^{\ell+1}} \left[\frac{n!}{\omega^{n+1}} - e^{-\omega r_2} \sum_{k=0}^n \frac{n!}{(n-k)!} \frac{r_2^{n-k}}{\omega^{k+1}} \right]$$

$$+ r_2^\ell e^{-\omega r_2} \sum_{k=0}^m \frac{m!}{(m-k)!} \frac{r_2^{m-k}}{\omega^{k+1}}$$

The electron charge density for electron 2 becomes

$$\chi_c(2) \, \chi_d^*(2) = \frac{k_2}{2\pi} R_2^{N-1} e^{-\zeta R_2} \sum_L \frac{(2L+1)}{2} \langle L_c, L_d, L \rangle P_L(\Theta_2)$$

with $k_2 = A_c A_d \left[(2L_c + 1)(2L_d + 1) \right]^{1/2} / 2$, $N = N_c + N_d - 1$, $\zeta = \zeta_c + \zeta_d$.

Noting the α-function expansion

$$R_2^{N-1} e^{-\zeta R_2} P_L(\Theta_2) = \frac{1}{\zeta^{N-1}} \sum_{\ell_L} \alpha_{\ell_L}^L P_{\ell_L}(\theta_2)$$

and taking into account orthogonality ($\ell_L = \ell$) we finally get [9]

$$J = \frac{k_1 k_2}{\zeta^{N-1}} \sum_L \sum_\ell \frac{(2L+1)}{(2\ell+1)} \langle L_c, L_d, L \rangle \langle L_a, L_b, \ell \rangle \int r^2 \, dr \, V_\ell \, \alpha_\ell^L.$$

6

The sums over L and ℓ are limited because of the triangular rule for the Gaunt coefficients.

For convenience, we divide the integral into three parts corresponding to the three terms of the potential [10].

Let $i_1 + i_2 + i_3 = \int r^2 \, dr \, V_\ell \, \alpha_\ell$. Thus,

$$i_1 = \sum_{i=0}^{N+L+\ell} \sum_{j=0}^{N+\ell} \frac{n!}{\omega^{n+1}} \; a^i \; \zeta^{i+j} \; C_\ell(i,j)$$

$$\times \left\{ (-1)^j \, e^{-\zeta a} \int_0^a dr \; r^{j-2\ell} \, e^{\zeta r} + (-1)^i \, e^{\zeta a} \int_a^\infty dr \; r^{j-2\ell} e^{-\zeta r} - e^{-\zeta a} \int_0^\infty dr \; r^{j-2\ell} e^{-\zeta r} \right\}$$

$$i_2 = \sum_i \sum_j \sum_{k=0}^{n} \frac{n!}{(n-k)!} \; a^i \; \zeta^{i+j} \; C_\ell(i,j)$$

$$\times \left\{ -(-1)^j \, e^{-\zeta a} \int_0^a dr \; r^{j-2\ell+n-k} \, e^{-(\omega-\zeta)r} - (-1)^i \, e^{\zeta a} \int_a^\infty dr \; r^{j-2\ell+n-k} \, e^{-(\omega+\zeta)r} \right.$$

$$\left. + e^{\zeta a} \int_0^\infty dr \; r^{j-2\ell+n-k} \, e^{-(\omega+\zeta)r} \right\}$$

$$i_3 = \sum_i \sum_j \sum_{k=o}^{m} \frac{m!}{(m-k)!} \; a^i \zeta^{i+j} \; C_\ell(i,j)$$

$$\times \left\{ (-1)^j \, e^{-\zeta a} \int_0^a dr \; r^{j+1+m-k} \, e^{-(\omega-\zeta)r} + (-1)^i \, e^{\zeta a} \int_a^\infty dr \; r^{j+1+m-k} \, e^{-(\omega-\zeta)r} \right.$$

$$\left. - e^{-\zeta a} \int_0^\infty dr \; r^{j+1+m-k} \, e^{-(\omega+\zeta)r} \right\}$$

Each term of the summation over ℓ and L is given by

$$\iota_{123} = (i_1 + i_2 + i_3)\,\frac{(2L+1)}{2}\,\langle L_a, L_b, \ell \rangle \langle L_c, L_d, L \rangle\,\frac{k_1 k_2}{\zeta^{N-1}}$$

$$\times\,\frac{1}{\zeta^{L+2\ell+2}\,a^{L+\ell+1}},$$

the $(2\ell+1)$ factor having been cancelled.

Basic integrals

To carry out the analytical evaluation of the Coulomb integral, the following basic formulas are used [11] (we have replaced the zero on the integrals by the infinitessimal ε).

$$g1(n,a) = \int_\varepsilon^a dr\; r^n = \frac{a^{n+1}}{n+1} - \frac{\varepsilon^{n+1}}{n+1}, \quad n \neq -1;$$

$$g1(n,a) = \ell na - \ell n\varepsilon, \quad n = -1$$

$$f1(n,a,b) = \int_\varepsilon^a dr\; r^n\, e^{-br}$$

$$f1(n,a,b) = -\frac{e^{-ba}}{b^{n+1}} \sum_{t=0}^{n} \frac{n!}{(n-t)!}\,(ba)^{n-t} + \frac{n!}{b^{n+1}}, \quad n \geq 0;$$

$$f1(n,a,b) = -(-b)^{-n-1} e^{-ba} \sum_{t=1}^{-n-1} \frac{(-n-t-1)!}{(-n-1)!}\,\frac{1}{(-ba)^{-n-t}} + \frac{(-b)^{-n-1}}{(-n-1)!}\,\mathrm{Ei}(-ba)$$

$$+ (-b)^{-n-1} \sum_{t=1}^{-n-1} \frac{(-n-t-1)!}{(n-1)!(-n-t)!} - \frac{(-b)^{-n-1}}{(-n-1)!}\,\big[\ell n|b| + \gamma + \ell n\varepsilon\big], \quad n < -1;$$

$$f1(n,a,b) = \mathrm{Ei}(-ba) - \big[\ell n|b| + \gamma + \ell n\varepsilon\big], \quad n = -1.$$

To obtain the ε limit, $e^{-b\varepsilon}$ has been expanded and all powers of ε, except ε^0, have been dropped [12]. From physical considerations, all inverse powers of ε and $\ell n\,\varepsilon$ must cancel, if all parts of the program are considered. The other needed integrals are:

$$f2(n,a,b) = \int_a^{\infty} dr\ r^n\ e^{-br}$$

$$f2(n,a,b) = -\frac{e^{-ba}}{b^{n+1}} \sum_{t=0}^{n} \frac{n!}{(n-t)!}\ (ba)^{n-t}\quad ,\quad n \geq 0;$$

$$f2(n,a,b) = (-b)^{-n-1}\ e^{-ba} \sum_{t=1}^{-n-1} \frac{(-n-t-1)!}{(-n-1)!}\ \frac{1}{(-ba)^{-n-t}} - \frac{(-b)^{-n-1}}{(-n-1)!}\ Ei(-ba),\ n < -1;$$

$$f2(n,a,b) = -Ei(-ba)\ ,\quad n = -1.$$

$$f3(n,b) = \int_{\varepsilon}^{\infty} dr\ r^n\ e^{-br}\ = \frac{n!}{b^{n+1}},\quad n \geq 0;$$

$$f3(n,b) = \sum_{t=1}^{-n-1} \frac{(-n-t-1)!}{(-n-1)!\,(-n-t)!}\ (-b)^{-n-1} - \frac{(-b)^{-n-1}}{(-n-1)!}\ \left[\ell n|b| + \gamma + \ell n\varepsilon\right],\quad n < 1;$$

$$f3(n,b) = -\left[\ell n|b| + \gamma + \ell n\varepsilon\right],\quad n = -1.$$

For the case of Coulomb integrals [10,13] we may drop all Ei and logarithm terms. Also, Euler's constant γ does not appear. Hence, our *Mathematica* progam does not include these terms.

Programming of the Coulomb integral

Mathematica is a high level language that has a remarkably close correspondence to standard mathematical notation. Thus

$$\sum_{i=imin}^{imax} \sum_{j=jmin}^{jmax} (\text{expression}) = \text{Sum}\left[\text{expression}, \{i, imin, imax, j, jmin, jmax\}\right]$$

$$\int_{xmin}^{xmax} f(x) dx = \text{Integrate}\left[f(x), \{x, xmin, xmax\}\right]$$

For added flexibility for iteration we may use Do-loops:

$$\text{Do}\left[\text{Do}[\text{equations}, \{i, imin, imax\}, \{j, jmin, jmax\}]\right].$$

It is convenient to use a Which statement that defines a function for various parameter values:

$$f[n\_, x\_]: = \text{Which}[\text{test 1, function 1, test 2, function 2, True, function 3}].$$

In this case, if test 1 and test 2 are unsatified, function 3 is selected.

After running the program of Table I, for the case of all 1s orbitals with equal screening constants ($\zeta_a = \zeta_b = \zeta_c = \zeta_d = 1$, w = ζ = 2, typing "coulomb" produces Roothaan's [13] formula ($2\rho = \zeta a = 2a$). Typing a = 1/100 and N[coulomb, 20] produces 0.62499166683332546. Typing N[coulomb,30] produces 0.624991666333325460009943731. Although we have requested 20 digits and 30 digits we get 17 and 27 digits computed. This is because of cancellation errors caused by the differencing of nearly equal numbers. *Mathematica* trys not to produce worthless numbers.

To conform to *Mathematica* protocol and for clarity in typing the following notation is used:

N_a = nna, L_a = hha, ζ_a = alpha; N_b = nnb, L_b = hhb, ζ_b = beta; M = mm; A_a = aa, A_b = ab, A_c = ac, A_d = ad; L = hh, ℓ = h.

10

The Gaunt coefficients are produced by explicitly integrating over three Legendre polynomials.

Results for unequal screening constants

Table II shows the results for several examples of Coulomb integrals. These examples deal with the more difficult case (for other methods) of $\zeta_a + \zeta_b \neq \zeta_c + \zeta_d$ (w $\neq$ zeta). In our programming we are only required to replace g1[j-2h+n-k, a) by f1[j-2h+n-k, a, w-zeta] and g1[j+1+m-k, a] by f1[j+1+m-k, a, w-zeta]. The first example produces the 12 digits given by the author [14] using a Taylor series expansion of a computer algebra formula using p and t (p = (w + ζ) a/2, t = (w - ζ)/ (w + ζ); p = 0.02, t = 0.01). Hence, we see that a closed formula can effectively control the word length of the computer. For the case with a=2, there is agreement with the seven decimal digits obtained by using expansions of the alpha-function [9,15] in a FORTRAN implementation for the Coulomb integral. Finally, we take two extreme examples using 4f, 3d, and 1s orbitals with separations of $a = 0.01$ and $a = 100$. With $a = 0.01$ we need to request 40 digits in order to get 21. The example with $a = 100$ shows that small values present no problems.

Conclusion

The examples shown in Table II with wide ranging parameters indicate that Coulomb integrals can be computed to arbitrary accuracy for all physical systems. It is important in developing fast alternative methods to have available completely trustworthy benchmarks for all parameter ranges. This is assured because *Mathematica* uses integer arithmetic.

Other multicenter molecular integrals are under study using symbolic programming.

Acknowledgment

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```mathematica
(* basic integrals *)

g1[n_,a_]:=Which[n>=0,a^(n+1)/(n+1),n<-1,a^(n+1)/(n+1),True,0];

f1[n_,a_,b_]:=Which[n>=0, (-Exp[-b*a]/b^(n+1)*Sum[n!/(n-t)!*(a*b)^
            (n-t),{t,0,n}]+n!/b^(n+1)),
            n<-1,
            ((-b)^(-n-1)*Sum[(-Exp[-b*a]*(-n-t-1)!/(-n-1)!
            /(-b*a)^(-n-t) + (-n-t-1)!/(-n-1)!/(-n-t)!),
            {t,1,-n-1}]),
            True,0];

f2[n_,a_,b_]:=Which[n>=0,Exp[-a*b]/b^(n+1)*Sum[n!/(n-t)!*(b*a)^(n-t)
            {t,0,n}],
            n<-1,
            -(-b)^(-n-1)*Sum[-Exp[-b*a]*(-n-t-1)!/(-n-1)!/
            (-b*a)^(-n-t),{t,1,-n-1}],
            True,0];

f3[n_,b_]:=Which[n>=0,n!/b^(n+1),
            n<-1,
            Sum[(-n-t-1)!/(-n-1)!/(-n-t)!*(-b)^(-n-1),{t,1,-n-1}],
            True,0];

(*data*)
nna=1;hha=0;  alpha=1
nnb=1;hhb=0;  beta=1
nnc=1; hhc=0;  gamma=1
nnd=1; hhd=0;  delta=1
mm=0;
(*constants*)
aa=Sqrt[(2*alpha)^(2nna+1)/(2nna)!];
ab=Sqrt[(2*beta)^(2nnb+1)/(2nnb)!];
ac=Sqrt[(2*gamma)^(2nnc+1)/(2nnc)!];
ad=Sqrt[(2*delta)^(2nnd+1)/(2nnd)!];
w=alpha+beta;
zeta=gamma+delta;
k1=aa*ab*Sqrt[(2hha+1)*(2hhb+1)]/2;
k2=ac*ad*Sqrt[(2hhc+1)*(2hhd+1)]/2;
nn=nnc+nnd-1;

coulomb=0;
```

Table I.   Program using *Mathematica* for the Coulomb integral.

```
(*do-loops for h and hh *)
Do[    Do[
           n=nna+nnb+h;
           m=nna+nnb-h-1;
             cpolynomial=Sum[a^(nn+hh+2h-2pp-2vp-2v-k-kp)*
                 r^(2pp+2v+2vp+kp)*(-1)^(v+qp+p+pp+hh)*(-1)^hh*
                 (2hh-2p)!*(2h-2pp)!/4^(hh+h-p-pp)/((hh-p)!*
                 p!*pp!*q!*qp!*v!*vp!*(hh+mm-2p-q-v)!)*
                 (nn-hh+2p+2q+2qp)!/((h-pp)!*(h-mm-2pp-qp-vp)!*
                 kp!*(nn-hh+2p+2q+2qp-k-kp)!),
                 {p,0,Floor[(hh+mm)/2]},{q,0,hh+mm-2p},
                 {v,0,hh+mm-2p-q},{pp,0,Floor[(h-mm)/2]},
                 {qp,0,h-mm-2pp},{vp,0,h-mm-2pp-qp},
                 {k,0,nn-hh+2p+2q+2qp},
                 {kp,0,nn-hh+2p+2q+2qp-k}];
    cmatrix=CoefficientList[cpolynomial,{a,r}];
    c=cmatrix;
    i1=Sum[n!/w^(n+1)*a^i*zeta^(i+j)*c[[i+1,j+1]]*
        ((-1)^j*Exp[-zeta*a]*f1[j-2h,a,-zeta]
        +(-1)^i*Exp[zeta*a]*f2[j-2h,a,zeta]
        -Exp[-zeta*a]*f3[j-2h,zeta]),
        {i,0,nn+hh+h},{j,0,nn+h}];
    i1=Simplify[i1];
    i2=Sum[n!/(n-k)!/w^(k+1)*zeta^(i+j)*a^i*c[[i+1,j+1]]*
        (-(-1)^j*Exp[-zeta*a]*g1[j-2h+n-k,a]
        -(-1)^i*Exp[zeta*a]*f2[j-2h+n-k,a,w+zeta]
        +Exp[-zeta*a]*f3[j-2h+n-k,w+zeta]),
        {i,0,nn+hh+h},{j,0,nn+h},{k,0,n}];
    i2=Simplify[i2];
    i3=Sum[m!/(m-k)!/w^(k+1)*zeta^(i+j)*a^i*c[[i+1,j+1]]*
        ((-1)^j*Exp[-zeta*a]*g1[j+1+m-k,a]
        +(-1)^i*Exp[zeta*a]*f2[j+1+m-k,a,w+zeta]
        -Exp[-zeta*a]*f3[j+1+m-k,w+zeta]),
        {i,0,nn+hh+h},{j,0,nn+h},{k,0,m}];
    i3=Simplify[i3];
i123=i1+i2+i3;
i123=Simplify[i123];
i123=i123/a^(hh+h+1)/zeta^(hh+2h+2)/zeta^(nn-1)*k1*k2*(2hh+1)/2*
     Integrate[LegendreP[hha,x]*LegendreP[hhb,x]*LegendreP[h,x],
     {x,-1,1}]*
     Integrate[LegendreP[hhc,x]*LegendreP[hhd,x]*LegendreP[hh,x],
     {x,-1,1}];
coulomb=coulomb+i123;
                              ,{hh,Abs[hhc-hhd],hhc+hhd,2},
                              {h,Abs[hha-hhb],hha+hhb,2} ]]
```

Table I   (continued)

a	$\chi_a(1)$				$\chi_b(1)$				$\chi_c(2)$				$\chi_d(2)$				Requested digits	Computed value
	N_a	L_a	M_a	ζ_a	N_b	L_b	M_b	ζ_b	N_c	L_c	M_c	ζ_c	N_d	L_d	M_d	ζ_d		
.01	1	0	0	.99	1	0	0	.99	1	0	0	1.01	1	0	0	1.01	20	.6249166670583
.01																	30	.62491667058300881498346
0.2	2	0	0	.8	2	0	0	.9	2	0	0	1.1	2	0	0	1.2	20	.34598364791661 04
2																	20	.305834662952360448
2	2	1	0	.8	2	1	0	.9	2	0	0	1.1	2	0	0	1.2	20	.32475644802549823
20																	20	.049846796378696259
.01	4	3	0	.8	1	0	0	.9	3	2	0	1.1	1	0	0	1.2	40	.000033435746571113613
100																	20	$1.32578247093629546 \times 10^{-10}$

Coulomb integrals. $\chi_a(1)$, $\chi_b(1)$ are at $(0,0,0)$ and $\chi_c(2)$, $\chi_d(2)$ are at $(0,0,a)$.

Analytic Löwdin Alpha-Function Method For
Two-Center Electron-Repulsion
Integrals Over Slater-Type Orbitals

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ABSTRACT

Using the Löwdin alpha-function method in which displaced orbitals are expanded in spherical harmonics, two-center, two-electron repulsion integrals of the Coulomb, hybrid, and exchange type are done analytically using Slater-type orbitals. Computer algebra and integer arithmetic are used to obtain analytic results and avoid cancellation errors by the generation of rational matrix elements for C, E, and F matrices that are used to express the α-function. The formulas for the integrals are kept simple by reversing the order of integration over each part of a split quadrant. Only two basic integrals are used which are first efficiently evaluated by using look-up tables and then used repeatedly.

I. INTRODUCTION

The need for basis sets to be constructed of Slater-type orbitals (STOs) when dealing with current problems of molecular reaction dynamics and variants of density functional theory has been voiced by several quantum chemists. And this need is still felt in the more traditional studies of bound state molecules.[1] The lack of analytic procedures have mitigated against the use of STOs in contrast to the almost universally used Gaussian-type orbitals (GTOs).

This paper deals with two-center two-electron repulsion integrals of the Coulomb, hybrid, and exchange type. The Löwdin alpha-function method[2] is used in which displaced STOs are expanded in spherical harmonics, as was first done by Collidge.[3] This method has been augmented by computer algebra and by the use of matrices with integer elements,[4] to avoid the ever present danger of computer cancellation errors.

In addition to presenting a method for doing all two-center integrals with the possibility of high speed and accuracy, our method has techniques that can be used in the solution of three- and four-center integrals.

Much of the early work on two-center integrals was done in elliptical coordinates.[5-8] Later work has used a variety of more general methods.[9]

II. ALPHA-FUNCTION REPRESENTATIONS

Every displaced STO may be expanded in an infinite series of spherical harmonics; the functional coefficients being designated as α- functions. Assume that a local coordinate system (R, Θ, φ) is displaced a distance a along the z-axis. In terms of the original coordinate system (r, θ, φ) we have[10]

$$\chi = A\, R^{N-1}\, e^{-\zeta R}\, Y_L^M(\Theta, \varphi)$$

$$\chi = \frac{A}{\zeta^{N-1}} \left[\frac{(2L+1)(L+M)!}{4\pi(L-M)!} \right]^{\frac{1}{2}} \sum_{l=M}^{\infty} \left[\frac{4\pi(l+M)!}{(2l+1)(l-M)!} \right]^{\frac{1}{2}} \tag{1}$$

$$\times (-1)^M\, \alpha_l^{NLM}(\zeta a, \zeta r)\, Y_l^M(\theta, \varphi)$$

where

$$\alpha_l^{NLM}(\zeta a,\, \zeta r) = \frac{(2l+1)(l-M)!}{2(l+M)!} \sum_{i=0}^{N+L+l} \sum_{j=0}^{N+l} \tag{2}$$

$$\times C_l^{NLM}(i,j) \cdot H_{ij} \cdot (\zeta a)^{i-L-l-1}\, (\zeta r)^{j-l-1}$$

2

and

$$
H_{ij} = \begin{cases} e^{-\zeta a}[(-1)^j\, e^{\zeta r} - e^{-\zeta r}], & r < a \\[2mm] e^{-\zeta r}[(-1)^i\, e^{\zeta a} - e^{-\zeta a}], & r > a \end{cases} \tag{3}
$$

The normalization constant $A = (2\zeta)^{N+1/2}\,[(2N)!]^{-1/2}$; N, L, and M are the quantum numbers of the orbital; ζ is the screening constant or the orbital exponent.

For small values of the parameters it is necessary to expand the exponentials in the α-function, and by use of computer algebra a triple sum is reduced to a double sum with an appropriate E or F matrix with rational elements.[11] Using these expansions our method is stable for arbitrary values of screening constants. Thus,

$$
\alpha_l(r) = \begin{cases} e^{-\zeta a}\displaystyle\sum_{i=0}^{N+L+l}\;\sum_{j=l}^{JMAX} E_l(i,j)\,(\zeta a)^{i-L-l-1}\,(\zeta r)^j, & r < a \\[4mm] e^{-\zeta r}\displaystyle\sum_{i=l}^{IMAX}\;\sum_{j=0}^{N+l} F_l(i,j)\,(\zeta a)^i\,(\zeta r)^{j-l-1}, & r > a \end{cases} \tag{4}
$$

In our examples $JMAX = IMAX = 36$ was sufficient.

A simplified working form of the α-function is obtained by leaving only the r variable intact, and storing one-dimensional $Y_l(j)$ and $Z_l(j)$ matrices.

$$
\alpha_l = \begin{cases} \displaystyle\sum_{j=l}^{JMAX} Y_l(j)\,r^j, & r < a \\[4mm] e^{-\zeta r}\displaystyle\sum_{j=0}^{N+l} Z_l(j)\,r^{j-l-1}, & r > a \end{cases} \tag{5}
$$

III. COULOMB INTEGRAL

The definition[5] of the Coulomb two-center, two-electron repulsion integral is

$$
J = \int\!\!\int \chi_a^*(1)\,\chi_b(1)\,r_{12}^{-1}\,\chi_c(2)\,\chi_d^*(2)\,dv_1\,dv_2 \tag{6}
$$

We superimpose $\chi_a(1)$ and $\chi_b(1)$ at the origin, and $\chi_c(2)$ and $\chi_d(2)$ at a distance of a along the z axis (o, o, a). The superimposed orbitals $\chi_c(2)$ and $\chi_d(2)$ may be merged and expressed as a linear sum of orbitals upon expanding the spherical harmonics.

The Coulomb integral may be written as

$$J = \int \chi_c(2) \, \chi_d^*(2) \, \vee (\vec{r}_2) \, dv_2 \tag{7}$$

with the potential given as

$$\vee(\vec{r}_2) = \int \chi_a^*(1) \, \chi_b(1) / \, r_{12} \, dv_1, \tag{8}$$

The Laplace expansion of r_{12}^{-1} is

$$\frac{1}{r_{12}} = \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \frac{4\pi}{2\lambda + 1} \, \frac{r_<^\lambda}{r_>^{\lambda+1}} \, Y_\lambda^\mu(\theta_1, \varphi_!) \, Y_\lambda^{\mu*}(\theta_2, \varphi_2), \tag{9}$$

where $r_<$ is the smaller of r_1, r_2 and $r_>$ is the larger.

Using orthogonality of spherical harmonics, the potential may be determined. In our developments, in order to avoid having to distinguish between real STOs and complex STOs, and to facilitate comparisons with the literature, only the case of orbitals with magnetic quantum $M = 0$ will be considered. This is a mild restriction easily removed once the chief problem of dealing with radial integrals is worked out. Thus the potential becomes[5]

$$\vee(r_2, \theta_2) = k_1 \sum \langle L_a, L_b, \lambda \rangle \, \vee_\lambda(r_2) \, P_\lambda(\theta_2), \tag{10}$$

where

$$\vee_\lambda(r_2) = \left\{ \frac{1}{r_2^{\lambda+1}} \int_0^{r_2} dr_1 \, r_1^n \, e^{-\omega r_1} + r_2^\lambda \int_{r_2}^\infty dr_1 \, r_1^m \, e^{-\omega r_1} \right\}, \tag{11}$$

with $\langle L_a, L_b, \lambda \rangle = \int P_{L_a}(\theta) \, P_{L_b}(\theta) \, P_\lambda(\theta) \sin\theta \, d\theta$, representing the Gaunt coefficients, and $\omega = \zeta_a + \zeta_b$, $n = N_a + N_b + \lambda$, $m = N_a + N_b - \lambda - 1, k_1 = A_a A_b \, [(2L_a + 1) \times (2L_b + 1)]^{\frac{1}{2}}/2$. Note that $Y_l^0(\theta, \varphi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\theta)$.

We perform the indicated integrations using the formula

$$\int e^{-\omega x} x^n \, dx = -e^{-\omega x} \sum_{k=0}^{n} \frac{n!}{(n-k)!} \frac{x^{n-k}}{\omega^{k+1}}, \tag{12}$$

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$$V_\lambda(r_2) = \frac{1}{r_2^{\lambda+1}} \left[\frac{n!}{\omega^{n+1}} - e^{-\omega r_2} \sum_{k=0}^{n} \frac{n!}{(n-k)!} \frac{r_2^{n-k}}{\omega^{k+1}} \right] + r_2^\lambda e^{-\omega r_2} \sum_{k=0}^{m} \frac{m!}{(m-k)!} \frac{r_2^{m-k}}{\omega^{k+1}} \tag{13}$$

The electron charge density for electron 2 becomes

$$\chi_c(2)\,\chi_d^*(2) = \frac{k_2}{2\pi}\, R_2^{N-1}\, e^{-\zeta R_2} \sum_L \frac{(2L+1)}{2} \langle L_c, L_d, L \rangle P_L(\Theta_2) \tag{14}$$

with $k_2 = A_c A_d [(2L_c+1)(2L_d+1)]^{\frac{1}{2}}/2$, $N = N_c + N_d - 1$, $\zeta = \zeta_c + \zeta_d$.

Noting the α-function expansion

$$R_2^{N-1}\, e^{-\zeta R_2}\, P_L(\Theta_2) = \frac{1}{\zeta^{N-1}} \sum_{l_L} \alpha_{l_L}^L\, P_l(\theta_2) \tag{15}$$

and taking into account orthogonality $(l_L = \lambda)$ we finally get

$$J = \frac{k_1 k_2}{\zeta^{N-1}} \sum_L \sum_\lambda \frac{(2L+1)}{(2\lambda+1)} \langle L_c, L_d, L \rangle \langle L_a, L_b, \lambda \rangle \int r^2 dr\, V_\lambda\, \alpha_\lambda^L \tag{16}$$

The sums over L and λ are limited because of the triangular rule for the Gaunt coefficients.

The Coulomb integral is reduced to evaluating basic integrals of the type

$$\int_0^a e^{-\omega x} x^n\, dx, \quad n \geq 0, \text{ and } \int_a^\infty e^{-\omega x} x^n\, dx, \quad n \geq 0, \text{ or } n < 0 \tag{17}$$

once the appropriate α-function representation and V_λ are substituted. These evaluations are done rapidly using look-up tables and computer memory (see Appendix).

To be explicit:

$$J = \frac{k_1\, k_2}{\zeta^{N-1}} \sum_L \sum_\lambda \frac{(2L+1)}{(2\lambda+1)} \langle L_c, L_d, L \rangle \langle L_a, L_b, \lambda \rangle$$
$$\times \left\{ \sum_{j=\lambda}^{JMAX} \left[\frac{n!}{\omega^{n+1}} Y_\lambda^L(j) \int_0^a r^{j-\lambda+1}\, dr \right. \right.$$

$$+ \sum_{k=0}^{n} \frac{n!}{(n-k)!} \frac{(-1)}{\omega^{k+1}} Y_{\lambda}^{L}(j) \int_{0}^{a} r^{n-k+j-\lambda+1} e^{-\omega r} dr$$

$$+ \sum_{k=0}^{m} \frac{m!}{(m-k)!} \frac{1}{\omega^{k+1}} Y_{\lambda}^{L}(j) \int_{0}^{a} r^{m-k+j+\lambda+2} e^{-\omega r} dr \Bigg] \qquad (18)$$

$$+ \sum_{j=0}^{N+\lambda} \left[\frac{n!}{\omega^{n+1}} Z_{\lambda}^{L}(j) \int_{a}^{\infty} r^{j-2\lambda} e^{-\zeta r} dr \right.$$

$$+ \sum_{k=0}^{n} \frac{n!}{(n-k)!} \frac{(-1)}{\omega^{k+1}} Z_{\lambda}^{L}(j) \int_{a}^{\infty} r^{n-k+j-2\lambda} e^{-(\omega+\zeta)r} dr$$

$$+ \sum_{k=0}^{m} \frac{m!}{(m-k)!} \frac{1}{\omega^{k+1}} Z_{\lambda}^{L}(j) \int_{a}^{\infty} r^{m-k+j+1} e^{-(\omega+\zeta)r} dr \Bigg] \Bigg\}$$

where

$$N = N_a + N_b - 1$$

$$n = N_a + N_b + \lambda$$

$$m = N_a + N_b - \lambda - 1 \qquad (19)$$

$$\omega = \zeta_a + \zeta_b$$

$$\zeta = \zeta_c + \zeta_d$$

IV. HYBRID INTEGRAL

All two-center, two-electron repulsion integrals are given by the same formula but they differ in the location of the orbitals. The hybrid integral[7] has three orbitals, $\chi_a(1), \chi_b(1)$ and $\chi_c(2)$, placed at the origin and one orbital $\chi_d(2)$ placed at (o,o,a). With this being the case the potential for the hybrid integral is identical to that of the Coulomb integral. The charge density $\chi_c(2) \chi_d^*(2)$ is somewhat simpler.

$$\chi_c(2) \chi_d^*(2) = \frac{k_2}{2\pi} \frac{1}{\zeta_d^{N_d-1}} e^{-\zeta_c r_2} r_2^{N_c-1} \sum_{l_d} \alpha_{l_d}^{d}(r_2) P_{l_d}(\theta_2) P_{L_c}(\theta_2) \qquad (20)$$

Integrating the density over the potential we get

$$I = \frac{k_1 k_2}{\zeta_d^{N_d-1}} \sum_{l_d} \sum_{\lambda} \langle L_a, L_b, \lambda \rangle \langle L_c, \lambda, l_d \rangle \int r^2 dr \ \vee_{\lambda} \ \alpha_{l_d}^{d} \ e^{-\zeta_c r} r^{N_c+1} \qquad (21)$$

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Again, the sum is limited by the triangular rule for Gaunt coefficients, and upon α-function and V_λ substitutions the hybrid integral reduces to evaluating basic integrals. To be explicit:

$$
I = \frac{k_1, k_2}{\zeta_d^{N_d-1}} \sum_\lambda \sum_{l_d} \langle L_a, L_b, \lambda \rangle \langle L_c, \lambda, l_d \rangle
$$

$$
\times \left\{ \sum_{j=l_d}^{JMAX} \left[\frac{n!}{\omega^{n+1}} Y_{l_d}^d(j) \int_0^a r^{N_c+j-\lambda} e^{-\zeta_c r} \, dr \right. \right.
$$

$$
+ \sum_{k=0}^n \frac{n!\,(-1)}{(n-k)!\,\omega^{k+1}} Y_{l_d}^d(j) \int_0^a r^{N_c+n-k+j-\lambda} e^{-(\zeta_c+\omega)r} \, dr
$$

$$
+ \sum_{k=0}^m \frac{m!}{(m-k)!} \frac{1}{\omega^{k+1}} Y_{l_d}^d(j) \int_0^a r^{N_c+m-k+j+\lambda-1} e^{-(\zeta_c+\omega)r} \, dr \Bigg] \tag{22}
$$

$$
+ \sum_{j=0}^{N_d+l_d} \left[\frac{n!}{\omega^{n+1}} Z_{l_d}^d(j) \int_a^\infty r^{N_c+j-\lambda-l_d-1} e^{-\zeta r} \, dr \right.
$$

$$
+ \sum_{k=0}^n \frac{n!}{(n-k)!} \frac{(-1)}{\omega^{k+1}} Z_{l_d}^d(j) \int_a^\infty r^{N_c+n-k+j-\lambda-l_d-1} e^{-(\zeta+\omega)r} \, dr
$$

$$
\left. \left. + \sum_{k=0}^m \frac{m!}{(m-k)!} \frac{1}{\omega^{k+1}} Z_{l_d}^d(j) \int_a^\infty r^{N_c+m-k+j+\lambda-l_d} e^{-(\zeta+\omega)r} \, dr \right] \right\}
$$

Symbols are as in the Coulomb case.

V. EXCHANGE INTEGRAL

For the exchange integral[5] we place $\chi_a(1)$ and $\chi_c(2)$ at the origin, and $\chi_b(1)$ and $\chi_d(2)$ at (o,o,a). We substitute in the following expressions, invoking orthogonality, and obtain an infinite series for the exchange integral, K.

$$
\chi_a(1) = A_a \, r_1^{N_a-1} \, e^{\zeta_a r_1} \, Y_{L_a}^0(\theta_1, \varphi_1)
$$

$$
\chi_b(1) = \frac{A_b \sqrt{2L_b+1}}{\zeta_b^{N_b-1}} \sum_{l_b} \frac{1}{\sqrt{2l_b+1}} \, \alpha_{l_b}^b(r_1) \, Y_{l_b}^0(\theta_1, \varphi_1)
$$

$$
\chi_c(2) = A_c \, r_2^{N_c-1} \, e^{-\zeta_2 r_1} \, Y_{L_c}^0(\theta_2, \varphi_2) \tag{23}
$$

$$
\chi_d(2) = \frac{A_d \sqrt{2L_d+1}}{\zeta_d^{N_d-1}} \sum_{l_d} \frac{1}{\sqrt{2l_d+1}} \, \alpha_{l_d}^d(r_2) \, Y_{l_d}^0(\theta_2, \varphi_2)
$$

$$\frac{1}{r_{12}} = \sum_{\lambda=0}^{\infty} \sum_{\mu-\lambda}^{\lambda} \frac{4\pi}{2\lambda+1} \frac{r_<^{\lambda}}{r_>^{\lambda+1}} Y_{\lambda}^{\mu*}(\theta_1,\varphi_1) Y_{\lambda}^{\mu}(\theta_2,\varphi_2) \qquad 24$$

$$K = \frac{k_1 k_2}{\zeta_b^{N_b-1} \zeta_d^{N_d-1}} \sum K_{\lambda}$$

with

$$K_{\lambda} = \sum_{l_d} \sum_{l_b} \langle L_c,\lambda,l_d \rangle \langle L_a,\lambda,l_b \rangle$$
$$\times \iint dr_1\, dr_2\, r_1^{N_a+1}\, e^{-\zeta_a r_1}\, \alpha_{l_b}^{b}(r_1) r_2^{N_c+1}\, e^{-\zeta_c r_2}\, \alpha_{l_d}^{d}(r_2) \frac{r_<^{\lambda}}{r_>^{\lambda+1}} \qquad (24)$$

On a previous occasion[12] we have first determined the potential, but this leads to di' cult basic integrals. To avoid this we shall split the (r_1, r_2) quadrant as in Figui 1, as was done by Lundquist and Löwdin.[13] For arbitrary functions $f(r_1)$ and $g(r_2)$ we get a more symmetry integration scheme. Thus,

$$\int_0^{\infty} \int_0^{\infty} dr_1\, dr_2\, f(r_1)\, g(r_2) \frac{r_<^{\lambda}}{r_>^{\lambda+1}} = \int_0^{\infty} dr_2\, g(r_2) \frac{1}{r_2^{\lambda+1}} \int_0^{r_2} dr_1\, f(r_1)\, r_1^{\lambda}$$
$$+ \int_0^{\infty} dr_1\, f(r_1) \frac{1}{r_1^{\lambda+1}} \int_0^{r_1} dr_2\, g(r_2)\, r_2^{\lambda} \qquad (25)$$

Therefore, we may write

$$K_{\lambda} = K_{\lambda}^{I} + K_{\lambda}^{II}, \qquad (26)$$

with

$$K_{\lambda}^{I} = \sum_{l_d} \sum_{l_b} \langle L_c,\lambda,l_d \rangle \langle L_c,\lambda,l_d \rangle$$
$$\times \int_0^{\infty} dr_2\, r_2^{N_c+1}\, e^{-\zeta_c r_2}\, \alpha_{l_d}^{d}(r_2) \frac{1}{r_2^{\lambda+1}} \int_0^{r_2} dr_1\, r_1^{N_a+1}\, e^{-\zeta_a r_1}\, \alpha_{l_b}^{b}(r_1)\, r_1^{\lambda}. \qquad (27)$$

In a analogous manner K_{λ}^{II} can be written.

To make our method analytic, the first integral for the "potential is done by a simple in-house version of computer algebra. Because two representations of the

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α-function must be used, depending on whether r is less than or greater than a, six regions of the quadrant must be addressed separately. The method will be sufficiently illustrated by just considering the first three regions, that is

$$K_\lambda^I = K_\lambda^1 + K_\lambda^2 + K_\lambda^3. \tag{28}$$

Region 1. Here we have $r < a$. Hence,

$$U_\lambda^1(r_2) = \frac{1}{r_2^{\lambda+1}} \int_0^{r_2} dr_1 \, r_1^{N_a+1} \, e^{-\zeta_a r_1} \, \alpha_{l_b}^b(r_2) \, r_1^\lambda$$

$$U_\lambda^1(r_2) = \frac{1}{r_2^{\lambda+1}} \sum_{j=l_b}^{JMAX} Y_{l_b}^b(j) \int_0^{r_2} dr_1 \, r_1^{N_a+1+j+\lambda} \, e^{-\zeta_a r_1} \tag{29}$$

Using the formula[5]

$$\int_0^r dx \, x^n \, e^{-\omega x} = r^{n+1} \, n! \, e^{-\omega r} \sum_{k=0}^{\infty} \frac{\omega^k \, r^k}{(n+k+1)!} \tag{30}$$

then,

$$U_\lambda^1(r_2) = n! \, e^{-\zeta_a r_2} \sum_{j=l_b}^{JMAX} \sum_{k=0}^{\infty} Y_{l_b}^b(j) \frac{\zeta_a^k \, r_2^{N_a+1+j+k}}{(n+k+1)!}, \tag{31}$$

where $n = N_a + 1 + j + \lambda$.

For our examples, we take the largest power of r_2 to be 36. The computer generates and stores the coefficients of r_2. Thus,

$$U_\lambda^1(r_2) = e^{-\zeta_a r_2} \sum_m^{36} C_1(\lambda, m) \, r_2^m, \tag{32}$$

The "potential" for Region 2 is simply

$$U_\lambda^2(r_2) = \frac{e^{-\zeta_a a}}{r_2^{\lambda+1}} \sum_m^{36} C_1(\lambda, m) \, a^{m+\lambda+1}, \tag{33}$$

$$U_\lambda^2(r_2) = \frac{C_2(\lambda)}{r_2^{\lambda+1}}. \tag{34}$$

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For Region 3 we have

$$U_\lambda^3(r_2) = \frac{1}{r_2^{\lambda+1}} \int_a^{r_2} dr_1 \, r_1^{N_a+1+\lambda} \, e^{-\zeta_a r_1} \, e^{-\zeta_b r_1} \sum_{j=0}^{N_b+l_b} Z_{l_b}^b(j) \, r_1^{j-l_b-1} \, r_1^\lambda. \quad (35)$$

Using the formula

$$\int_a^{r_2} dx \, x^n \, e^{-\omega x} = -e^{-\omega r_2} \sum_{k=0}^n \frac{n!}{(n-k)!} \frac{r_2^{n-k}}{\omega^{k+1}} + e^{-\omega a} \sum_{k=0}^n \frac{n!}{(n-k)!} \frac{a^{n-k}}{\omega^{k+1}} \quad (36)$$

with $\omega = \zeta_a + \zeta_b$ and $n = N_a + j + \lambda - l_b$ we get

$$\begin{aligned}
U_\lambda^3(r_2) = &\frac{(-1)}{r_2^{\lambda+1}} \sum_j \sum_k e^{-\omega r_2} Z_{l_b}^b(j) \frac{n!\,(-1)}{(n-k)!} r_2^{n-k} \\
&+ \frac{1}{r_2^{\lambda+1}} \sum_j \sum_k e^{-\omega a} Z_{l_b}^b(j) \frac{n!}{(n-k)!} a^{n-k}
\end{aligned} \quad (37)$$

and by computer algebra

$$U_\lambda^3(r_2) = \frac{e^{-\omega r_2}}{r_2^{\lambda+1}} \sum_{m=0}^{2N_a+\lambda} C_{3R}(\lambda,m) \, r_2^m + \frac{C_{3A}(\lambda)}{r_2^{\lambda+1}}, \quad (38)$$

where $C_{3R}(\lambda,m)$ and $C_{3A}(\lambda)$ are stored arrays of coefficients.

Finally, substituting in the proper α-functions for the second integration we get

$$\begin{aligned}
K_\lambda^1 &= \sum_{j=l_d}^{36} \sum_m Y_{l_d}^d(j) \, C_1(\lambda,m) \int_0^a dr \, r^{N_c+1+j+m} \, e^{-(\zeta_a+\zeta_c)r} \\
K_\lambda^2 &= \sum_{j=0}^{N_d+l_d} Z_{l_d}^d(j) \, C_2(\lambda) \int_a^\infty dr \, e^{-(\zeta_c+\zeta_d)r} r^{N_c-1+j-l_b-\lambda} \\
K_\lambda^3 &= \sum_{j=0}^{N_d+l_d} \sum_{m=0}^{2N_a+\lambda} Z_{l_d}^d(j) \, C_{3R}(\lambda,m) \int_a^\infty dr \, e^{-(\omega+\zeta)r} r^{N_c-1+j-l_d-\lambda} \\
&\quad + \sum_{j=0}^{N_d+l_d} Z_{l_d}^d(j) \, C_{3A}(\lambda) \int_a^\infty dr \, e^{-(\zeta_c+\zeta_d)r} r^{N_c-1+j-l_d-\lambda}
\end{aligned} \quad (39)$$

These integrals are readily identified as composed of our two basic integrals.

VI. DISCUSSION

Table I shows the results of evaluating two-center Coulomb, hybrid and exchange integrals using various combinations of $1s$, $2s$, and $2p$ orbitals with arbitrary screening constants. Our method is completely stable for these permutations, as is to be expected. The Coulomb and hybrid integrals are assembled from a finite number of terms as determined by the triangular rule for Gaunt coefficients; the exchange integrals are approximated to 7 decimal digits by using 12 harmonics. These calculations were made on a CDC CYBER 850 computer. E and F matrices and look-up tables for $A_n(z)$ and $E_n(z)$ are considered as data which is put into fast memory at run time. The "set-up" time or "overhead" is in the generation of Y and Z one-dimensional matrices, the production of basic integrals, and Gaunt coefficients. This overhead requires about 3 s of Central Processing Unit time (CPU) for the exchange integrals and about 2 s for the Coulomb and hybrid integrals. Some of the same values are needed for all of these integrals. In a SCF calculation, the set-up time would only be needed once for a large number of integrals. The CPU time of the subroutines for the Coulomb and hybrid integrals was about 0.25 and 0.4 s, respectively. The CPU time to generate 12 harmonics for the exchange integrals was about 0.7 s.

CONCLUSION

The analytical method outlined here for two-center STO integrals can be implemented with parallel processing or vector processing. And with improved programming it should be possible to significantly reduce computer time. In addition, analytic and semi-analytic methods for three- and four-center integrals for STOs can use some of the strategies developed here.

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APPENDIX

The speed of our method depends on the rapid evaluation of the basic integrals. These basic integrals occur many times, so generally speaking, they need only be evaluated for the highest harmonic and then stored in fast computer memory to be used repeatedly. The initial evaluations of the basic integrals are done using look-up tables.

All the basic integrals needed can be written in a simple form after an obvious change in variable. Thus,[5]

$$E_n(z) = \int_0^1 e^{-zx} x^n \, dx, \quad n \geq 0 \tag{1}$$

and

$$A_n(z) = \int_1^\infty e^{-zx} x^n \, dx, \quad n \geq 0 \text{ or } n < 0 \tag{2}$$

These basic integrals are accurately evaluated over a z-grid with $\Delta z = 0.1$ over a range sufficient to cover all the electron repulsion integrals to be investigated. These tables are stored on magnetic tape and put into fast memory at run time.

Silver and Rudenberg[6] showed how look-up tables may be generated and $E_n(z)$ evaluated by interpolation using a Taylor series whose derivatives are given by a shift upward in n.

We found that this approach can also be used for $A_n(z)$ even when n is negative. The simplicity of this procedure is shown by first writing the lth derivative of $E_n(z)$ and $A_n(z)$.

$$\frac{d^l}{dz^l} E_n(z) = (-1)^l E_{n+l}(z)$$
$$\frac{d^l}{dz^l} A_n(z) = (-1)^l A_{n+l}(z) \tag{3}$$

Then

$$E_n(z+h) = E_n(z) + \frac{d\,E_n(z)}{d\,z} h + \frac{d\,E_n(z)}{d\,z^2} \frac{h^2}{2!} + \cdots + \frac{d^l}{d\,z^l} E_n(z) \frac{h^l}{l!} \tag{4}$$

and

$$E_n(z+h) = E_n(z) - E_{n+1}(z)h + E_{n+2}(z)\frac{h^2}{2!} + \cdots + (-1)^l E_{n+l}(z)\frac{h^l}{l!} \tag{5}$$

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Similarly,

$$A_n(z + h) = A_n(z) - A_{n+1}(z)\,h + A_{n+2}(z)\frac{h^2}{2!} + \cdots + (-1)^l\,A_{n+l}(z)\frac{h^l}{l!} \quad (6)$$

Five terms of the Taylor series give sufficient accuracy. In our examples, n varies from -22 to 6, but we extend n to 10 so as to use a full Taylor series in every case. Hence, derivatives need not be stored.
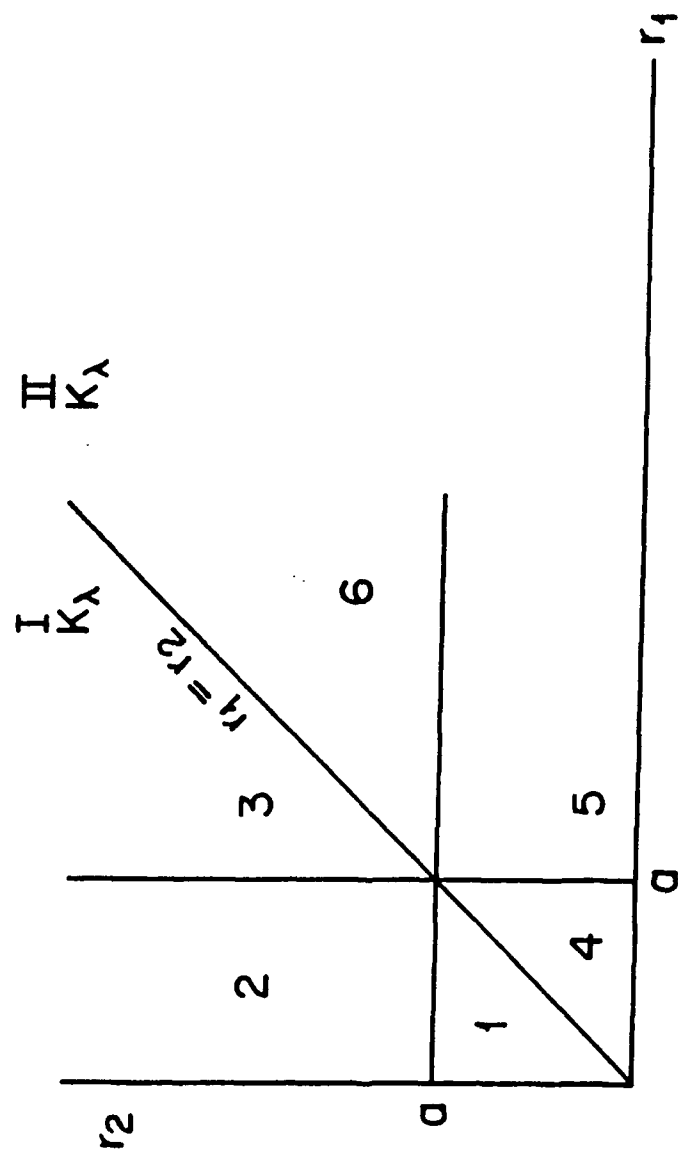
Figure 1. The six regions of the (r_1, r_2) quadrant that must be treated separately to analytically evaluate arbitrary two-center exchange integrals.

	a	N_a	L_a	M_a	ζ_a	N_b	L_b	M_b	ζ_b	N_c	L_c	M_c	ζ_c	N_d	L_d	M_d	ζ_d	Computed Value	Comparison
		$\chi_a(1)$				$\chi_b(1)$				$\chi_c(2)$				$\chi_d(2)$					
EXCHANGE																			
$(0,0,0)$:	2.0	2	1	0	1.0	2	1	0	1.0	2	1	0	1.0	2	1	0	1.0	.0439910	.0439915[a]
$\chi_a(1),\chi_c(2)$.	2.0	2	1	0	0.8	2	1	0	0.9	2	1	0	1.1	2	1	0	1.2	.0407474	
$(0,0,a)$:	1.0	2	1	0	1.0	1	0	0	1.0	2	1	0	1.0	1	0	0	1.0	.1720662	.1720662[b]
$\chi_b(1),\chi_d(2)$.	1.0	2	1	0	0.8	1	0	0	0.9	2	1	0	1.1	1	0	0	1.2	.1236365	.
COULOMB																			
$(0,0,0)$:	2.0	2	0	0	1.0	2	0	0	1.0	2	0	0	1.0	2	0	0	1.0	.3178164	.31782[c]
$\chi_a(1),\chi_b(1)$.	2.0	2	0	0	0.8	2	0	0	0.9	2	0	0	1.1	2	0	0	1.2	.3058347	
$(0,0,a)$:	2.0	2	1	0	1.0	2	1	0	1.0	2	0	0	1.0	2	0	0	1.0	.3311916	.33122[c]
$\chi_c(2),\chi_d(2)$.	2.0	2	1	0	0.8	2	1	0	0.9	2	0	0	1.1	2	0	0	1.2	.3247565	
HYBRID																			
$(0,0,0)$:	2.0	2	0	0	1.0	2	0	0	1.0	2	0	0	1.0	2	1	0	1.0	.2046695	.20466[c]
$\chi_a(1),\chi_b(1),\chi_c(2)$.	2.0	2	0	0	0.8	2	0	0	0.9	2	0	0	1.1	2	1	0	1.2	.1823044	
$(0,0,a)$:	2.0	2	1	0	1.0	2	1	0	1.0	2	1	0	1.0	2	0	0	1.0	.1615456	.161546[c]
$\chi_d(2)$.	2.0	2	1	0	0.8	2	1	0	0.9	2	1	0	1.1	2	0	0	1.2	.1805822	

Table I. Two-center, two-electron repulsion integrals. Comparision: a) Reference 14; b) Reference 8; c) Reference 15.

Semi-Analytical Method for Four-Center Molecular Integrals over Slater-Type Orbitals

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Abstract

A strategy for the evaluation of four-center molecular integrals over Slater-type orbitals is developed using the Löwdin alpha-function approach in which displaced orbitals are expanded in spherical harmonics. The harmonic potentials are produced analytically and evaluated along a grid. The harmonic charge distributions are given an analytical formulation and are evaluated over the common grid and numerical integrations are performed, for each harmonic. Using an example with 1s orbitals, only nine harmonics are needed for good results.

Computer algebra and integer arithmetic are used to generate C, E, and F matrices that are stored as part of the data base. T and X one-dimensional matrices are introduced as an aid in computation. The employment of look-up tables, and vector and parallel processing promises to make this method, which can be generalized, practical.

Introduction

It is generally agreed [1] that it would be desirable to use Slater-type orbitals (STOs), because of their more physical nature, in ab initio quantum chemistry and moleuclar physics as well as the almost universally employed Gaussian-type orbitals (GTOs). Advances toward this long sought goal have recently been made [2], but a comprehensive STO computer code competitive with GTO codes has yet to be written.

The author has continued to follow the path of the Löwdin alpha-function method in which displaced orbitals are expanded about a single-center in an infinite series of spherical harmonics with functional coefficients (Löwdin α-functions) [3]. This basic method has been augmented by computer algebra and integer arithmetic to avoid the pitfalls of cancellation errors due to the finite word length of computers [4]. A modified closed formula [5] for the α-function led to a C-matrix with integer elements [6,7]. To deal with small parameter values, the exponentials in the α-function were expanded using computer algebra leading to rational elements for E and F matrices [8].

The α-function method has been applied to four-center integrals to obtain formulas [9] and analytical procedures [10]. However, there were several difficult basic integrals that had to be dealt with and one that had to be done numerically. A pragmatic view seems to demand that we abandon a formula approach or an all analytic approach for this case and adopt a semi-analytical method in which the first integral (potential) is done analytically and the second integral (energy) is done numerically, for each harmonic. (An all numerical method has been done [11], but its lack of speed confines it to a checking role.)

That a semi-analytical method can lead to good accuracy was demonstrated by McLean [12] and Clementi [13] using elliptical coordinates for an analytic potential, followed by two numerical integrations for linear molecules. This procedure was proved effective for the general case by Musso and Magnasco [14], in which a three-dimensional numerical integration is required. The advantage of the α-function method to be presented here is that it only requires a one-dimensional numerical integration for each harmonic used. This, together with the better systematics of the method, promises to raise it to the level of practicality.

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Our method will be illustrated by an example using 1s-orbitals. The generalization to higher angular momentum is straightforward [15].

Alpha-Function Representations

A 1s orbital in its coordinate system is given by $\chi = \zeta^{3/2}\ e^{-\zeta R}/\sqrt{\pi}.$ If it is displaced a distance b along the z axis it may be expanded in spherical harmonics or Legendre polynomials in the original coordinate system as

$$\chi = \frac{\zeta^{3/2}}{\sqrt{\pi}} \sum_{\ell=0}^{\infty} \alpha_\ell P_\ell(\cos\theta), \tag{1}$$

where

$$\alpha_\ell = \frac{2\ell+1}{2} \sum_{i=0}^{\ell+1} \sum_{j=0}^{\ell+1} C_\ell(i,j)\ H_{ij}\ (\zeta b)^{i-\ell-1}\ (\zeta r)^{j-\ell-1} \tag{2}$$

and

$$H_{ij} = \begin{cases} e^{-\zeta b}\ [(-1)^j\ e^{\zeta r} - e^{-\zeta r}], & r < b \tag{3}\\[2em] e^{-\zeta r}\ [(-1)^i\ e^{\zeta b} - e^{-\zeta b}], & r > b. \tag{4} \end{cases}$$

The E matrix results when $e^{\zeta r}$ and $e^{-\zeta r}$ are expanded and the triple sum is reduced to a double sum by computer algebra. The F matrix results when $e^{\zeta b}$ and $e^{-\zeta b}$ are expanded. In our example, a 36 term expansion was found to be sufficient.

Thus

$$\alpha_\ell = \begin{cases} e^{-\zeta b} \sum_{i=0}^{\ell+1} \sum_{j=\ell}^{36} E_\ell(i,j)\ (\zeta b)^{i-\ell+1}\ (\zeta r)^j, & r < b \tag{5}\\[2em] e^{-\zeta r} \sum_{j=0}^{\ell+1} \sum_{i=\ell}^{36} F_\ell(i,j)\ (\zeta b)^{i-\ell+1}\ (\zeta r)^{j-\ell-1}, & r > b \tag{6} \end{cases}$$

A further simplification results by just keeping r intact,

$$Y_\ell(j) = \zeta^j \sum_{i=0}^{\ell+1} E_\ell(i,j) (\zeta b)^{i-\ell-1} e^{-\zeta b} \tag{7}$$

$$Z_\ell(j) = \zeta^{j-\ell-1} \sum_{i=\ell}^{36} F_\ell(i,j) (\zeta b)^i , \tag{8}$$

leading to

$$\alpha_\ell = \begin{cases} \displaystyle\sum_{j=\ell}^{36} Y_\ell(j)\, r^j , & r < b \tag{9} \\[2em] \displaystyle e^{-\zeta r} \sum_{j=0}^{\ell+1} Z_\ell(j)\, r^{j-\ell-1}, & r > b \tag{10} \end{cases}$$

When it is necessary to evaluate the α-function over a grid for large values of ζb it is expedient to introduce two more one-dimensional matrices immediately derived from the general C matrix:

$$T_\ell(j) = \frac{(2\ell+1)(\ell-M)!}{2(\ell+M)!}\ e^{-\zeta b}\ \zeta^{j-\ell-1} \sum_{i=0}^{N+L+\ell} C_\ell^{NLM}(i,j) (\zeta b)^{i-L-\ell-1} \quad r < b \tag{11}$$

$$X_\ell(j) = \frac{(2\ell+1)(\ell-M)!}{2(\ell+M)!}\ \zeta^{j-\ell-1} \sum_{i=0}^{N+L+\ell} C_\ell^{NLM}(i,j) [(-1)^i - e^{-\zeta b}] (\zeta b)^{i-L-\ell-1}, \quad r > b. \tag{12}$$

Hence,

$$\alpha_\ell^{NLM} = \begin{cases} \displaystyle\sum_{j=0}^{N+\ell} T_\ell(j) [(-1)^j e^{\zeta r} - e^{-\zeta r}]\, r^{j-\ell-1} , & r < b \tag{13} \\[2em] \displaystyle e^{-\zeta r} \sum_{j=0}^{N+\ell} X_\ell(j)\, r^{j-\ell-1}, & r > b \tag{14} \end{cases}$$

These various representation's of the α-function considerably simplify our programming and also speed up its execution.

Four-Center Integrals for 1s Orbitals

The formalism for the radial part of any STO is essentially the same, therefore we may sufficiently illuminate our method by use of an example using 1s orbitals, given by Trivedi and Steinborn [16]. In this case, 1s orbitals with screening constants of $\zeta = 1$ are located as follows:

$\chi_a(1)$ at (0,0,0), $\chi_b(1)$ at (0,0,b), $\chi_c(2)$ at (c,0,0), and $\chi_d(2)$ at (0,d,0), with b = c = d = 1.0. The method to be shown is valid for arbitrary b, c, and d, as well as ζ_a, ζ_b, ζ_c, and ζ_d. Because of our use of the E matrix expansion, our methods are stable for nearly equal or equal values of ζ_a and ζ_b. Since our method is partly numerical, no problems can originate with the relative values of ζ_c and ζ_d.

Our task is to evaluate the integral

$$I = \int \chi_a(1)^* \chi_b(1) \, r_{12}^{-1} \, \chi_c(2)^* \chi_d(2) \, dv_1 \, dv_2 \tag{15}$$

in which each orbital is at one of four separate locations. We orient the molecule so that $\chi_a(1)$ is at the origin and $\chi_b(1)$ is along the z axis at a distance of b from the origin. Using potential, we have

$$I = \int V \, \chi_c(2)^* \chi_d(2) \, dv_2 \tag{16}$$

with

$$V(r_2) = \int \chi_a(1)^* \chi_b(1) \, r_{12}^{-1} \, dv_1 \,. \tag{17}$$

Substituting in the Laplace expansion for $1/r_{12}$, the expansion for χ_b, and invoking orthogonality we obtain [10]

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$$V(r_2, \theta_2) = \sum_{\ell} V_{\ell}(r_2) \, P_{\ell}(\cos \theta_2),\tag{18}$$

with

$$V_{\ell}(r_2) = 4 \, (\zeta_a \zeta_b)^{3/2} \int dr_1 \, r^2 \, e^{-\zeta_a r_1} \, \frac{r_{<}^{\ell}}{r_{>}^{\ell+1}} \, \alpha_{\ell}^{b}(r_1)\tag{19}$$

where $r_{>}$ is the larger of r_1 and r_2, and $r_{<}$ is the smaller.

Explicitly,

$$V_{\ell}(r_2) = \frac{4 \, (\zeta_a \zeta_b)^{3/2}}{2\ell+1} \left\{ \frac{1}{r_2^{\ell+1}} \sum_{j=\ell}^{36} Y_{\ell}^{b}(j) \int_{o}^{r_2} dr \, r^{\ell+j+2} \, e^{-\zeta_a r} \right.$$

$$+ \, r_2 \sum_{j=\ell}^{36} Y_{\ell}^{b}(j) \int_{r_2}^{b} dr \, r^{j+1-\ell} \, e^{-\zeta_a r}$$

$$\left. + \, r_2 \sum_{j=0}^{\ell+1} Z_{\ell}^{b}(j) \int_{b}^{\infty} dr \, r^{j-2\ell} \, e^{-(\zeta_a + \zeta_b)r} \right\}, \quad r_2 < b\tag{20}$$

$$V_{\ell}(r_2) = \frac{4 \, (\zeta_a \zeta_b)^{3/2}}{2\ell+1} \left\{ \frac{1}{r_2^{\ell+1}} \sum_{j=\ell}^{36} Y_{\ell}^{b}(j) \int_{o}^{b} dr \, r^{\ell+j+2} \, e^{-\zeta_a r} \right.$$

$$+ \, \frac{1}{r_2^{\ell+1}} \sum_{j=0}^{\ell+1} Z_{\ell}^{b}(j) \int_{b}^{r_2} dr \, r^{j+1} \, e^{-(\zeta_a + \zeta_b)r}$$

$$\left. + \, r_2^{\ell} \sum_{j=0}^{\ell+1} Z_{\ell}^{b}(j) \int_{r_2}^{\infty} dr \, r^{j-2\ell} \, e^{-(\zeta_a + \zeta_b)r} \right\}, \quad r_2 > b.\tag{21}$$

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We will evaluate each of the harmonic potentials V_ℓ along a hundred point grid with a spacing of 0.1 units. This is accomplished, after an obvious change of variables, by use of the following basic formulas [17,18]

$$\int_o^1 x^n \; e^{-Zx} \; dx \; = \; n! \; e^{-Z} \; \sum_{k=0}^{\infty} \; \frac{z^k}{(n+k+1)!} \; . \tag{22}$$

$$\int_1^{\infty} x^n \; e^{-Zx} \; dx \; = \; e^{-Z(x)} \sum_{k=0}^{\infty} \; \frac{n!}{(n-k)!} \; . \; \frac{1}{z^{n+1}} \; . \tag{23}$$

$$\int_1^{\infty} \; \frac{e^{-Zx}}{x^n} \; dx \; = \; e^{-Z} \sum_{k=1}^{n-1} \; \frac{(n-k-1)!}{(n-1)!} \; (-z)^{k-1} \; - \; \frac{(-z)^{n-1}}{(n-1)!} \; Ei(-z) \tag{24}$$

Next, we must numerically integrate the potential over the charge density. Using spherical coordinates, take the center of χ_c to be at (c, Γ, γ) and χ_d to be at (d, Δ, δ). Then [9]

$$\chi_c \; = \; 2 \; \sum_{m=0}^{\infty} \; \sum_{\mu=-m}^{m} \; \frac{(4\pi)^{1/2}}{2m+1} \; \alpha_m^c \; Y_m^\mu \; (\Gamma, \gamma) \; Y_m^\mu \; (\theta_2, \varphi_2)^* \tag{25}$$

and

$$\chi_d \; = \; 2 \; \sum_{n=0}^{\infty} \; \sum_{\nu=-n}^{n} \; \frac{(4\pi)^{1/2}}{2n+1} \; \alpha_n^d \; Y_n^\nu \; (\Delta, \delta)^* \; Y_n^\nu \; (\theta_2, \varphi_2) \tag{26}$$

Substituting in V, χ_c, and χ_d into the equation for I and invoking orthogonality, we get

$$I \; = \; \sum \; I_\ell \tag{27}$$

with

$$I_\ell \; = \; \int r^2 \; dr \; V_\ell \; \rho_\ell \tag{28}$$

and

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$$\rho_{\ell}(r_2) = \sum_m \sum_n \frac{2\,\alpha_m^c}{2m+1} \frac{2\,\alpha_n^d}{2n+1} \frac{(4\pi)^{3/2}}{(2\ell+1)^{1/2}} \sum_\mu \sum_\nu Y_\ell^\mu (\Gamma, \gamma)^*$$

$$\times \quad Y_n^\nu (\Delta, \delta) \; < m, \mu \mid \ell, 0 \mid n, \nu > \qquad (29)$$

The angular brackets represent the integration of the product of three spherical harmonics [19].

In our example, the values of ℓ, m, and n are taken from 0 to 8 and we have $\Gamma = \Delta = \delta = 90^o$ and $\gamma = 0^o$. The numerical integrations are done by Simpson's Rule, obtaining I = 0.345538, which agrees with the four digits supplied by Trivedi and Steinborn. As an internal check of our method, we set $\Gamma = \Delta = \delta = \gamma = 0^o$, and obtain I = 0.50703 which compares well with the exact value for the hybrid integral I_h = 0.50704 [20]. Table I lists the harmonics and their sums for our two runs. The Central Processing Unit time on a Cyber 850 Computer was 11.4 s in each case. The basic integrals were pre-calculated, stored, and reused. The matrices C, E, and F are considered as part of the data base.

Conclusion

A feasible strategy has been formulated to evaluate the general four-center molecular integral using Slater-type orbitals. Both objectives of sufficient accuracy and speed appear within reach. Working within the framework of the Löwdin α-function method, careful elimination of computer cancellation errors by use of computer algebra has proven decisive. The rapid and accurate implementation of programmes is assured by pre-calculated exact matrix elements and look-up tables as well as computer vector and parallel processing. Improvements in algorithms and numerical integrations are under development.

Acknowledgments

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Harmonic	Exchange integral Orbital locations $\Gamma = \Delta = \delta = 90^0\ \gamma = 0^0$	Hydrid integral Orbital locations $\Gamma = \Delta = \gamma = \delta = 0^0$
ℓ	I_ℓ	I_ℓ
0	.3465644	.4573980
1	.0000000	.0444000
2	-.0010363	.0045491
3	.0000000	.0005674
4	.0000108	.0000911
5	.0000000	.0000188
6	-.0000004	.0000048
7	.0000000	.0000014
8	.0000000	.0000005
Sum	.3455385	.5070311

Table I. Four 1s orbitals are located by polar coordinates as indicated:
$\chi_a(1)$ at $(0, 0, 0)$, $\chi_b(1)$ at $(1.0, 0, 0,)$, $\chi_c(2)$ at $(1.0, \Gamma, \gamma)$, and $\chi_d(2)$ at $(1.0, \Delta, \delta)$. Screening constants are equal to 1.0. The harmonics and their sums are given for the two cases.

Multicenter Molecular Integrals Using Harmonic Expansions of Slater-Type Orbitals and Numerical Integrations

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Abstract

Formula and analytic methods have previously been explored for the evaluation of multicenter molecular integrals over Slater-type orbitals by employing the Löwdin α-function approach. These procedures are greatly simplified by numerical integrations. The programming of this numerical approach is straightforward and hence can serve as a check on future developments.

Introduction

As is well known [1], the general problem of the evaluation of multicenter molecular integrals using Slater-type orbitals (STOs) in basis sets is still not competitive with the use of Gaussian-type orbitals (GTOs) in quantum chemistry. However, investigators [2,3] continue to strive to bring this about because of their belief in the inherent superiority of STO basis sets.

By use of the Löwdin alpha-function method [4], a formula that involves an assembly of a triply infinite sum of formulae has been produced for the four-center (the most centers needed) multicenter integral using 1s orbitals and equal screening constants [5]. An analytical version of this formula has been produced [3] that is much easier to program because all of the parameters are "ground up," except the radial variable, to produce a simplified α-function. This paper shows how the multicenter molecular integral problem can be further simplified by use of numerical integration that leads to very transparent programming and reduced computer time. However, here, we only achieve about five-decimal digit accuracy. But, of course, accuracy and time is dependent on the numerical integration scheme. Nevertheless, for the efficient writing of new programs, a first run using simplified and reasonably fast programs is greatly desired; certainly the method to be presented meets this criteria.

Expansion of Displaced Orbitals

To illustrate our procedure, it is sufficient to use all 1s orbitals, with screening constants equal to 1 ($\zeta = 1$).

We shift an orbital $\chi = (\pi)^{-1/2} e^{-r}$ from the origin to a distance a along the z-axis. Now, with respect to the origin we have [6]

$$\chi = (\pi)^{-1/2} \sum_{l=0} \alpha_l P_l(\cos \vartheta),$$

(1)

where

$$\alpha_l = \frac{2l+1}{2} \sum_{i=0}^{l+1} \sum_{j=0}^{l+1} C_l(i, j) H_{ij} a^{l-l-1} r^{j-l-1}$$

(2)

and

$$H_{ij} = \begin{cases} e^{-a}[(-1)^j e^r - e^{-r}], & r < a \\ e^{-r}[(-1)^i e^a - e^{-a}], & r > a \end{cases}$$

(3)

For accurate evaluation of the α-function at small radial distances, we must expand $\exp(r)$ and $\exp(-r)$ for $r < a$ and thereby obtain a power series representation with coefficients given by an E matrix [7]. For the case of $r > a$, an expansion of $\exp(a)$ and $\exp(-a)$ leads to an F matrix (for s-orbitals the F matrix is the transpose of the E matrix).

Thus

$$\alpha_l = \begin{cases} \dfrac{e^{-a}}{a^{l+1}} \sum_{i=0}^{l+1} \sum_{j=l}^{\text{JMAX}} E_l(i, j) a^i r^j, & r < a \\[2ex] \dfrac{e^{-r}}{r^{l+1}} \sum_{i=l}^{\text{IMAX}} \sum_{j=0}^{l+1} F_l(i, j) a^i r^j, & r > a \end{cases}$$

(4)

A further simplification results by just keeping r intact. Defining

$$Y_l(j) = \sum_{i=0}^{l} E_l(i, j) a^{l-l-1} e^{-a}$$

(5)

and

$$Z_l(j) = \sum_{i=l}^{\text{IMAX}} F_l(i, j) a^i$$

(6)

we may finally write

$$\alpha_l = \begin{cases} \displaystyle\sum_{j=l}^{\text{JMAX}} Y_l(j) r^j, & r < a \\[2ex] e^{-r} \displaystyle\sum_{j=0}^{l+1} Z_l(j) r^{j-l-1}, & r > a \end{cases}$$

(7)

In the case $a = 2$, we get convergence over the grid from 0 to 2 ($r < a$), and from 2 to 10 ($r > a$). The grid values of α_l are accurate to 12 decimal digits by taking JMAX and IMAX to be 36. We choose a grid of 0.1 throughout.

Examples of Various Multicenter Molecular Integrals

Overlap

The simplest multicenter integral is the overlap

$$S = \int X_a(1)X_b(1)\,dv_1 \tag{8}$$

Locating X_a at the origin and X_b at $(0,0,a)$, we have

$$X_a = (\pi)^{-1/2}e^{-r} \tag{9}$$

and

$$X_b = (\pi)^{-1/2}\sum_l \alpha_l P_l(\cos \vartheta) \tag{10}$$

Using orthogonality of Legendre polynomials,

$$S = 4\int dr\, r^2 e^{-r}\alpha_l \tag{11}$$

The exact formula in this case is

$$S = e^{-a}(1 + a + a^2/3) \tag{12}$$

For $a = 2$, $S = 0.58645289$.

Using a 100 point grid and Simpson's rule for numerical integration, we get

$$S = 4\int_0^{10} dr\, r^2 e^{-r}\alpha_l = 0.58645185 \tag{13}$$

The grid spacing, 0.1, and grid length, 10, have been chosen to achieve five-decimal digit accuracy, thereby including 99.9998% of the charge with the requisite accuracy. The overlap is done in order to choose a proper grid. This task was accomplished with 0.65 s of central processing unit (CPU) time, on a CDC Cyber 850 computer.

Three-Center Nuclear-Attraction Integral (Electrostatic Potential)

These two integrals (three-center nuclear attraction and electrostatic potential) differ by only a constant. Working with the potential, we seek its value at the point (r_2, ϑ_2) due to a charge density given as the product of two orbitals, X_a located at the origin and X_b at $(0,0,a)$:

$$V(r_2, \vartheta_2) = \int dv_1\, X_a(1)X_b(1)/r_{12} \tag{14}$$

We substitute the Laplace expansion for $1/r_{12}$,

$$\frac{1}{r_{12}} = 4\pi \sum_{\lambda=0}^{\infty} \sum_{m=-\lambda}^{\lambda} (2\lambda + 1)^{-1} \frac{r_<^\lambda}{r_>^{\lambda+1}} Y_\lambda^{m*}(\vartheta_1, \varphi_1)Y_\lambda^m(\vartheta_2, \varphi_2) \tag{15}$$

where $r_>$ is the larger of r_1 and r_2 and $r_<$ is the smaller. Recognizing the orthogonality of the spherical harmonics, we get

$$V(r_2, \vartheta_2) = \sum_l V_l(r_2)P_l(\cos \vartheta_2) \tag{16}$$

with

$$V_l(r_2) = \frac{4}{2l + 1} \int_0^\infty dr_1 \, r_1^2 e^{-r_1} \frac{r_<^l}{r_>^{l+1}} \alpha_l(r_1) \tag{17}$$

Assuming $r_2 = 0.5$ and $\vartheta_2 = 0$ with $a = 2$, we have, dropping unnecessary subscripts,

$$V_l(r_2) = \frac{4}{2l + 1} \frac{1}{r_2^{l+1}} \int_0^{0.5} dr \, r^2 e^{-r} r^l \alpha_l(r) + \frac{4r_2^l}{2l + 1} \int_{0.5}^{10} dr \, \frac{r^2 e^{-r}}{r^{l+1}} \alpha_l(r) \tag{18}$$

Hence,

$$V(0.5, 0) = \sum_{l=0}^{5} V_l = 0.45038 \tag{19}$$

This value is obtained by using six harmonics and numerical integration. This is to be compared with the exact value [8] of 0.44996.

The CPU time used was 0.69 s.

Exchange Integral

For the two-center exchange integral we use the same orbitals and their locations as before. But now the potential is needed at 100 points along the r_2 grid that is similar to the r_1 grid. Hence,

$$V_l(r_2) = \frac{4}{2l + 1} \frac{1}{r_2^{l+1}} \int_0^{r_2} dr \, r^2 e^{-r} r^l \alpha_l(r) + \frac{4r_2^l}{2l + 1} \int_{r_2}^{10} dr \, r^2 e^{-r} r^{l+1} \alpha_l(r) \tag{20}$$

This requires computation at 10,000 grid points formed by a two-dimensional (r_1, r_2) lattice. This was done using 4.62 s of CPU time.

The exchange integral is given by

$$K = \iint \chi_a(1)\chi_b(1)r^{-1}\chi_c(1)\chi_d(1) \, dv_1 \, dv_2 \tag{21}$$

where χ_a and χ_c coincide as well as χ_b and χ_d.

The exchange integral is equivalent to

$$K = \int dv_2 \, \chi_c(2)\chi_d(2)V(r_2, \vartheta_2) \tag{22}$$

Using the α-function expansion of χ_b and χ_d and the Laplace expansion of $1/r_{12}$ together with the orthogonal properties of spherical harmonics, one obtains [9]

$$K = \sum K_l \tag{23}$$

with

$$K_l = \frac{4}{2l + 1} \int dr\, r^2 V_l e^{-r} \alpha_l \tag{24}$$

Using five harmonics and numerical integration, we get $K = 0.184190$, which required 4.45 s of CPU time. The exact value obtained by using the closed formula of Sugiura [10] is $K = 0.184156$.

Four-Center Integral

We finally solve a four-center two-electron-repulsion problem having three 1s orbitals located on a sphere of radius 1, and one at the origin [11].

This problem has been done by formula [5] and also analytically [9]. The orbital $\chi_a(1)$ is located at the origin and $\chi_b(1)$ at a distance of 1 along the z-axis. The orbitals are used to produce the potential as shown. Orbitals $\chi_c(2)$ and $\chi_d(2)$ are off-axis with center locations given by spherical coordinates (a, γ, Γ) and (a, δ, Δ), respectively, with $a = 1$. Using the Legendre addition theorem, the expansions take the form

$$\chi_c = 2 \sum_{m=0}^{\infty} \sum_{\mu=-m}^{m} \frac{(4\pi)^{1/2}}{2m + 1} \alpha_m Y_m^\mu(\Gamma, \gamma) Y_m^\mu(\vartheta_1, \varphi_1)^* \tag{25}$$

and

$$\chi_d = 2 \sum_{n=0}^{\infty} \sum_{\nu=-n}^{n} \frac{(4\pi)^{1/2}}{2n + 1} \alpha_n Y_n^\nu(\Delta, \delta)^* Y_n^\nu(\vartheta_2, \varphi_2) \tag{26}$$

Making the proper substitution, we may write the resulting integral as the sum of the product of radial functions I_{lmn} multiplied by angular functions A_{lmn}. Thus

$$I = \sum_l \sum_m \sum_n I_{lmn} A_{lmn} \tag{27}$$

where

$$I_{lmn} = \int dr\, r^2 V_l \alpha_m \alpha_n \tag{28}$$

and

$$A_{lmn} = \frac{(4\pi)^{3/2}}{(2l + 1)^{1/2}} \sum_\mu \sum_\nu Y_m^\mu(\Gamma, \gamma)^* Y_n^\nu(\Delta, \delta) \langle m, \mu | l, 0 | n, \nu \rangle \tag{29}$$

where the angular brackets represent Gaunt coefficients. (Γ, γ) and (Δ, δ) are the angular locations of the center of the orbitals. The evaluation of I_{lmn} is quite similar to that of K_l, except that the formula is not closed. Reasonable answers are obtained by taking l from 0 to 4 and m and n from 0 to 6 with $m + n \le 6$.

To determine the accuracy of this integral, we set $\gamma = \Gamma = \delta = \Delta = 0$ and get a hybrid integral whose value is known ($I = 0.507045$). The numerical result here is $I = 0.506284$.

Conclusion

It has been demonstrated that the multicenter integral problem is readily programmed and evaluated by numerical methods. A different numerical integration algorithm might conceivably lead to acceptable accuracy and increased speed. In any event, the ease in implementation of the herein described method, at least as far as 1s orbitals are concerned, ensures that it can serve as a first check on any new developments in molecular integrals.

Acknowledgments

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Analytical method for two- and three-center molecular integrals over Slater-type s-orbitals using expansions in spherical harmonics

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ABSTRACT

Using the Löwdin alpha-function method in which displaced orbitals are expanded in spherical harmonics, two-center and three-center electron-repulsion integrals of the exchange and Coulomb type over Slater-type s-orbitals are evaluated. By means of computer algebra, analytical procedures are implemented and no numerical integration is needed. The formulas for the integrals are kept simple by reversing the order of integration over each part of a split quadrant. Orbitals of the 1s and 2s type are used to illustrate the method, which can be generalized.

I. Introduction

Almost all recent calculations in ab initio molecular physics and quantum chemistry are done using basis sets made up of Gaussian-type orbitals (GTOs), characterized by $\exp(-R^2)$, because of the ease of computation of their multicenter molecular integrals. It is recognized[1] that basis sets composed of Slater-type orbitals (STOs), characterized by $\exp(-R)$, are more representative of physical orbitals, however, their molecular integrals have the reputation of being "intractable". Yet, progress continues to be made toward the solution of the STO integral problem.[2]

In this paper, the method of the Löwdin alpha-function[3] is used again[4] in which displaced orbitals are expanded about a common origin or single-center in terms of spherical harmonics with functional coefficients (alpha-functions). This time, the analytic method is simplified by defining a "potential" in various regions of a split (r_1, r_2) quadrant. Now these "potentials" do not contain the Ei function, but only powers and exponentials. Hence, the second integration for energy (Coulomb or exchange) can always be done analytically and only three types of integration formulas are needed. As an illustration of this method, two- and three-center exchange and Coulomb-type integrals are done for 1s and 2s orbitals.

In the Löwdin α-function method all terms separate into radial and angular parts; our C, E, and F matrices for higher quantum numbers only differ in their numerical elements. Hence, s-orbitals can serve as an adequate prototype for the general two- and three-center problem.

A simple form of computer algebra is used in our approach so that the radial variable "r" remains identifiable, thereby making the method analytic. Integer arithmetic is used to generate our C, E, and F matrices so as to avoid cancellation errors (these matrices are considered as input data).

II. Alpha-Function Representations

Every displaced STO may be expanded in an infinite series of spherical harmonics; the functional coefficients being designed as α-functions. For a s-orbital in its own coordinate system (R,Θ,φ), $\chi = A\, R^{N-1}\, e^{-\zeta R}\, Y_0^0(\Theta,\varphi)$, where the normalization constant $A = (2\zeta)^{N+1}\, [2N)!]^{-1/2}$, ζ is the screening constant or orbital exponent, and the spherical harmonic $Y_0^0(\Theta,\varphi)$ equals $(4\pi)^{-1/2}$. If the orbital is placed at a distance of a along the z-axis of a (r,θ,φ) coordinate system its representation in this coordinate system is[5]

$$\chi = A/(\zeta^{N-1}) \sum_{\ell=0}^{\infty} (2\ell+1)^{-1/2}\ \alpha_\ell(r)\, Y_\ell^0(\theta,\varphi)$$

where

$$\alpha_\ell(r) = \frac{2\ell+1}{2} \sum_{i=0}^{N+\ell} \sum_{j=0}^{N+\ell} C_\ell(i,j)\, H_{ij}\, (\zeta a)^{i-\ell-1}\, (\zeta r)^{j-\ell-1}$$

and

$$H_{ij} = \begin{cases} e^{-\zeta a}\, [(-1)^j\, e^{\zeta r} - e^{-\zeta r}], & r<a \\[2em] e^{-\zeta r}\, [(-1)^i\, e^{\zeta a} - e^{-\zeta a}], & r>a. \end{cases} \tag{1}$$

If the exponentials in the α-function are expanded, we get a representation in $\mathbf{E}$ and $\mathbf{F}$ matrices:[6]

$$\alpha_\ell(r) = \begin{cases} e^{-\zeta a} \sum_{i=0}^{N+\ell} \sum_{j=\ell}^{JMAX} E_\ell(i,j)\, (\zeta a)^{i-\ell-1}\, (\zeta r)^j, & r<a \\[2em] e^{-\zeta r} \sum_{i=\ell}^{IMAX} \sum_{j=0}^{N+\ell} F_\ell(i,j)\, (\zeta a)^i\, (\zeta r)^{j-\ell-1} & r>a. \end{cases} \tag{2}$$

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A final simplification results by substituting in the numerical values of the parameters to obtain $Y_\ell(j)$ and $Z_\ell(j)$, which are coefficients of the polynomials in r.

$$\alpha_\ell(r) = \begin{cases} \sum_{j=\ell}^{JMAX} Y_\ell(j)\, r^j & , \quad r<a \\[4ex] e^{-\zeta r} \sum_{j=0}^{N+\ell} Z_\ell(j)\, r^{j-\ell-1} & , \quad r>a. \end{cases} \tag{3}$$

In this paper we have used 36 for IMAX and JMAX.

III. Three-Center Exchange Integral

The two-electron repulsion integral is defined as

$$K = \iint dv_1\, dv_2 \; \chi_a(1)\, \chi_b(1)\, r_{12}^{-1}\, \chi_c(2)\, \chi_d(2). \tag{4}$$

The locations of the orbitals for the three-center exchange integral is given in Figure 1. We let a be the distance to $\chi_b(1)$ and b be the distance to $\chi_d(2)$; θ is the angle between a and b. In their local coordinate systems the orbitals are given as

$$\chi_a(1) = A_a\, e^{-\alpha r_1}\, Y_0^0(\theta_1, \varphi_1) \qquad \chi_b(1) = A_b\, e^{-\beta R_1}\, Y_0^0(\Theta_1, \varphi_1)$$

$$\chi_c(2) = A_c\, e^{-\gamma r_2}\, Y_0^0(\theta_2, \varphi_2) \qquad \chi_d(2) = A_d\, e^{-\delta R_2}\, Y_0^0(\Theta_2, \varphi_2). \tag{5}$$

We write the expansion of $\chi_b(1)$:

$$\chi_b(1) = A_b \sum_{\ell_b=0}^{\infty} (2\ell+1)^{-1/2}\, \alpha_{\ell_b}^b(1)\, Y_{\ell_b}^0(\theta_1, \varphi_1). \tag{6}$$

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By use of the Legendre addition theorem we have[7]

$$\chi_d(2) = A_d \sum_{\ell_d=0}^{\infty} \sum_{\mu=-\ell_d}^{\ell_d} (4\pi)^{1/2} (2\ell_d+1)^{-1} \alpha_{\ell_d}^d (2) Y_{\ell_d}^\mu (\theta_1, \varphi_1) Y_{\ell_d}^{\mu*} (\theta_2, \varphi_2) \quad (7)$$

Now,

$$1/r_{12} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} (2\ell+1)^{-1} \frac{r_<^\ell}{r_>^{\ell+1}} Y_\ell^{m*} (\theta_1, \varphi_1) Y_\ell^m (\theta_2, \varphi_2), \quad (8)$$

where $r_<$ is the lesser of r_1 and r_2, and $r_>$ is the greater. We will use

$$Y_\ell^0 (\theta, \varphi) = ((2\ell+1)/4\pi)^{1/2} P_\ell (\cos \theta). \quad (9)$$

Substituting these expressions into the formula for the exchange integral and using the orthogonal properties of spherical harmonics, we get

$$K = \Sigma K_\ell P_\ell (\cos \theta) \quad (10)$$

where

$$K_\ell = A_\ell \iint dr_1 dr_2 r_1^2 r_2^2 e^{-\alpha r_1} e^{-\gamma r_2} \alpha_\ell^b (1) \alpha_\ell^d (2) r_<^\ell / r_>^{\ell+1} r_1^{N_a-1} r_2^{N_c-1} \quad (11)$$

and

$$A_\ell = \frac{A_a A_b A_c A_d}{\beta^{N_b-1} \delta^{N_d-1}} (2\ell+1)^{-2}. \quad (12)$$

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To simplify the integrations necessary for K_ℓ we divide the (r_1, r_2) quadrant into nine regions as shown in Figure 2.

Now we may write[8]

$$K_\ell = \overset{I}{K_\ell} + \overset{II}{K_\ell} \tag{13}$$

$$\overset{I}{K_\ell} = A_\ell \int_0^\infty r_2^{N_c+1} dr_2 \ e^{-\gamma r_2} \ \alpha_\ell^d(2) \frac{1}{r_2^{\ell+1}} \int_0^{r_2} r_1^{N_a+1} dr_1 \ e^{-\alpha r_1} \alpha_\ell^b(1) \ r_1^\ell , \tag{14}$$

$$\overset{II}{K_\ell} = A_\ell \int_0^\infty r_1^{N_a+1} dr_1 \ e^{-\alpha r_1} \ \alpha_\ell^b(1) \frac{1}{r_1^{\ell+1}} \int_0^{r_1} r_2^{N_c+1} dr_2 \ e^{-\gamma r_1} \alpha_\ell^d(2) \ r_2^\ell . \tag{15}$$

We take the "potential" in the various regions to be

$$\overset{1}{V_\ell} = \frac{1}{r_2^{\ell+1}} \int_0^{r_2} dr_1 \rho_\ell^{(1)} r_1^\ell$$

$$\overset{2}{V_\ell} = \frac{1}{r_2^{\ell+1}} \int_0^a dr_1 \rho_\ell^{(1)} r_1^\ell$$

$$\overset{3}{V_\ell} = \frac{1}{r_2^{\ell+1}} \int_a^{r_2} dr_1 \rho_\ell^{(1)} r_1^\ell$$

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$$\overset{4}{V}_\ell = \overset{2}{V}_\ell$$

$$\overset{5}{V}_\ell = \overset{3}{V}_\ell$$

$$\overset{6}{V}_\ell = \frac{1}{r_1^{\ell+1}} \int_0^{r_1} dr_2 \, \rho_\ell^{(2)} \, r_2^\ell$$

$$\overset{7}{V}_\ell = \overset{6}{V}_\ell$$

$$\overset{8}{V}_\ell = \frac{1}{r_1^{\ell+1}} \int_0^b dr_2 \, \rho_\ell^{(2)} \, r_2^\ell$$

$$\overset{9}{V}_\ell = \frac{1}{r_1^{\ell+1}} \int_b^{r_1} dr_2 \, \rho_\ell^{(2)} \, r_2^\ell$$

where

$$\rho_\ell^{(1)} = r_1^{N_a+1} \, e^{-\alpha r_1} \, \alpha_\ell^b(1)$$

and

$$\rho_\ell^{(2)} = r_2^{N_c+1} \, e^{-\gamma r_2} \, \alpha_\ell^d(2). \tag{16}$$

We take note of the various expressions for the α-function in the various regions:

$$\alpha_\ell^b(1) = \sum_{j=\ell}^{JMAX} Y_\ell^b(j) \, r^j \qquad , \qquad r_1 < a \tag{17}$$

$$\alpha_\ell^b(1) = e^{-\beta r_1} \sum_{j=0}^{N_b+\ell} Z_\ell^b(j) \, r_1^{j-\ell-1} \quad , \quad r_1 > a \tag{18}$$

$$\alpha_\ell^d(2) = \sum_{q=\ell}^{JMAX} Y_\ell^d(q) \, r_2^q \quad , \quad\quad r_2 < b \tag{19}$$

$$\alpha_\ell^d(2) = e^{-\delta r_2} \sum_{j=0}^{N_d+\ell} Z_\ell^d(q) \, r_2^{q-\ell-1} \quad , \quad r_2 > b. \tag{20}$$

We write

$$\overset{I}{K}_\ell = \sum_{i=1}^{5} \overset{i}{K}_\ell \tag{21}$$

and

$$\overset{II}{K}_\ell = \sum_{i=6}^{9} \overset{i}{K}_\ell \tag{22}$$

with

$$\overset{1}{K}_\ell = A_\ell \int_0^a dr_2 \, \rho_\ell^{(2)} \overset{1}{V}_\ell \qquad\qquad \overset{2}{K}_\ell = A_\ell \int_a^b dr_2 \, \rho_\ell^{(2)} \overset{2}{V}_\ell$$

$$\overset{3}{K}_\ell = A_\ell \int_a^b dr_2 \, \rho_\ell^{(2)} \overset{3}{V}_\ell \qquad\qquad \overset{4}{K}_\ell = A_\ell \int_b^\infty dr_2 \, \rho_\ell^{(2)} \overset{4}{V}_\ell$$

$$\overset{5}{K}_\ell = A_\ell \int_b^\infty dr_2 \, \rho_\ell^{(2)} \overset{5}{V}_\ell \qquad\qquad \overset{6}{K}_\ell = A_\ell \int_0^a dr_1 \, \rho_\ell^{(1)} \overset{6}{V}_\ell$$

$$\overset{7}{K}_{\ell} = A_{\ell} \int_{a}^{b} dr_1 \, \overset{1)}{\rho}_{\ell} \, \overset{7}{V}_{\ell} \qquad\qquad \overset{8}{K}_{\ell} = A_{\ell} \int_{b}^{\infty} dr_1 \, \rho_{\ell}^{(1)} \, \overset{8}{V}_{\ell}$$

$$\overset{9}{K}_{\ell} = A_{\ell} \int_{b}^{\infty} dr_1 \, \rho_{\ell}^{(1)} \, \overset{9}{V}_{\ell} . \qquad\qquad (23)$$

Three basic formulas for integrals are needed (the first one given by Silverstone[9]):

$$\int_{0}^{1} x^n \, e^{-zx} \, dx = \sum_{k=0}^{\infty} \frac{(-Z)^k}{k! \, (n+k+1)} \qquad\qquad (24)$$

$$\int_{1}^{\infty} x^n \, e^{-zx} \, dx = e^{-z} \sum_{k=0}^{n} \frac{n!}{(n-k)!} \frac{1}{z^{n+1}}, \qquad n \geq 0 \qquad\qquad (25)$$

$$\int_{1}^{\infty} \frac{e^{-zx}}{x^n} \, dx = e^{-Z} \sum_{k=1}^{n-1} \frac{(n-k-1)!}{(n-1)!} (-Z)^{k-1} - \frac{(-z)^{n-1}}{(n-1)!} Ei(-z), \quad n > 0. \qquad (26)$$

Taking note of the different expressions for the α-function in the various regions and making the appropriate change of variable in the basic integrals, we get analytic expressions for the potentials:

$$\overset{1}{V}_{\ell} = \sum_{j=\ell}^{JMAX} \sum_{k=0}^{\infty} \frac{(-\alpha)^k}{k! \, (n+k+1)} \, Y_{\ell}^{b}(j) \, r_2^{N_a+j+k+1}$$

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$$\overset{1}{V}_\ell = \left(e^{-\alpha r_2}\right) \overset{JMAX}{\underset{m=N_a+\ell+1}{\Sigma}} \overset{1}{P}_{\ell m} \ r_2^m$$

$$\overset{2}{V}_\ell = \frac{1}{r_2^{\ell+1}} \overset{JMAX}{\underset{j=\ell}{\Sigma}} \ \overset{\infty}{\underset{k=0}{\Sigma}} \ \frac{(-\alpha)^k}{k!(n+k+1)} \ Y_\ell^b(j) \ a^{N_a+\ell+j+k+2}$$

$$\overset{2}{V}_\ell = \frac{\overset{2}{P}_\ell}{r_2^{\ell+1}}$$

with $n = N_a + \ell + j + 1$.

$$\overset{3}{V}_\ell = \frac{1}{r_2^{\ell+1}} \overset{N_b+\ell}{\underset{j=0}{\Sigma}} \ Z_\ell^b(j) \int_a^{r_2} dr_1 \ r_1^n \ e^{-(\alpha+\beta)r_1}$$

$$\overset{3R}{V}_\ell = - \ \frac{e^{-(\alpha+\beta)r2}}{r_2^{\ell+1}} \ \overset{N_b+\ell}{\underset{j=0}{\Sigma}} \ \overset{n}{\underset{k=0}{\Sigma}} \ Z_\ell^b(j) \ \frac{n!}{(n-k)!} \ \frac{r_2^{n-k}}{(\alpha+\beta)^{k+1}}$$

$$\overset{3A}{V}_\ell = \frac{1}{r_2^{\ell+1}} \ \overset{N_b+\ell}{\underset{j=0}{\Sigma}} \ \overset{n}{\underset{k=0}{\Sigma}} \ Z_\ell^b(j) \ \frac{n!}{(n-k)!} \ \frac{a^{n-k}}{(\alpha+\beta)^{k+1}} e^{-(\alpha+\beta)a}$$

$$\overset{3}{V}_\ell = \overset{3R}{V}_\ell + \overset{3A}{V}_\ell = \frac{e^{-(\alpha+\beta)r_2}}{r_2^{\ell+1}} \overset{N_a+N_b+\ell}{\underset{m=0}{\Sigma}} \overset{3R}{P}_{\ell m} \ r_2^m + \frac{\overset{3A}{P}_\ell}{r_2^{\ell+1}}$$

with $n = N_a + j$.

$$\overset{6}{V}_\ell = \sum_{q=\ell}^{JMAX} \sum_{k=0}^{\infty} \frac{(-\gamma)^k}{k!\,(n+k+1)}\, Y_\ell^d(q)\, r_1^{N_c+q+k+1}$$

$$\overset{6}{V}_\ell = e^{-\gamma r_1} \sum_{m=N_c+\ell+1}^{JMAX} \overset{6}{P}_{\ell m}\, r_1^m$$

$$\overset{7}{V}_\ell = \overset{6}{V}_\ell$$

$$\overset{8}{V}_\ell = \frac{1}{r_1^{\ell+1}} \sum_{q=\ell}^{JMAX} \sum_{k=0}^{\infty} \frac{(-\gamma)^k}{k!\,(n+k+1)}\, e^{-\gamma b}\, Y_\ell^d(q)\, b^{N_c+\ell+k+q+2}$$

$$\overset{8}{V}_\ell = \frac{\overset{8}{P}_\ell}{r_1^{\ell+1}} \bigg|_{r_1}$$

with $n = N_c + \ell + q + 1$.

$$\overset{9}{V}_\ell = \frac{1}{r_1^{\ell+1}} \sum_{q=0}^{N_d+\ell} Z_\ell^d(q) \int_b^{r_1} dr_2\, r_2^{N_c+q}\, e^{-(\gamma+\delta)\,r_2}$$

$$\overset{9R}{V}_\ell = -\frac{e^{-(\gamma+\delta)\,r_1}}{r_1^{\ell+1}} \sum_{q=0}^{N_d+\ell} \sum_{k=0}^{n} \frac{Z_\ell^d(q)\,n!}{(n-k)!}\, \frac{r_1^{n-k}}{(\gamma+\delta)^{k+1}}$$

$$\overset{9B}{V}_\ell = \frac{1}{r_1^{\ell+1}} \sum_{q=0}^{N_d+\ell} \sum_{k=0}^{j+1} \frac{Z_\ell^d(q)\,n!}{(n-k)!}\, \frac{b^{n-k}\, e^{-(\gamma+\delta)\,b}}{(\gamma+\delta)^{k+1}}$$

$$\overset{9}{V}_{\ell} = \overset{\Re}{V}_{\ell} + \overset{\Re B}{V}_{\ell}$$

$$\overset{9}{V}_{\ell} = \frac{e^{-(\gamma+\delta)\,r_1}}{r_1^{\ell+1}} \sum_{m=0}^{\ell+2} \overset{\Re}{P}_{\ell m}\ r^m + \frac{\overset{9B}{P}_{\ell}}{r_1^{\ell+1}} \tag{27}$$

with $n = N_c + q$

The coefficients $\overset{1}{P}_{\ell m}$, $\overset{2}{P}_{\ell}$, $\overset{3R}{P}_{\ell m}$, $\overset{3A}{P}_{\ell}$, $\overset{6}{P}_{\ell m}$, $\overset{8}{P}_{\ell}$, $\overset{9R}{P}_{\ell m}$, and $\overset{3B}{P}_{\ell}$

are generated by computer and stored.

Now, we put together the final integrals:

$$\overset{1}{K}_{\ell} = A_{\ell} \sum_{q} \sum_{m} Y_{\ell}^d (q)\ \overset{1}{P}_{\ell m} \int_{o}^{a} dr\ e^{-\gamma r}\ r^{N_c+q+m+1}$$

$$\overset{2}{K}_{\ell} = A_{\ell} \sum_{q} Y_{\ell}^d (q)\ \overset{2}{P}_{\ell} \int_{a}^{b} dr\ e^{-\gamma r}\ r^{N_c+q-\ell}$$

$$\overset{3}{K}_{\ell} = \overset{3R}{K}_{\ell} + \overset{3A}{K}_{\ell}$$

$$\overset{3R}{K}_{\ell} = A_{\ell} \sum_{q} \sum_{m} \left(Y_{\ell}^d \right)(q)\ \overset{3R}{P}_{\ell m} \int_{a}^{b} dr\ e^{-(\alpha+\beta+\gamma)r}\ r^{N_c+q+m-\ell}$$

$$\overset{3A}{K}_{\ell} = A_{\ell} \sum_{q} Y_{\ell}^d (q)\ \overset{3A}{P}_{\ell} \int_{a}^{b} dr\ e^{-\gamma r}\ r^{N_c+q-\ell}$$

$$\overset{4}{K_\ell} = A_\ell \underset{q}{\Sigma} \; Z_\ell^d (q) \; \overset{2}{P_\ell} \int_b^\infty dr \; e^{-(\gamma+\delta)r} \; r^{N_c - 1 + q - 2\ell}$$

$$\overset{5}{K_\ell} = \overset{5R}{K_\ell} + \overset{5A}{K_\ell}$$

$$\overset{5R}{K_\ell} = A_\ell \underset{q}{\Sigma} \underset{m}{\Sigma} \; Z_\ell^d (q) \; \overset{3R}{P_\ell} \int_b^\infty dr \; e^{-(\alpha+\beta+\gamma+\delta)r} \; r^{N_c - 1 + q + m - 2\ell}$$

$$\overset{5A}{K_\ell} = A_\ell \underset{q}{\Sigma} \; Z_\ell^d (q) \; \overset{3A}{P_\ell} \int_b^\infty dr \; e^{-(\gamma+\delta)} \; r^{N_c - 1 + q - 2\ell}$$

$$\overset{6}{K_\ell} = A_\ell \underset{j}{\Sigma} \underset{m}{\Sigma} \; Y_\ell^b (j) \; \overset{6}{P_{\ell m}} \int_o^a dr \; e^{-\alpha r} \; r^{N_a + j + m + 1}$$

$$\overset{7}{K_\ell} = A_\ell \underset{j}{\Sigma} \underset{m}{\Sigma} \; Z_\ell^b (j) \; \overset{6}{P_{\ell m}} \int_a^b dr \; e^{-(\alpha+\beta)r} \; r^{N_a + j + m - \ell}$$

$$\overset{8}{K_\ell} = A_\ell \underset{j}{\Sigma} \; Z_\ell^b (j) \; \overset{8}{P_\ell} \int_b^\infty dr \; e^{-(\alpha+\beta)r} \; r^{N_a - 1 + j - 2\ell}$$

$$\overset{9}{K_\ell} = \overset{9R}{K_\ell} + \overset{9B}{K_\ell}$$

$$\overset{9R}{K_\ell} = A_\ell \underset{j}{\Sigma} \underset{m}{\Sigma} \; Z_\ell^b (j) \; \overset{9R}{P_{\ell m}} \int_b^\infty dr \; e^{-(\alpha+\beta+\gamma+\delta)r} \; r^{N_a - 1 + j + m - 2\ell}$$

$$\overset{9B}{K_\ell} = A_\ell \underset{j}{\Sigma} \; Z_\ell^b (j) \; \overset{3B}{P_\ell} \int_b^\infty dr \; e^{-(\alpha+\beta)r} \; r^{N_a - 1 + j - 2\ell} \qquad (28)$$

In the summations, the maximum power of r used was 36.

As an example of the three-center exchange integral we take the case of $a =$

$\sqrt{2}$, $b = 2$, $\theta = 45^o$, and $\alpha = \beta = \gamma = \delta = 1.2$. Table I shows the results of our

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computations. The last columns give the sum of the preceding columns. We multiply each last column value by P (cos θ) and add. Hence, K = .1099365 and K = .0845324, and therefore K = .1944689. (The Central Processing Unit time was 93 s on a Cyber 760). This value agrees with the six figures given by Trivedi and Steinborn[10], and Graovac, et al.[11]

We may readily specify the three-center exchange integral to the two-center exchange integral. As an example we set $a = b = 2$, $\theta = 0^o$, and keep all screening constants the same. Because of symmetry considerations we may write K = 2K, and the problem reduces to integration over three regions. The value computed was K = .1433972 (17 s CPU time). This compares well with the exact value of K = .1433970 obtained by use of Sugiura's formula.[12] This kind of comparison is an excellent check on our method.

Let us consider two additional examples. For a two-center exchange integral take $\chi_a(1)$ to be a 2s orbital with $\chi_b(1)$, $\chi_c(2)$, and $\chi_d(2)$ to be 1s orbitals, with all screening constants equal to 1.0. Let the displacement distance be $a = 1.0$. Then we get K = 0.35678082, which agrees with the seven digits given by Maslen and Trefry.[13] If we interchange $\chi_a(1)$ and $\chi_b(1)$, we get the same answer, which demonstrates the consistency of our method. In the second example, we study a three-center exchange integral with all 2s orbitals, $a = \sqrt{2}$, $b = 2.0$, $\theta = 60^o$, $\alpha = 0.5$, $\beta = 1.0$, $\gamma = 1.2$, and $\delta = 1.5$. We find that K = 0.13960560.

IV. Three-Center Coulomb Integral

Coulomb integrals are simpler to formulate than the corresponding exchange integrals. This is because we may merge the two orbitals of the same electron and place it at the origin. Then, the potential due to these orbitals can be

immediately written as an analytical expression.[14,15]

For the three-center Coulomb integral we use the same geometry as before (Fig. 1), but now we interchange the positions of orbitals $\chi_b(1)$ and $\chi_c(2)$. In this case, we may consider the product of the two orbitals at the origin as a single charge distribution. Thus

$$\chi_a(1)\, \chi_b(1) = A_a\, A_b\, r_1^{N_a + N_b - 2}\, e^{-(\alpha + \beta)r_1}\, Y_0^0(\theta_1, \varphi_1) / (4\pi)^{1/2} \tag{29}$$

The true potential is

$$V(r_2) = \int dv_1\, \chi_a(1)\, \chi_b(1) / r_{12} \tag{30}$$

The integration is easily carried out getting

$$V(r_2) = \frac{8\,(\alpha\,\beta)^{3/2}}{(\alpha+\beta)^{3/2}} \left\{ \frac{1}{r_2} - e^{-(\alpha+\beta)r_2} \left(\frac{\alpha+\beta}{2} \quad \frac{1}{r_2} \right) \right\} \tag{31}$$

We write each term as a separate potential

$$\overset{1}{V}(r_2) = \frac{1}{r_2} \tag{32}$$

$$\overset{2}{V}(r_2) = \frac{e^{-(\alpha+\beta)r_2}}{r_2} \tag{33}$$

$$\overset{3}{V}(r_2) = -\frac{(\alpha+\beta)}{2}\, e^{-(\alpha+\beta)r_2} \tag{34}$$

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The definition of the Coulomb integral is

$$J = \iint dv_1\, dv_2\ \chi_a^*(1)\ \chi_b(1)\ r_{12}^{-1}\ \chi_c^*(2)\ \chi_d(2). \tag{35}$$

In our case

$$J = \int dv_2\ V(r_2)\ \chi_c(2)\ \chi_d(2). \tag{36}$$

Substituting in the appropriate α-functions and taking orthogonality into account we get

$$J = \Sigma\ A_\ell\ J_\ell\ P_\ell(\cos\theta)$$

with

$$J_\ell = \int r^2\, dv\ V(r)\ \alpha_\ell^c(r)\ \alpha_\ell^d(r). \tag{37}$$

This time,

$$A_\ell = \frac{32\,(\alpha\beta\gamma\delta)^{3/2}}{(\alpha+\beta)^3}\ \frac{1}{2\ell+1}$$

Now, we simply write

$$J_\ell = \int r^2\, dr\ \alpha_\ell^c\ \alpha_\ell^d\ \{\overset{1}{V} + \overset{2}{V} + \overset{3}{V}\} \tag{38}$$

Taking into account the range of validity of each α-function, we write

$$J_\ell = \overset{I}{J_\ell} + \overset{II}{J_\ell} + \overset{III}{J_\ell}$$

with

$$\overset{I}{J_\ell} = \int_o^a r^2\, dr\, \alpha_\ell^c\, \alpha_\ell^d\, \{ \overset{1}{V} + \overset{2}{V} + \overset{3}{V} \}$$

$$\overset{II}{J_\ell} = \int_a^b r^2\, dr\, \alpha_\ell^c\, \alpha_\ell^d\, \{ \overset{1}{V} + \overset{2}{V} + \overset{3}{V} \}$$

$$\overset{III}{J_\ell} = \int_b^\infty r^2\, dr\, \alpha_\ell^c\, \alpha_\ell^d\, \{ \overset{1}{V} + \overset{2}{V} + \overset{3}{V} \} \qquad (39)$$

Furthermore, let each region I, II, and III define three $\overset{i}{J_\ell}$ values corresponding to the three potentials.

Thus, finally $\quad J_\ell = \sum_{i=1}^{9} \overset{i}{J_\ell}.$ $\qquad (40)$

Table II tabulates J_ℓ for 13 harmonics. The last column corresponds to J_ℓ. Multiplying the last column by $P_\ell(\cos\theta)$ and adding we get $J = .343848$ (CPU time is 164 s).

We may check our procedures by setting $a = b = 2$ and $\theta = 0^0$. This gives the result $J = .454950$. Closed formulas are available[16] for two-center Coulomb integrals. For this example, the formula gives $J = .455049$.

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V. Two-Center Coulomb Integral

The two-center coulomb integral forms an exceptionally simple case with our method. With s-orbitals only one harmonic is needed, namely, $\ell = 0$. This comes about if we merge orbitals $\chi_c(2)$ and $\chi_d(2)$. Thus,

$$\chi_c(2)\,\chi_d(2) = (4\pi)^{-1/2}\ A_c\ A_d\ e^{-(\gamma+\delta)R_2}\ Y_0^0(\Theta,\phi) \tag{41}$$

We consider this charge density as essentially a 1s orbital with a screening constant of $\gamma+\delta$. We write its α-function as α_ℓ^{CD}. Hence,

$$\chi_c(2)\,\chi_d(2) = Y_0^0\ A_c\ A_d\ \Sigma\ (2\,\ell+1)^{-1/2}\ \alpha_\ell^{CD}(2)\ Y_0^0(\theta_2,\varphi_2) \tag{42}$$

Substituting this expression into the formula for the Coulomb integral and invoking orthogonality, only the $\ell = 0$ term survives. Thus we get

$$J = A_o \sum_{j=0}^{JMAX} Y_0^{CD}(j) \int_0^a dr\ r^{j+2}\ V + A_o \sum_{j=0} Z_0^{CD}(j) \int_a^\infty dr\ r^{j+1}\ V\ e^{-(\gamma+\delta)r}$$

with

$$A_o = 32\,(\alpha\,\beta\,\gamma\,\delta)^{3/2}\,/\,(\alpha+\beta)^3. \tag{43}$$

The computed value is $J = .455049$, the same as the formula value.

VI. Conclusion

All expansion methods necessarily have their limitations; in our case the number of harmonics required depend upon the magnitude of the product of each orbital screening constant and the displacement of the orbital from the origin.[17] However, when one relates this basic consideration to realistic physical problems, the constraint is not as severe as might be supposed. In most of our examples, we achieved excellent results with use of only 13 harmonics. We note that exchange integrals become very small and may be discarded when displacement distances or screening constants become large; also, when the charge overlap between orbitals is essentially zero its Coulomb interaction may be calculated on the basis of multipoles.[18]

The efficiency of this generalizable method for the evaluation of STO multicenter molecular integrals may be significantly improved by better programming, the use of look-up tables, and vector processing.

VII. Acknowledgment

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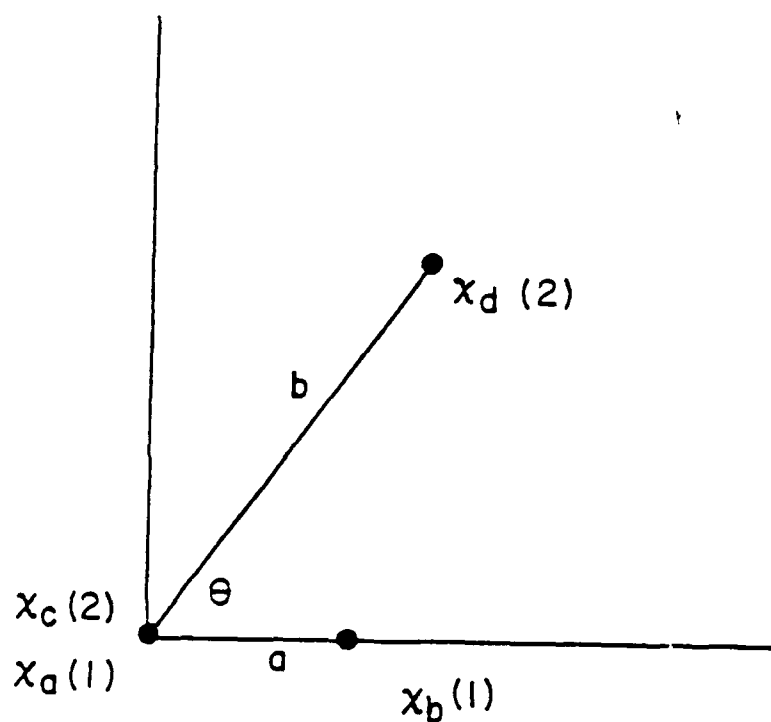Figure 1.   Location of orbitals $\chi_a(1)$, $\chi_b(2)$, $\chi_c(2)$, and $\chi_d(2)$ for the determination of the three-center exchange integrals.
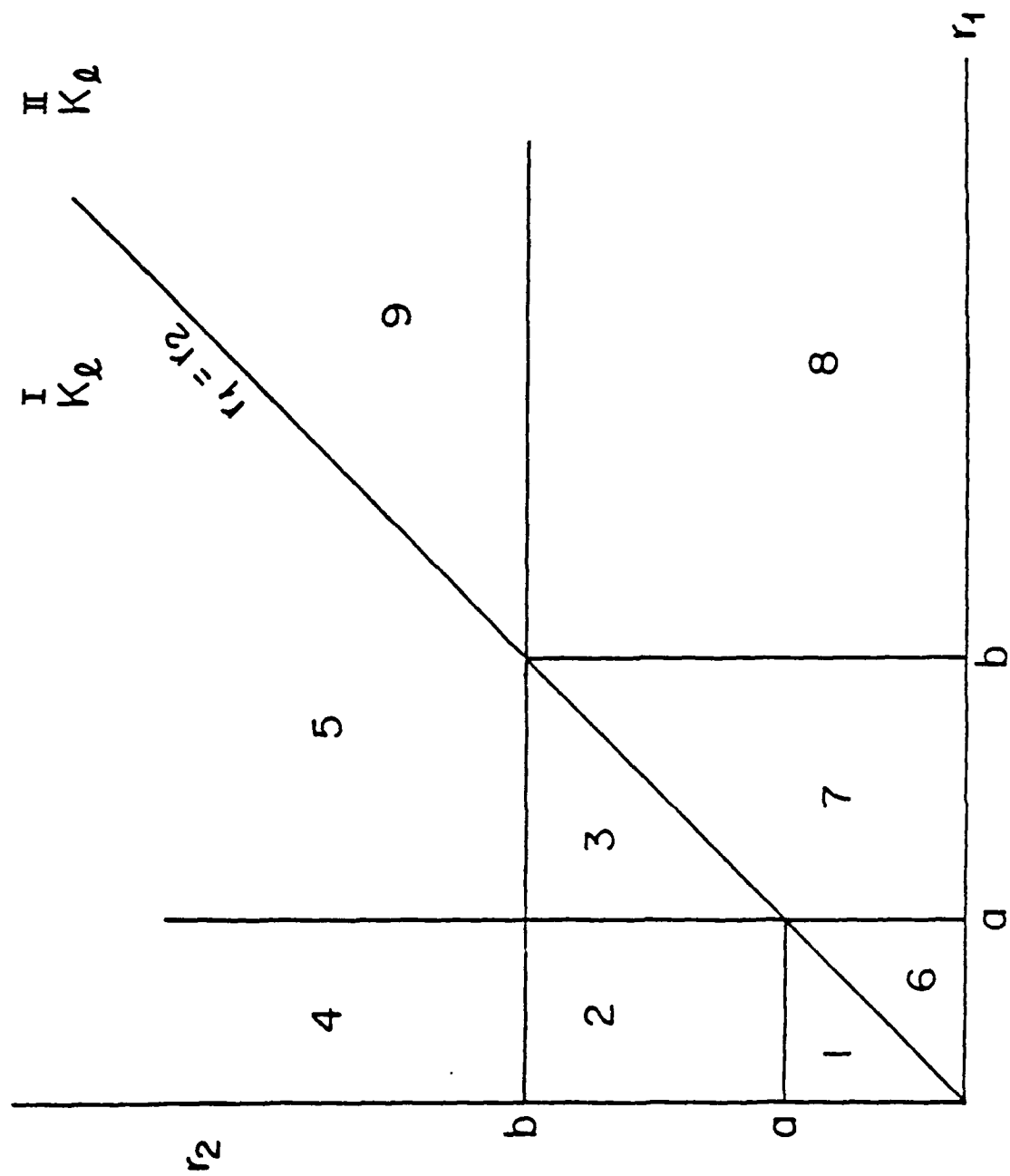
Figure 2.   The nine regions of space separately calculated for the evaluation of the three-center exchange integral.

ℓ	1 K_ℓ	2 K_ℓ	3 K_ℓ	4 K_ℓ	5 K_ℓ	I K_ℓ
0	.02845745	.02617458	.00728394	.02148834	.01697119	.10037551
1	.00238985	.00303369	.00180182	.00191656	.00384017	.01298209
2	.00023898	.00038652	.00037769	.00018840	.00071014	.00190172
3	.00003101	.00006034	.00008476	.00002266	.00013414	.00033290
4	.00000516	.00001165	.00002173	.00000340	.00002810	.00007003
5	.00000106	.00000270	.00000637	.00000062	.00000657	.00001742
6	.00000025	.00000073	.00000210	.00000013	.00000179	.00000500
7	.00000007	.00000022	.00000076	.00000003	.00000053	.00000162
8	.00000002	.00000007	.00000030	.00000001	.00000017	.00000058
9	.00000001	.00000003	.00000012	.00000000	.00000006	.00000022
10	.00000000	.00000001	.00000005	.00000000	.00000002	.00000009
11	.00000000	.00000000	.00000002	.00000000	.00000001	.00000004
12	.00000000	.00000000	.00000001	.00000000	.00000000	.00000002

ℓ	6 K_ℓ	7 K_ℓ	8 K_ℓ	9 K_ℓ	II K_ℓ
0	.02661260	.02610242	.02012826	.00454913	.07739241
1	.00221363	.00369237	.00258891	.00121171	.00970662
2	.00021777	.00055076	.00033792	.00024236	.00134881
3	.00002777	.00009714	.00005040	.00004644	.00022175
4	.00000455	.00002064	.00000892	.00000947	.00004358
5	.00000092	.00000518	.00000187	.00000214	.00001010
6	.00000022	.00000149	.00000045	.00000054	.00000270
7	.00000006	.00000048	.00000012	.00000015	.00000081
8	.00000002	.00000017	.00000004	.00000005	.00000027
9	.00000001	.00000006	.00000001	.00000001	.00000010
10	.00000000	.00000003	.00000000	.00000001	.00000004
11	.00000000	.00000001	.00000000	.00000000	.00000002
12	.00000000	.00000000	.00000000	.00000000	.00000001

Table I.   The values of thirteen harmonics for the three-center exchange integral over the top half of the quadrant, and the bottom half.

ℓ	$^1J_\ell$	$^2J_\ell$	$^3J_\ell$	$^4J_\ell$	$^5J_\ell$	$^6J_\ell$	$^7J_\ell$	$^8J_\ell$	$^9J_\ell$	J_ℓ
0	.10838061	-.01660707	-.01261811	.07407333	-.00024205	-.00065682	.07371521	-.00136200	-.00266670	.22201641
1	.04115240	-.00356584	-.00396141	.07087906	-.00022892	-.00062224	.06022382	-.00107799	-.00212706	.16067182
2	.00940986	-.00062554	-.00080369	.02757856	-.00009200	-.00024944	.02273402	-.00039719	-.00078849	.05676607
3	.00218328	-.00012497	-.00017280	.00841543	-.00003011	-.00008111	.00758842	-.00013052	-.00026015	.01738746
4	.00056905	-.00002960	-.00004274	.00246417	-.00000963	-.00002573	.00262208	-.00004468	-.00008928	.00541365
5	.00016799	-.00000817	-.00001215	.00075128	-.00000321	-.00000850	.00097531	-.00001653	-.00003308	.00181294
6	.00005528	-.00000256	-.00000388	.00024549	-.00000114	-.00000299	.00039112	-.00000661	-.00001324	.00066148
7	.00001990	-.00000089	-.00000137	.00008636	-.00000043	-.00000112	.00016760	-.00000283	-.00000567	.00026158
8	.00000771	-.00000033	-.00000052	.00003254	-.00000017	-.00000044	.00007595	-.00000128	-.00000257	.00011088
9	.00000317	-.00000013	-.00000021	.00001302	-.00000007	-.00000018	.00003605	-.00000061	-.00000122	.00004982
10	.00000137	-.00000006	-.00000009	.00000549	-.00000003	-.00000008	.00001779	-.00000030	-.00000060	.00002349
11	.00000062	-.00000003	-.00000004	.00000242	-.00000001	-.00000004	.00000907	-.00000015	-.00000031	.00001154
12	.00000029	-.00000001	-.00000002	.00000111	-.00000001	-.00000002	.00000476	-.00000008	-.00000016	.00000586

Table II. The values of thirteen harmonics for the three-center Coulomb integral over partial potentials and regions.